IMPACT ASSESSMENT
WORK GROUP I

UNITED STATES — CANADA

MEMORANDUM OF INTENT
ON
TRANSBOUNDARY AIR POLLUTION

FINAL REPORT
JANUARY 1983

WORK GROUP I

IMPACT ASSESSMENT

FINAL REPORT

Work Group Co-Chairmen

G.E. Bangay, Canada
C. Riordan, United States

February 1983

Submitted to the Coordinating Committee in fulfillment of the requirements of the Memorandum of Intent on Transboundary Air Pollution signed by Canada and the United States.

TO: Co-Chairmen
Canada/United States
Coordinating Committee

FROM: Co-Chairmen
Impact Assessment Work Group I

We are pleased to submit our final report completing the Phase III activities of the Impact Assessment Work Group I. Although we have reached agreement on the majority of information and conclusions found in the report, there are a number of instances when Canadians and Americans could not reach agreement. These differences are confined to the aquatic section of the report (Section 3) and has required the preparation of separate summary statements in Section 1. Those portions of the text which represent a lack of Canada/United States consensus are typed in italics.

This report completes our activities under the terms of reference contained in the Memorandum of Intent and as such represents the joint efforts by representatives of our two countries to provide information to the negotiators.

Sincerely yours,

G.E. Bangay
Canadian Co-Chairman

Courtney Riordan
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 acidic deposition.

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 hae 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 1 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.

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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 do the following.

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 ecoloigcal stablity 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 (e.g., 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 (e.g., annual, seasonal, episodic) which would be necessary to protect identified sensitive areas.

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SECTION I

SUMMARY

SECTION 1

SUMMARY

1.1 INTRODUCTION

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

During the Work Group's assessment of these effects it has been necessary to conduct the work along strictly disciplinary lines. Thus the presentation of our findings follows a sectoral approach (i.e., aquatic, terrestrial). While this approach has been useful for organizing and presenting our findings, it has also limited our consideration of the interactions which exist among these sectors. These effects do not occur in isolation.

The following sections summarize findings of the Work Group with respect to impacts on aquatic and terrestrial sectors of the biosphere, health and visibility, and man-made structures. There are also summary statements with regard to methodologies for estimates of economic benefits of controls, natural and material resource inventory, and liming.

1.2 AQUATIC ECOSYSTEM EFFECTS - CANADA

The potential effects from the deposition of acid and associated ions and compounds (sulphur dioxide, sulphate, nitrate, ammonia, and others) on water quality, and on the aquatic ecosystem, appear to be more fully quantified and understood than for terrestrial ecosystems. Data have been drawn from a number of study areas in eastern North America including Labrador, Newfoundland, Nova Scotia, New Brunswick, the southern part of the Canadian Shield in Quebec, and Ontario. Primary study areas in the U.S. are found in New Hampshire and southern Maine, Adirondack Park in New York, the Boundary Waters Canoe Area of Minnesota, and numerous lakes in north-central Wisconsin.

The findings and conclusions of the Work Group with respect to acidification effects are contained in the following statements:

> *Sulphuric acid has been identified as the dominant compound contributing to the long-term surface water acidification process. Nitric acid contributes to the acidity of precipitation, but is less important in eastern North America than sulphuric acid in long-term acidification of surface waters. Nitric acid contributes to pH depression of surface waters during periods of snowmelt and heavy rain runoff in some areas.*

Studies of lakes in eastern North America have provided evidence that atmospheric deposition accounts for sulphate levels in excess of those expected from natural processes. In the absence of effects from mine drainage and industrial waste water, the symptoms of acidification (e.g., pH depressions of surface waters and loss of fish populations), have been observed only in lakes and rivers where the accompanying elevated concentrations of surface water sulphate (and nitrate in some cases) indicate atmospheric deposition of these ions. Land use changes, such as fires, logging, and housing developments have taken place in many areas with sensitive (low alkalinity) surface waters, but the symptoms of acidification have not been observed unless there is an accompanying increase in surface water sulphate concentrations. Nitrate concentrations also increase in some areas, especially during snowmelt.

In eastern Canada, the surface waters which have elevated excess sulphate occur in areas which have high atmospheric deposition of sulphate. All of the surface waters sampled in northeastern North America that have experienced loss of alkalinity also have elevated excess sulphate concentrations. In areas with less acidic deposition, loss of alkalinity in surface waters has not been observed. In Quebec, sulphate concentrations in surface waters decrease towards the east and north in parallel with deposition patterns. Sulphate concentrations are equal to or greater than the bicarbonate concentration in lakes in the southwest part of the Province. This indicates that the surface water chemistry has been altered by atmospheric sulphur deposition.

Observed Historical Changes

Sediments from lakes in Maine, Vermont, and New Hampshire indicate increased atmospheric acidic deposition has affected terrestrial and aquatic ecosystems as measured by changes in metal concentrations and diatom populations. It has been inferred from the sediment record that the rate of acidification of aquatic ecosystems has increased since the late 1800s as measured by declines in metals (zinc, copper, iron, calcium, magnesium and manganese) in the sediments. Conditions of low pH maintain metals in the water column, where they can be flushed out of the system before being deposited in the sediments. Diatom data are less complete, but they also indicate a statistically significant pH decline since the early 1900s.

In this report numerous historical chemistry records have been examined for waters not influenced by local urban or industrial discharges. Reviews have been conducted for 2 rivers in Newfoundland and 6 in Nova Scotia; 7 lakes in Nova Scotia and 3 in New Brunswick; 40 lakes in Adirondack Park, New York; 250 lakes in New England; 2 streams in New Jersey Pine Barrens; and 275 lakes in Wisconsin. Historical records which are available from areas of soils and bedrock with a low potential to reduce acidity exposed to acidic deposition, show an increase in sulphate and corresponding decrease in alkalinity and pH. Areas of similar lithology and land use practices, but not receiving significant acidic deposition do not show similar losses of alkalinity.

Lakes in the Adirondack Mountain range have some of the lowest alkalinity values and are located in watersheds with a low potential to reduce acidity. They are located in the eastern U.S. in a zone receiving high acidic deposition (26-40 kg/ha.yr of sulphate in precipitation 1978-81). Historical data on fish and pH are available for 40 high elevation Adirondack lakes. In the 1930s, only 8% of these lakes had pH less than 5.0; 10% had no fish whereas in the 1970s, 48% had pH less than 5.0 and 52% had no fish. In some cases, entire fish communities consisting of brook trout, lake trout, white sucker, brown trout, and several cyprinid species apparently have been eliminated over the 40-year period. The New York Department of Environmental Conservation has concluded that at least 180 former brook trout ponds are acidic and no longer support brook trout. The relative contribution of natural and anthropogenic sources to acidification of these lakes is not known.

In New England, deposition of wet sulphate has been measured to be 17-40 kg/ha.yr. A study of 95 lakes for which there are historical pH data from the 1930s to the 1960s has indicated that 36% either had the same pH or higher while 64% now have lower pHs. For 56 lakes, a comparison of historical alkalinities to modern values indicated that 30% of the lakes had increased and 70% had decreased in alkalinity. Over the period of record, measured alkalinity values have decreased by an average of 100 μeq/L. The lakes were small to medium size oligotrophic to mesotrophic with moderately to very transparent water, low to moderate concentrations of humic solute, low alkalinity and conductance and with moderately disturbed to pristine watersheds. For four rivers in Nova Scotia data from 1980-81 showed a decrease in bicarbonate, an increase in sulphate and hydrogen ion concentrations when compared to 1954-55 data.

Short-Term pH Depressions

While the rate of change of water quality of lakes (i.e., the time required for a lake to become acidified) is one of the least well-defined aspects of the acidification process, there is evidence that current acid loadings are damaging to fish populations and other biota due to short-term pH depressions following snowmelt and storm runoff. Both sulphate and nitrate are associated with short-term changes in water chemistry but in the majority of surveyed cases sulphate appears to be the larger contributor to the total acidity.

Short-term pH depressions, and elevated concentrations of metals, particularly aluminum, have been observed during periods of high infiltration or runoff. Metal accumulation in surface waters (Al, Mn, Fe, Zn, Cd, Cu, Pb, and Ni), first noted in streams and lakes of Scandinavia, also has been reported from such places as Hubbard Brook, the Adirondacks, and the Great Smoky Mountains of the U.S., and the southern Precambrian Shield area of Ontario, Canada. Artificial acidification of a lake in the Experimental Lakes Area of Ontario has also shown rapid mobilization of metals from lake sediments to the water column.

Data for 57 headwater streams in Muskoka-Haliburton show that 65% experience minimum pH values less than 5.5 and 26% have minimum pH values less than 4.5. Some inlet streams were observed to have pH values below 4.0 during spring snowmelt.

Data from intensive studies of 16 lakes in the Muskoka-Haliburton area of Ontario currently receiving about 23-29 kg/ha.yr sulphate in precipitation have shown that lakes which have summer alkalinity values up to about 40 μeq/L, experience pH depressions to values below about 5.5 during snowmelt. In Ontario and Quebec there are about 1.5 million lakes on the Precambrian Shield. In Ontario, of the 2,260 lakes sampled on the Precambrian Shield, 19% have alkalinities below 40 μeq/L. In the Shield area of Quebec, a 1981 survey of 162 lakes indicated 37% were extremely sensitive to acidification (CSI greater than 5.0), while 15% had summer pH values less than 5.0 (alkalinity less than 0).

A very large number of surface waters are being affected by acidic deposition, even though the total number of lakes and rivers in eastern North America which are known to have been acidified (alkalinity less than 0) by atmospheric acidic deposition is a relatively small percentage of the total aquatic resource.

Biological Effects

Detailed studies of watersheds have been carried out in sensitive regions of North America and Scandinavia under a range of sulphate deposition rates. The results of the studies conducted in North America are described below.

Observed changes in aquatic life have been both correlated with measured changes in the pH of water and compared for waters of different pH values. Differences have been documented in species composition and dominance and size of plankton communities in lakes of varying pH. Study results show that the number of species is lower in low pH lakes compared to lakes of higher pH. These alterations may have important implications for organisms higher in the food chain. Individual lakes often experience several symptoms of acidification at the same time. For example, in Ontario, Plastic Lake inlet streams have low pH *and high aluminum concentrations during spring runoff and extensive growth of filamentous green algae, and fish kills have been observed in Plastic Lake.*

For those regions currently receiving loadings of sulphate in precipitation of less than 17 kg/ha.yr (Wisconsin, Minnesota and northwestern Ontario), there have been no observed detrimental chemical or biological effects.

For regions currently receiving between 20 and 30 kg/ha.yr sulphate in precipitation there is evidence of chemical alteration and acidification. In Nova Scotia rivers which currently have pH less than 5 there have been salmon population reductions as documented by 40 years of catch records. Fish stocks have remained viable in adjacent rivers with pH values presently greater than 5. Water chemistry records (1954-55 to 1980-81) have indicated a decline in pH to values presently less than 5 for other rivers in the same area. In Maine there is evidence of pH declines over time and loss of alkalinity from surface waters. In Muskoka-Haliburton there is historical evidence of loss of alkalinity for one study lake and there is documentation of pH depressions in all study lakes and streams with low alkalinity. Fish kills were observed in the shore zone of a study lake during spring melt. In the Algoma region there are elevated sulphate and aluminum levels in some headwater lakes.

For regions currently experiencing loading greater than 30 kg/ha.yr there are documented long-term chemical and/or biological effects and short-term chemical effects in sensitive (low alkalinity) surface waters.

In the Adirondack Mountains of New York, comparison of data from the 1930s with recent surveys has shown that some more lakes have been acidified. Fish populations have been lost from 180 lakes. Elevated aluminum concentrations in surface waters have been associated with low pH and survival of stocked trout is reduced by the aluminum.

In the Hubbard Brook study area in New Hampshire where the influx of chemicals is limited principally to precipitation and dry deposition there are pH depressions in streams during snowmelt of 1 to 2 units. Elevated levels of aluminum were observed in headwater streams.

Many species of frogs, toads and salamanders breed in temporary pools formed by the mixture of spring rains and snowmelt. Such pools are subjected to pH depression. Embryonic deformities and mortalities in the yellow spotted salamander which breeds in temporary meltwater pools have been observed in New York State where the acidity of the meltwater pools was 1.5 pH units lower than that of nearby permanent ponds. Population densities of *the bullfrog and woodfrog were reduced in acidic streams and ponds in Ontario.*

A lake acidification experiment in northwestern Ontario clearly shows that alterations to aquatic food chains begin at pH values slightly below 6.0. The remarkable agreement between these whole-lake experiments and observational studies in Scandinavia and eastern North America provides strong evidence that the observed declines in fisheries are caused by acidification and not by other ecological stresses.

Extent of Effects

The terrestrial mapping analysis for eastern Canada supported by surface water chemistry has demonstrated that the watersheds of sensitive (low alkalinity) aquatic ecosystems where effects have been observed have a low potential to reduce acidity and are representative, in terms of soil and geological characteristics, of much larger areas of eastern Canada.

Similarly, using related but different criteria, maps have been developed which characterize considerable areas of the northeastern United States as having low potential to reduce acidity. Therefore, there is reason to expect that there are sensitive surface waters in these other areas which would experience similar effects if subjected to deposition rates comparable to those in the study areas. However, quantification of the number of lakes and rivers susceptible to acidification in both countries will require validation of the terrestrial mapping methodologies and increased information on the chemistry of lakes and streams.

The present empirical evidence covers a broad spectrum of physical and climatological conditions across northeastern North America and therefore provides a reasonable basis on which to make judgements on potential loading effect relationships. However the data do have some deficiencies. More data on historical trends of deposition and associated chemical and biological characteristics would improve our understanding of long-term rates and effects of acidification. In addition, a better understanding of all the mechanisms involved in the acidification process will enhance our ability to estimate loading/response relationships precisely. Therefore any estimates of loading/response relationships should be strengthened in the light of new scientific information as it becomes available.

Target Loadings

Sulphate in precipitation has been used as a surrogate for total acid loading. Sulphate in precipitation can be reliably measured. It is recognized that dry deposition of sulphate and sulphur dioxide, and the wet and dry deposition of nitrogen oxides, nitric acid, particulate nitrate and ammonia, as well as other compounds also contribute to acidic deposition. Based on documented effects, wet and dry deposition of sulphur compounds dominate in long-term acidification.

Sulphur deposition also predominates in the majority of cases surveyed involving short-term pH depressions and associated effects. Insufficient data are available to relate nitrate deposition to short-term water quality effects. Therefore, we are unable to determine a nitrate dose-response relationship.

The models, which are based on theory, that have been considered, permit a quantification of the target loadings in terms of geochemical basin sensitivity. Although these models require further validation, the derived loading estimates are generally supportive of the empirical observations for the study areas discussed above.

Based on the results of the empirical studies, interpretation of long-term water quality data, studies of sediment cores and models that have been reviewed, we conclude that acidic deposition has caused long-term and short-term acidification of sensitive (low alkalinity) surface waters in Canada and the U.S. The Work Group concludes on the basis of our understanding of the acidification process that reductions from present levels of total sulphur deposition in some areas would reduce further damage to sensitive (low alkalinity) surface waters and would lead to eventual recovery of those waters that have already been altered chemically or biologically. Loss of genetic stock would not be reversible.

The Canadian members of the Work Group propose that present deposition of sulphate in precipitation be reduced to less than 20 kg/ha.yr in order to protect all but the most sensitive aquatic ecosystems in Canada. In those areas where there is a high potential to reduce acidity and surface alkalinity is generally greater than 200 µeq/L, the Canadian members recognize that a higher loading rate is acceptable.

As loading reductions take place and additional information is gathered on precipitation, surface water chemistry and watershed response, it may be possible to refine regional loading requirements.

1.2 AQUATIC ECOSYSTEM EFFECTS - UNITED STATES

Acidic deposition has been reported in the literature as a cause of both long-term and short-term episodic depressions in pH and loss in alkalinity in some lakes and streams in the U.S. and Canada.

Elevated concentrations of toxic elements, such as aluminum, and biological effects including losses in fish populations have been reported to accompany some of these pH depressions. In most of the reported cases, clear relationships were not established between acidic deposition and observed effects. Conclusions are based on an understanding of the acidification process although mechanisms which control this process are often not completely understood.

The following summary statements are observations reported to be occurring in areas receiving acidic deposition.

> *Both sulphuric and nitric acid contribute to the acidity of precipitation. It appears, however, that sulphuric acid contributes more to long-term acidification of surface waters than does nitric acid. Nitric acid can contribute to pH depression of surface waters during periods of snowmelt and heavy rain runoff in some areas. Studies of lakes in eastern North America indicate that atmospheric deposition accounts for sulphate levels in some waters in excess of those expected from natural processes. Lake study areas are located in Labrador, Newfoundland, Nova Scotia, New Brunswick, the southern part of the Canadian Shield in Quebec, and in eight regions of Ontario. Primary study areas in the U.S. are found in New Hampshire and southern Maine, Adirondack Park in New York, the Boundary Waters Canoe Area of Minnesota, and numerous lakes in north-central Wisconsin.*
>
> *There is evidence of long-term reductions of pH and alkalinity and other water quality changes for some low alkalinity surface waters. The rate of change of pH and alkalinity in lakes is one of the least well defined aspects of the acidification process. However, there is evidence of short-term pH depressions in some waters following high runoff from snowmelt and storm activity. Both sulphate and nitrate are associated with short-term changes in water chemistry but, in the majority of surveyed cases, sulphate appears to be the larger contributor to total acidity.*
>
> *Short-term pH depressions and elevated concentrations of metals, particularly aluminum, iron, zinc, and manganese have been observed during periods of high runoff. Metal mobilization from some watersheds, first noted in streams and lakes of Scandinavia, also has been reported from such places as Hubbard Brook, the Adirondacks, and the Great Smokey Mountains of the U.S., and Sudbury, Muskoka, and Plastic Lake in Ontario, Canada. Artificial acidification of a lake in the Experimental Lakes Area of Ontario has shown mobilization of metals from lake sediments to the water column.*
>
> *Sediments from lakes in Maine, Vermont, and New Hampshire suggest increased acidity in aquatic ecosystems. It has been inferred from declines in metals (zinc, copper, iron, calcium, magnesium and manganese) in the sediments that the acidity of the water increased since the late 1800s. Low pH maintains*

metals in the water column, where they can be flushed out of the system before being deposited in the sediments. Diatom data are less complete, but they also indicate a pH decline since the early 1900s.

There are few historical records of chemistry of low alkalinity waters not influenced by local urban or industrial discharges (i.e., 6 rivers in Nova Scotia; 7 lakes in Nova Scotia and 3 in New Brunswick; 40 lakes in Adirondack Park, New York; 250 lakes in New England; 2 streams in the New Jersey Pine Barrens; 270 lakes in Wisconsin). The above locations are exposed to various levels of acidic deposition. Some surface waters in these areas have shown a decrease in alkalinity and/or pH. In Wisconsin, however, most lakes surveyed had increased in alkalinity and pH.

The total number of lakes and rivers in eastern North America that are thought to have been acidified by acidic deposition is a very small percentage of the total aquatic resource. In the absence of effects from mine drainage and industrial waste water, the symptoms of acidification (e.g., long-term pH declines and/or short-term pH depressions of surface waters with loss of fish populations) have been observed only in clearwater lakes and streams with accompanying elevated concentrations of sulphate and/or nitrate. Natural acidification processes do occur but their effects appear greatest in coloured surface waters. Land use changes, such as fires, logging, and housing developments, have taken place in many areas with low alkalinity surface waters. However, the symptoms of acidification have not been observed in clearwater lakes and streams except in areas receiving high levels of acidic deposition.

Lakes in the Adirondack Mountain range exhibit some of the lowest alkalinity values found in the eastern United States and are located in a zone presently receiving high acidic deposition (30-40 kg/ha.yr of sulphate in precipitation). In this area, 52% of the 214 high elevation lakes sampled in 1975 had pH values less than 5.0. Seven percent had pH values between 5.0 and 6.0. The New York Department of Environmental Conservation has concluded that at least 180 former brook trout ponds are acidic and no longer support brook trout. The factors causing these population extinctions have not been demonstrated.

New England currently receives wet sulphate deposition loadings of 17-40 kg/ha.yr. A study of 95 relatively small low alkalinity lakes in New England for which historical data were available showed that 64% had decreased in pH. However, accompanying historical deposition data are not available. A comparison of present alkalinity values with historical values for 56 lakes indicated that 70% had decreased in alkalinity. Two other studies have indicated pH declines in some lakes surveyed in Maine. The relative contributions of natural and anthropogenic sources to acidification of these lakes is not known.

Data from intensive studies of 17 lakes in the Muskoka-Haliburton area of Ontario currently receiving about 20-30 kg/ha.yr sulphate in precipitation have shown that some lakes with summer alkalinity values up to about 40 µeq/L experience pH depressions to values below 5.5 during snowmelt. One inlet stream was observed to have pH values as low as 4.1 during spring snowmelt. Other inlet streams had pH depressions but pH did not drop as low. Of 2,624 lakes surveyed in Ontario, 50% had alkalinity of less than 200 µeq/L, a value that may be regarded as the upper limit for potential effects of acidic deposition; 13% of the lakes sampled in the province had alkalinities below 40 µeq/L. While these lakes may be representative of the areas sampled, they may not be representative of lakes located elsewhere in the Shield. In another survey of 199 lakes of the Precambrian Shield of Quebec 7.5% had alkalinity of approximately 50 µeq/L or less. There are about 1.5 million lakes on the Precambrian Shield in the provinces of Ontario and Quebec; but it is not possible at present to extrapolate results of the surveys to the total population of lakes.

Observed changes in aquatic life have both been correlated with measured changes in the pH of water and inferred by comparisons of waters of different pH values. Differences have been documented in species composition and dominance and size of plankton communities in lakes of varying pH. Study results show that the number of species is lower in low pH lakes compared to lakes of higher pH. These differences may have important implications for organisms higher in the food chain, but studies to date have not been done that might establish this connection.

Many species of frogs, toads and salamanders breed in temporary pools formed by the mixture of spring rains and snowmelt and subject to pH depression. Embryonic deformities and mortalities in the yellow spotted salamander, which breeds in temporary meltwater pools, have been observed in New York State where the acidity of the meltwater pools was 1.5 pH units lower than that of nearby permanent ponds. Population densities of the bullfrog and woodfrog were lower in acidic streams and ponds than in those of higher pH sampled in Ontario. These data are very limited and therefore the extent of the problem is unknown.

Atlantic salmon populations have disappeared from nine rivers in Nova Scotia but remain in rivers in the same area having higher pH due to greater alkalinity. Decreases in alkalinity and the pH of water over time have been observed in some low pH rivers in Nova Scotia. However, historical chemical data do not exist for the period of major decline in angling success nor do they exist for rivers in which fish declined.

Detailed studies of watersheds and clusters of lakes have been carried out in regions of North America and Scandinavia containing low alkalinity lakes and streams under a range of sulphate deposition *rates. The results of those studies conducted in North America are summarized below.*

There have been no reported chemical or biological effects for regions currently receiving loadings of sulphate in precipitation at rates less than about 20 kg/ha.yr.

Evidence of chemical change exists for some waters in regions currently estimated or measured to be receiving between about 20-30 kg/ha.yr sulphate in precipitation. In Nova Scotia rivers, 40 years of historical records document reductions in angling success for Atlantic salmon in nine rivers of low pH. Records over later periods for other nearby rivers document decreases in alkalinity and pH. In Maine there is evidence of pH declines over time and loss of alkalinity from some surface waters. In Muskoka-Haliburton historical evidence documents loss of alkalinity for one lake and pH depressions in a number of lakes and streams. Fish confined to the inlet of one lake died during spring melt. In the Algoma region there are elevated sulphate and aluminum levels in some headwater lakes.

Long-term chemical and/or biological effects and short-term chemical effects have been observed in some low alkalinity surface waters experiencing loadings greater than about 30 kg/ha.yr. In Quebec, sulphate concentrations in surface waters decrease towards the east and north in parallel with the deposition pattern of sulphate. Sulphate concentrations are equal to or greater than the bicarbonate concentration in some lakes in the southwest part of the province. In the Adirondack Mountains of New York comparison of data from the 1930s with recent surveys has shown that more lakes are now in low pH categories. The relative contribution of natural and anthropogenic sources to acidification of these lakes is not known. The New York Department of Environmental Conservation has concluded that at least 180 former brook trout ponds are acidic and no longer support brook trout, although a direct association with acidic deposition has not been established. In the Hubbard Brook study area in New Hampshire there are pH depressions in some streams during snowmelt of 1 to 2 units.

In the watershed studies summarized above, sulphate in precipitation was used as a surrogate for total acid loading. Sulphate in precipitation can be reliably measured. It is recognized that dry deposition of sulphate and sulphur dioxide, and the wet and dry deposition of nitrogen oxides, nitric acid, particulate nitrate and ammonia, as well as other compounds, also contribute to acidic deposition. The use of a single substance as a surrogate for acidic loadings adds unknown error owing to site-to-site variability in: (1) composition of deposition, and (2) ability of watersheds to neutralize incoming acidity. Wet and dry deposition of sulphur compounds appeared to predominate in long-term acidification.

Insufficient data are available to related nitrate deposition to short-term water quality effects. Therefore, we are unable to develop nitrate loading/response relationships.

The terrestrial mapping analysis for eastern Canada has demonstrated that the watersheds in which some surface waters have been observed to experience effects are representative, in terms of soil and geological characteristics, of larger areas of eastern Canada. The level of variability within terrain classes is not known.

An alkalinity map of the U.S. shows the location of regions where the mean alkalinity of most of the sampled surface waters is less than 200 μeg/L. There is reason to believe that some of these low alkalinity surface waters could experience effects similar to those noted in detailed study sites receiving similar total acidic deposition loadings. However, quantification of the number of lakes and rivers in both countries susceptible to acidification at specific loading rates would require validation of mapping methodologies and increased information on loading rates and the chemistry of lakes and streams. The present empirical evidence covers a broad spectrum of physical and climatological conditions across northeastern North America and therefore provides a basis on which to make only qualitative judgements regarding relationships between acidic loading rates and effects.

Based on the results of the empirical studies, interpretation of long-term water quality data and studies of sediment cores that have been reviewed, we conclude that acidic deposition has caused long- and short-term acidification of some low alkalinity surface waters in Canada and the U.S. Based on our understanding of the acidification process the Work Group concludes that reductions from present levels of total sulphur deposition would reduce further chemical and biological alterations to low alkalinity surface waters currently experiencing effects and would lead to eventual recovery of those waters that have been altered by deposition.

The U.S. members conclude that reductions in pH, loss of alkalinity, and associated biological changes have occurred in areas receiving acidic deposition, but cause and effects relationships have often not been clearly established. The relative contributions of acidic inputs from the atmosphere, land use changes, and natural terrestrial processes are not known. The key terrestrial processes which provide acidity to the aquatic systems and/or ameliorate atmospheric acidic inputs are neither known or quantified. The key chemical and biological processes which interact in aquatic ecosystems to determine the chemical environment are not known or quantified. Based on this status of the scientific knowledge, the U.S. Work Group concludes that it is not now possible to derive quantitative loading/effects relationships.

1.3 TERRESTRIAL ECOSYSTEM IMPACTS

The effects of transboundary air pollution on terrestrial ecosystems have been reviewed on the basis of direct effects on vegetation, effects on soils, and effects on wildlife.

1.3.1 Effects on Vegetation

Three main pollutants are of concern with regard to vegetation effects. These pollutants are sulphur dioxide, ozone, and acidic deposition. Ozone and acidic deposition occur at concentrations above background levels at long distances from emission sources. Sulphur dioxide is more of a concern to vegetation in proximity to point sources of emissions than at long distances, where dispersion effects can reduce atmospheric levels to those of background.

1.3.1.1 Sulphur Dioxide

Near point sources, the adverse effects of sulphur dioxide on vegetation can be both visible and subtle (without development of visible foliar injury). Visible effects can be associated with both doses of high concentrations of sulphur dioxide over short periods of time and low concentrations over extended periods. However, in a few specific cases, atmospheric sulphur dioxide deposition may have beneficial effects on agricultural vegetation grown on borderline or sulphur deficient soils.

Visible effects of sulphur dioxide have occurred on pine forests in Canada subjected to average growing season concentrations of sulphur dioxide of 0.017 ppm. Visible injury to the perennial foliage of coniferous trees results in premature needle drop, reduced radial and volume growth and early death of trees. Reduced growth and yield of crops without the development of visible injury have also been found in certain field experiments.

Annual doses of sulphur dioxide of 0.02 ppm have been associated with habitat modifications in grasslands and the elimination of certain sensitive species of lichens near point sources. Lichens may be markedly affected by sulphur dioxide and are considered as bioaccumulators of very low level sulphur dioxide exposures. Direct effects including visible injury, effects on reproductive capacity and species mortality have been encountered in the field at concentrations of sulphur dioxide as low as 0.006 - 0.03 ppm annual average.

Despite such documented evidence of instances of direct effects, obviously not all, but probably most exposures to sulphur dioxide on a regional scale are below levels producing phytotoxic reactions. However, long-term, low-dose studies have demonstrated direct effects on lichen communities and indirect effects on several plant species.

1.3.1.2 Ozone

Ozone is the most important long-range transported pollutant with respect to vegetation effects. Air masses carry ozone and its precursors over long distances and can affect crops and forests in rural areas remote from sources. As a specific example, ozone related crop injuries in southern Ontario have been reported associated with high ozone levels in air masses moving across Lake Erie. In the U.S., experimentally derived crop yield losses ranging from 2 to 56% (crop dependent) were equated with seasonal 7 hr/day mean ozone concentrations of 0.06 - 0.07 ppm. Yield losses in the various crops were as follows: kidney bean 2%, soybean 10%, peanut 14-17%, and lettuce 53-56%. Although direct effects of ozone have been documented on forest growth, an estimate of loss is difficult to calculate because of the limitations stated in the main report.

1.3.1.3 Acidic Deposition

Acidic deposition in the form of simulated rain has been demonstrated to induce a variety of direct and indirect effects on plants grown under greenhouse or semicontrolled conditions. Foliar injury, growth reductions, and growth stimulations have been found under these growing conditions following treatment with simulated acidic precipitation. However, visible foliar injury has not been documented in the field for vegetation exposed to ambient levels of acidic precipitation. The potential effects of acidic deposition on forest growth have been difficult to assess because of the complicating influence of other environmental and climatic factors. To date, there have been too few studies to establish a clear relationship on the interactions of acidic deposition/sulphur dioxide/ozone to reach a definitive conclusion on effects.

1.3.2 Effects on Terrestrial Wildlife

Direct effects of acidic deposition on terrestrial wildlife have not been reported and are not considered likely. Nevertheless, in some instances, indirect effects have been suggested through three possible mechanisms:

1) contamination by heavy metals mobilized by acidity;
2) reduction in nutritional value of browse or food source; and
3) loss of browse species or impairment of habitats.

1.3.3 Effects on Soil

Soils vary widely with respect to their properties, 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. The following effects of acidic deposition probably occur and in some cases are supported by observation, although the number of field situations where investigators have been able to attribute acidity to precipitation or to compare present with former soil pH value is small.

On soils derived from calcareous parent materials, the effects of acidic deposition will lead to only insignificant increases in lime requirement, except in situations near strong point emitters. Heavy metal deposition from these same point source emitters may also cause soil toxicities.

On acid soils, the absence of clear effects upon tree growth from radial-increment measurements covering several decades suggests there will be no short-term effects attributable to acidic deposition.

From the few field situations where earlier investigations permit a comparison over a reasonable time-frame, there is evidence that less acutely acid soils increase in acidity and lose bases at a faster than normal weathering rate. For acutely acid soils, pH may show only minor changes, while over the same period moderate to appreciably larger amounts of soil aluminum are mobilized. These depend upon whether the forest cover is deciduous (e.g., beech) or coniferous (e.g., spruce).

From one comprehensive field investigation, it has been suggested that the additional amounts of aluminum brought into solution kill feeding roots and permit the invasion of fungi causing tree "dieback", but it is not known whether this phenomenon would occur on other sites and soils. What appears well established from a variety of hydrological, limnological and catchment studies is that acidic deposition can lead to the release of additional amounts of soluble aluminum, thus disturbing previous aluminum/calcium ratios in soils, sediments and streamwaters. An eventual reduction in base status and fertility is suggested.

The sulphate component of acidic deposition appears to be adsorbed by soils containing active aluminum and iron oxides, but where these are absent or present in limited amounts, sulphate functions as a balancing anion, leading to the leaching loss of bases and other cations.

The fate of the nitrate component depends upon wet precipitation/snowmelt characteristics. Nitrate, reaching the surface organic horizons of acid forest soils is held there for assimilation by tree roots during the growing season. There are, however, forested catchments in the northeast where nitrate is passed to water bodies.

The lack of appropriate experimental approaches from which the effects of acidic deposition on soil might be assessed and safe deposition ceilings estimated, has caused scientists to exploit indirect or special situations. These include working near strong point sources, studying soils treated with acidifying fertilizers, and designing lysimetric experiments incorporating simulated acid rains. From such approaches, a variety of soil effects have been demonstrated, usually of an undesirable nature, but at the present time the problem remains of quantifying the dose-response reactions in the field situations.

1.3.4 Sensitivity Assessment

Regions which may be sensitive to acidic deposition have one or more components (i.e., forests, aquatic life, soil, or water) susceptible to degradation under the influence of acidic deposition. Relative sensitivity of these components is reflected in the rate at which an ecosystem component degrades under a particular acidic deposition loading. Different underlying criteria have to be used to represent sensitivity for the different ecosystem components, such as rate of tree growth, characterization of the soil-base status, or water alkalinity. Because so little is known about the acidic deposition dose-response relationships, the underlying criteria are often imprecise. Therefore, relative sensitivity can only be approximately represented or mapped, and then perhaps for only a few species, ecosystems or theoretical effects.

Attention is focused on the sensitivity of soils and bedrock because results from studies which address vegetation and ecosystem effects are limited and not well understood at this time. In the approach used, the emphasis has been to map a combination of potentially important soil attributes as a best available indicator of relative sensitivity. Soil attributes incorporated include texture, depth to carbonate, pH and cation exchange capacity, as well as glacial and bedrock features. Incompleteness of survey data for certain important properties (e.g., sulphate adsorption capacity, internal proton production, and the role of dry deposition) precludes their use in identifying detailed sensitivities of land or aquatic resources. As far as possible, the eastern parts of the United States and Canada are mapped using a similar conceptual framework which indicates the general extent of areas of different possible sensitivities to the effects of acidic deposition. The significance of these categories will increase as more effects are documented.

1.4 HUMAN HEALTH AND VISIBILITY

1.4.1 Health

Available information gives little cause for concern over direct health effects from acidic deposition. The potential indirect health effects associated with transboundary air pollution discussed are: (1) contamination of the food chain with metallic substances, especially mercury; (2) leaching of watersheds and corrosion of storage and distribution systems, leading to elevated levels of toxic metals; and (3) health implications of recreational activities in impacted waters.

The principal conclusions of the report are as follows:

> Acidification of lakes is a concern because it may be related to increased mercury contamination of the food chain, thus increasing the health risks associated with high levels of consumption of contaminated organisms. A correlation exists between low pH in lakes and higher mercury concentrations in some species of fish, although the mechanism for this accumulation is not presently known. In addition to the effects produced by acidic deposition, the increased input of anthropogenic sources (air or water effluents) of mercury and other heavy metals may further complicate the issue and lead to health problems when affected fish are consumed by humans in large amounts.
>
> Acidic deposition may liberate metals in some groundwaters, surface drinking water supply systems and cisterns. However, groundwater may also be acidic due to increased partial pressure of CO_2 at depths of a few metres or more. This should not be confused with acidity due to atmospheric deposition. Elevated metal concentrations in acidified drinking water supplies have been found. Lead levels in tap water from cisterns were much higher than those found in the source water; about 16% of the households sampled in one western Pennsylvanian county had tap water levels in excess of the United States drinking water standards. Surface drinking water supplies which are not treated (i.e., small communities or individual water supplies) are susceptible. No adverse health effects resulting from consumption of such water have been reported. Concern has been expressed that recreational activities in acidified waters, such as swimming, may prove to cause eye irritation. To date, no compelling evidence has been forthcoming that indicates that humans are being adversely affected by these waters in their current state.
>
> With respect to the direct inhalation of transported air pollutants for which standards exist (i.e., particulate matter, photochemical oxidants, sulphur oxides, and nitrogen oxides), no adverse human health effects are anticipated, providing the ambient air quality standards are not exceeded (see Table 5-2). However, in regions where transboundary air pollution contributes to the violation of the standard, health related problems cannot be ruled out.
>
> Although some concern has been expressed over the effects of acid sulphates on mortality/morbidity, the available data appear insufficient to single out this species as the sole pollutant of

concern in the sulphur-particulate complex. As with the gaseous pollutants, the long-range transport of particulate matter should only be viewed as a concern when violation of the ambient air quality standards occur.

1.4.2 Visibility

Effects of transboundary air pollution on visibility are related to fine particle air quality and only indirectly to acidic deposition. The major precursors of acid deposition that can significantly affect visibility are sulphuric acid and various ammonium sulphate aerosols. These form a large fraction of the fine particle loadings that dominate visibility impairment from anthropogenic sources. Available data do not suggest that nitrates (predominantly in the vapour phase) play a significant role in impairment of visibility, but visible brown plumes from NO_2 have been reported at a distance of 100 km from a few isolated point sources.

From available information on background and incremental fine particle 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 the eastern U.S. and portions of southern and eastern Canada between 1950 and 1975, with stable or small improving trends since that time. These changes may be associated with changes in the level and distribution patterns of sulphur oxide emissions.

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. Studies of the value of visibility and public perception indicate that the public cares about visibility and is willing to pay for maintaining or improving it. Accurate economic assessments are not, however, available for eastern North America.

1.5 MAN-MADE STRUCTURES

Certain airborne chemicals can accelerate deterioration of materials. There is evidence that materials in urban areas of Europe and North America have suffered and are suffering from exposure to these pollutants. Materials at risk include statuary and structures of cultural value as well as commonly used construction materials. In the present discussion, exterior surfaces are the focus of interest.

It is reasonable to assume that acidic 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 mask the effects resulting from long-range transport of acidic deposition.

The principal findings of the Work Group are:

The majority of sensitive materials tend to be located in urban/suburban areas. However, materials at risk cannot be assumed to be proportional to population density.

Relationships between concentration of corrosive gases and damage are better documented than relationships between acidic precipitation or particulates and deterioration.

The main groups of materials which are damaged by outdoor air pollutants are: metals, coatings and masonry. The pollutants are delivered to the surfaces in wet and dry form.

It is generally accepted that SO_2 is the primary species causing damage to materials. The importance of nitrogen compounds is closely related to its particular species and may increase with the predicted increases in NO_x emissions relative to SO_2 emissions.

Chemical degradation processes include deterioration of calcareous building materials by the removal of calcium carbonate through conversion to calcium sulphate and the removal of protective corrosion products on metals, particularly zinc and copper.

Mechanical deterioration of masonry occurs when calcium sulphate enters the porous material and causes internal rupturing due to the pressure of crystallization or hydration.

Regional field studies, chamber tests and atmospheric corrosion sites have indicated the nature and extent of accelerated corrosion associated with metal-pollutant interactions. Dose-response relations have been determined for SO_2 and low-carbon steel and zinc. In some areas of eastern North America, urban centres have experienced extensive and significant deterioration of zinc coverings.

Common materials of construction at risk include, limestone, carbon steel and galvanized steel sheet. Carbon steels must be coated in order to provide useful service life and, thus the coating becomes the material at risk.

Dose-response relations have been determined for sulphur dioxide and ozone for some paints and coatings. In some urban centres, ozone can have a significant impact on the durability of elastomers.

For porous materials such as masonry, the long-term accumulation of pollutants is a major concern especially for deterioration associated with sulphate.

Materials at risk and some active corrosion agents have been identified in numerous field and laboratory tests. Confidence in dose-response relationships is weakened in some cases because of incomplete monitoring of air quality and meteorological parameters in field tests.

1.6 METHODOLOGIES FOR 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.

The following are the conclusions of the Work Group:

A number of methodologies have been reviewed but presently the basic conclusion of this effort is that application of available approaches for conducting a benefit/cost analysis must either omit real but intangible benefits or include a wide uncertainty range. Despite these real limitations, these methodologies can provide a useful estimate of benefits for some sectors.

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 most of these techniques at this time. For some sectors, differences in producers' income may provide benefit estimates even in the absence of explicit dose-response data.

The value of the secondary benefits can be estimated for specific economic sectors and regions, to derive a partial 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 issues of property rights.

The initial design of future research efforts to document the effects of acidic deposition should reflect the data requirements for an economic benefit estimate. Interdisciplinary cooperation at the design stage is the best way to ensure results which are amenable to economic analysis.

1.7 NATURAL AND MATERIAL RESOURCE INVENTORY

1.7.1 Introduction

A natural and material resource inventory is a necessary component of an assessment of the benefits of emission reductions. Consequently, the Work Group attempted to compile an inventory for aquatic, terrestrial and man-made resources.

In all cases, the sectoral inventories are incomplete and sometimes lacking in sufficient detail. For example, not only does the aquatic inventory not include an accurate accounting of lakes and streams with their associated alkalinity, but it also does not include a consideration of the population size and diversity of aquatic organisms depending on the maintenance of a stable aquatic environment. Similarly the terrestrial inventory has been limited to only a consideration of hardwoods and softwoods because a comprehensive inventory at the species level is presently lacking.

The inventory has been established on the basis of sulphate deposition regimes coincident with the location of terrestrial features such as soils and bedrock which have a limited capacity to reduce the impact of acidic deposition on aquatic regimes. In no cases were there sufficient data to indicate which particular resources are being damaged by acidic deposition. Thus, this inventory is a categorization of resources potentially at risk, rather than a list of resources now adversely affected by acidic deposition. The completion of this inventory has served to underline the considerable weakness which exists in our ability to adequately quantify the extent of the resource at risk.

1.7.2 Aquatic - United States

Approximately 36,000 km^2 of the eastern U.S. surface water area (25%) is located in areas of low and moderate potential to reduce acidity (high and moderate sensitivity) and of deposition greater than 20 kg/ha.yr sulphate in precipitation. Only 24% are located in areas with a high potential to reduce acidity (low sensitivity) and of deposition greater than 20 kg/ha.yr sulphate in precipitation. The actual surface water area would be more restricted if data had been available on surface water chemistry (i.e., alkalinity). Additional refinements on the inventory should include data on this variable as well as more accurate measurements of surface water area.

1.7.3 Aquatic - Canada

Approximately 52,000 km^2 of surface water area is estimated to be at risk in areas with deposition exceeding 20 kg/ha.yr. Of this total, about 54% (28,000 km^2) is located in areas with a low potential to reduce acidity (high sensitivity). The inventory could be improved by better data availability on actual surface areas of waters and kilometres of rivers and streams. Moreover, actual data on aquatic alkalinity and aquatic biota will be required to define more accurately the extent of the resource at risk.

1.7.4 Agriculture - United States

Major crops in the eastern U.S. (corn, soybeans, hay, wheat, tobacco and potatoes) are grown under varying sulphate deposition regimes. Soybeans and tobacco are the only ones, however, with approximately 20% of their yield grown under sulphate deposition greater than 40 kg/ha.yr. For the other crops, less than 10% of their total yield is grown under sulphate deposition greater than 40 kg/ha.yr.

1.7.5 Agriculture - Canada

Many of Canada's most valuable crops are grown in areas of high deposition. These include both grains and vegetables. Importantly, for 6 of the 12 crop types included in the inventory, more than 50% of their individual total yields is grown in areas where sulphate deposition exceeds 40 kg/ha.yr. Only 4% or less of each crop is grown in areas experiencing annual deposition levels of 10-20 kg/ha.yr sulphate in precipitation.

1.7.6 Forests - United States

The annual forest growth in those states east of the 100° meridian in 1977 was 476 million m^3. Approximately 10% of this combined hardwood and softwood growth occurs under sulphate deposition regimes greater than 40 kg/ha.yr. Over 75% of the growth occurs under sulphate deposition regimes between 20-40 kg/ha.yr.

1.7.7 Forests - Canada

Canadian forest growth occurs in a slightly different pattern than in the U.S. Of the total annual yield of 150 million m^3, about 10% of the hardwood growth is located in the highest deposition area, but only 1% of the softwood growth and 8% of the mixed growth.

Approximately 64% of the hardwood and 70% of the mixed growth occurs in the area of moderate deposition, but only 28% of the softwood growth.

1.7.8 Man-Made Materials - United States

There is no adequate U.S. inventory of renewable or cultural resources. Past efforts to create an inventory of renewable resources have combined per capita material estimates and census data on population distribution. These per capita estimates have been shown to be very site specific and are not an adequate basis for creating a national inventory. The only inventory prepared by the Work Group is one on historic resources exposed to various levels of ambient sulphur dioxide.

1.7.9 Man-Made Materials - Canada

As in the case in the U.S., Canada has no adequate inventory of renewable materials or cultural resources. The historic resources inventory includes historical landmarks, buildings and monuments and parks. The inventory presented here indicates the numbers of each of these which are located in 2 categories of deposition: greater than 40 kg/ha.yr and under 40 kg/ha.yr. Geographically, these resources are located in the area around Quebec City, one of the earliest towns in Canada, and in southwestern Ontario (Windsor-Sarnia).

1.8 LIMING

Mitigation of the effects of acidic deposition by adding neutralizing agents to the receptors has been an obvious action to be considered. Limestone is most often used although other chemicals have been tried. The term "liming" has often been used to describe such treatments and in this section will be used to describe artificial neutralization experiments regardless of the chemical or chemicals actually used.

Extensive work has been carried out on aquatic systems affected by acidic deposition. However, the application of lime products to aquatic resources will not address the potential for damage to forests or buildings and structures.

1.8.1 Aquatic Systems

Liming will not eliminate all problems associated with acidification of surface waters but may be necessary on a limited basis as a means of temporarily mitigating the loss of important aquatic ecosystem components. However, it cannot be used in all situations.

Further, its long-term viability and impact on fish populations needs additional study.

The following observations support this overall conclusion:

> Liming can only treat certain aquatic situations, mostly lakes, and must be repeated periodically. It is not practical to locate and treat small temporary meltwater pools because of their large number and widespread occurrences. These pools, however, are an important habitat for amphibians and dependent wildlife. The technology for reliably treating high discharge rivers (such as the salmon rivers of the eastern North American coast) is not available.
>
> Swedish experimental liming programs report some success in being able to promote the growth and reproduction of fish populations. However, all results to date are from experiments which have been run for five years or less. The long-term effectiveness of liming to protect aquatic ecosystems is not known. As a result of liming acidic waters, aluminum poisoning of salmon and rainbow trout has been encountered.
>
> No experimental data on liming are available for surface waters containing some of the important sport fish species in North America, such as muskellunge, walleye and bass.
>
> Anthropogenic acidic deposition will alter the original uniqueness of "wilderness" aquatic environments. The additions of neutralizing agents will further modify the character of these ecosystems and will not preserve the "wilderness" nature of these waters.

1.8.2 Terrestrial Liming

The liming of forest lands to neutralize potential acidic deposition effects on terrestrial ecosystems has serious limitations. These include evidence that liming would not prevent direct foliar injury; that under certain conditions lime additions can disrupt important soil biological relationships and adversely affect forests; and that the area coverage required would tend to be so large as to be economically prohibitive.

1.8.3 Drinking Water Supply

Liming techniques have been effectively applied to the treatment of low pH municipal supplies. The per capita costs range from $0.18 to $0.57.

SECTION 2

INTRODUCTION

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 acidic 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 ACIDIC DEPOSITION AND POTENTIAL FOR LARGE-SCALE EFFECTS

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

Over most of this area, acidic deposition, 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 compounds. Although acidic components of acidic 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.

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 altered 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. The hydrogen ion load (mass per area per time) affects the extent of chemical reactions in soils and other materials whereas the concentration affects the rates of reactions. For example, the total amounts of chemical constituents leached from soils annually is more closely related to the annual load on hydrogen ion than to the concentration in any precipitation event. The load is also used in the following ways: (1) in comparison with loads of acid-forming ions to determine the influence of acid neutralizing materials in atmospheric deposition; (2) to simulate the acidity of streams receiving snowmelt runoff from an accumulated snowpack; and (3) to determine the acidity of lakes which average the inflow from a number of runoff events.

The effect of acidic deposition 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 acidic deposition are characterized as having thin soils, low in exchangeable bases and cation exchange capacity, overlying granitic bedrock (noncalcareous). Figure 2-1 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 3.5 and 4.5 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 portions of the Precambrian Shield areas of Ontario and Quebec. Other areas may be considered sensitive based on soil characteristics or other variables.

What is known of the complexity and geographic range of acidic deposition ecosystem interaction and long distance transport of air pollutants pose a significant dilemma for federal, state and provincial regulatory agencies. Aquatic life is apparently being damaged by regional air emissions, but air quality standards were not designed to protect water quality. Nevertheless, important resources over a large part of the continent appear to be at risk and new multinational control approaches may be required.

2.1.1 Methods of Measuring Effects

Lakes, rivers, and watersheds act as "collectors" of atmospheric pollution. Therefore, one research approach has been to study lakes and watersheds as large-scale "calibrated" collectors since the surface environment experiences a total loading that is 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 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

Figure 2-1. Regions of North America containing lakes that may be sensitive to acidification by acidic deposition, based on bedrock geology, showing where calibrated watershed studies on sensitive areas are in progress (modified from Galloway and Cowling 1978).

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 2-1).

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 acidic 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), show this factor plus dry deposition to be 1.9 for central Norway. Regions of proportionately high evaporative losses are expected to have higher observed sulphate concentrations in lake water than are predicted by the Henriksen equations for a given atmospheric loading rate (Glass and Brydges 1981). These processes vary with precipitation and temperature patterns between regions, from one watershed to the next, and from areas having strong topography.

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 acidity in rainfall 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 uses of home wood burning stoves 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 3B (Table 2-1).

Substantial increases in these emissions are expected if consumption of fossil fuels continues to increase. Estimated emission rates for other constituents from the burning of coal are presented in Table 2-2. A recent U.S. National Academy of Sciences report (NAS 1978) further estimated that from 25 to 30% 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. Rasmussen et al. (1975) estimated that greater than 90% of the global anthropogenic SO_2 is emitted from the Northern Hemisphere. 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. 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 information about these factors since sensitive receptor areas are often located at considerable distances from the pollutant source regions.

TABLE 2-1. CURRENT EMISSIONS IN THE U.S. AND CANADA (10^6 Tons)

	U.S.A. (1980 Estimated)		CANADA 1979[a]		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
Nonferrous Smelters	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

[a] Inco, Sudbury at 1980 emission rate.

From: Canada/United States Work Group 3A Interim Report "Strategies Development & Implementation" Feb. 1981, Ottawa, Ont.

TABLE 2-2. AIR EMISSIONS FROM A TYPICAL 1000 MW COAL-FIRED STEAM PLANT[a]

Constituent	Mean concentration in coal[b]		Annual air emission (kg/yr)
Major			
Ash	11.4	(%)	2.5×10^6
Total carton	70.3	(%)	10^{10} (as CO_2) 10^7 (as CO)
Total sulphur	3.3	(%)	65×10^6
Water	9.	(%)	450×10^6
Total nitrogen	1.3	(%)	10^6 (as NO_x)
Al	1.3	(%)	0.24×10^6
Ca	0.77	(%)	0.14×10^6
Cl	0.14	(%)	7×10^6 (mostly vapor)
Fe	0.9	(%)	0.31×10^6
K	0.16	(%)	0.062×10^6
Mg	0.05	(%)	0.014×10^6
Na	0.05	(%)	0.02×10^6
Si	2.49	(%)	0.54×10^6
Ti	0.07	(%)	0.034×10^6
Minor			
Organic C	-		5,000.
Fluoranthane	-		35.
Benzo(ghi)perylene	-		14.
Benzo(a)pyrene	-		13.
Benzo(a)pyrene	-		7.
Pyrene	-		13.
Perylee	-		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)	640.
Cr	13.8	(ppm)	1,700.
Cu	15.2	(ppm)	915.
F	61.	(ppm)	15,000. (40% as vapor)
Ga	3.1	(ppm)	172.
Ge	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.
Ra			0.1 (Ci)
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)	2,600.
Th	3.1	(ppm)	96.
Tl	680.	(ppm)	33,000.
U	5.	(ppm)	250.
V	32.7	(ppm)	3,400.
W	3.	(ppm)	90.
Zn	272.	(ppm)	37,000.
Zr	72.5	(ppm)	2,200.

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

[b] 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[a]	Major Source		Estimated Emission kg/yr			Major Identified Sinks	Residence Time[b]
	Anthropogenic	Natural	Anthropogenic	Natural	Concentration $g\ m^{-3}$		Days
SO_2	Combustion of coal and oil (North America)[c]	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 stratosphere; 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; Combustion of oil	Biological processes in forests	27×10^9	175×10^9	1	Photochemical oxidation	-

From:

[a] Rasmussen et al. 1975
[b] Robinson and Robbins 1970
[b] Rodhe 1978
[b] Soderlund and Svensson 1976
[b] Spadding 1972
[b] Stewart et al. 1978
[b] Sze 1977
[b] Liu 1978
[b] Kellogg et al. 1972
[b] Junge 1972, 1974, 1977
[b] Gramat et al. 1976
[c] Galloway and Whelpdale 1980

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 (Figures 2-2 a and 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. Figures 2-3 a and b show isopleths of precipitation for the North American continent. The numbers on the contours represent the average number of centimetres 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 Figures 2-3 a and b 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 or turnover time varies between constituents. A large percentage of compounds with relatively short residence times (a few days) are deposited within tens to hundreds of kilometres from the point of emission. Compounds with longer residence times may travel thousands of kilometres. 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

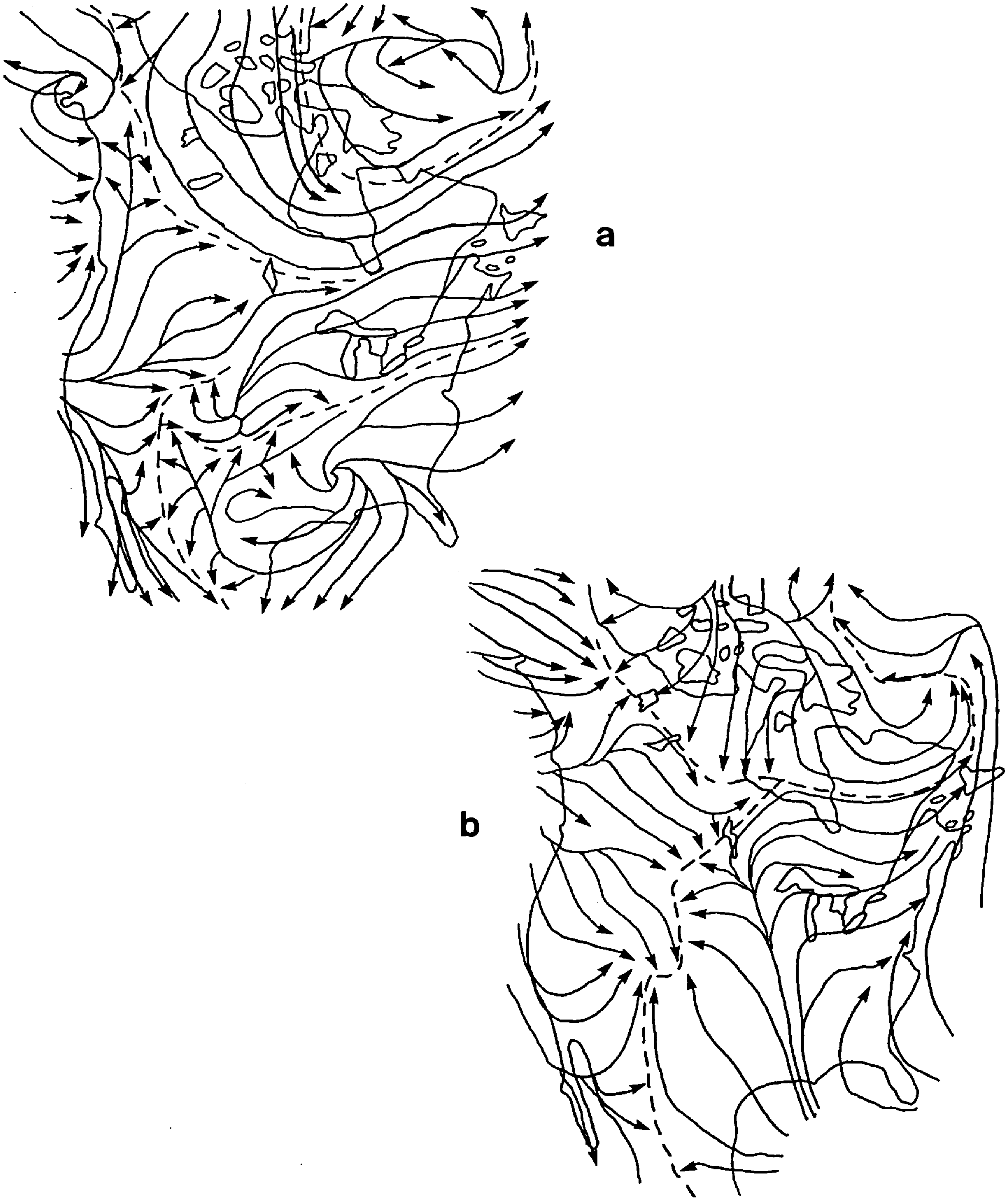


Figure 2-2. Wind patterns for North America based on surface stream-lines for (a) January and (b) July (Bryson and Hare 1974).

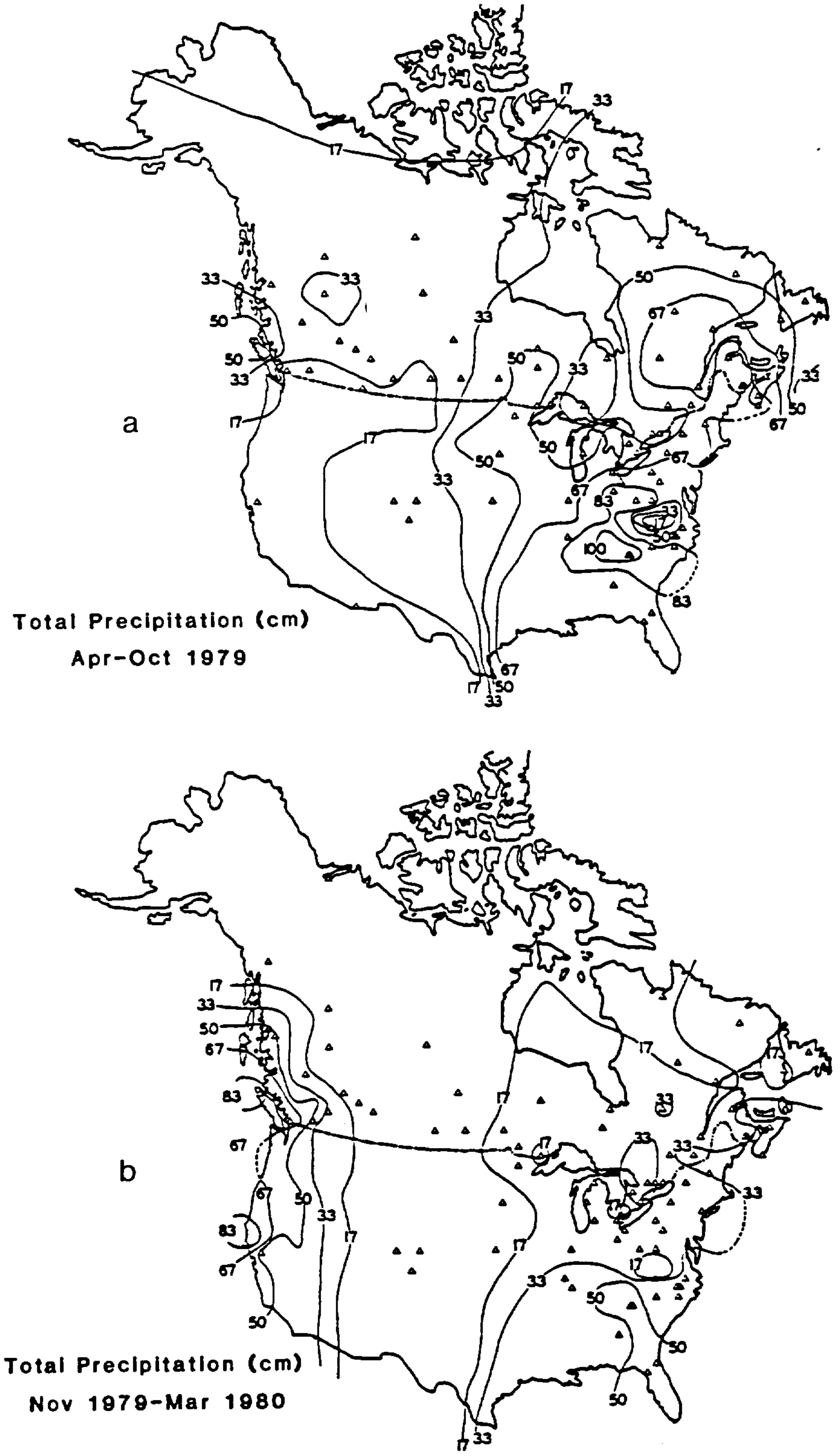


Figure 2-3. Seasonal precipitation for North America patterns, total precipitation as water depth (cm), shown for (a) "Summer" April - October 1979, and (b) "Winter" November 1979 - March 1980. Data reporting sites (△) are from NADP and CANSAP precipitation monitoring networks (Glass and Brydges 1982).

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 (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 Schumann (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 et al. (1979) 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. 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.

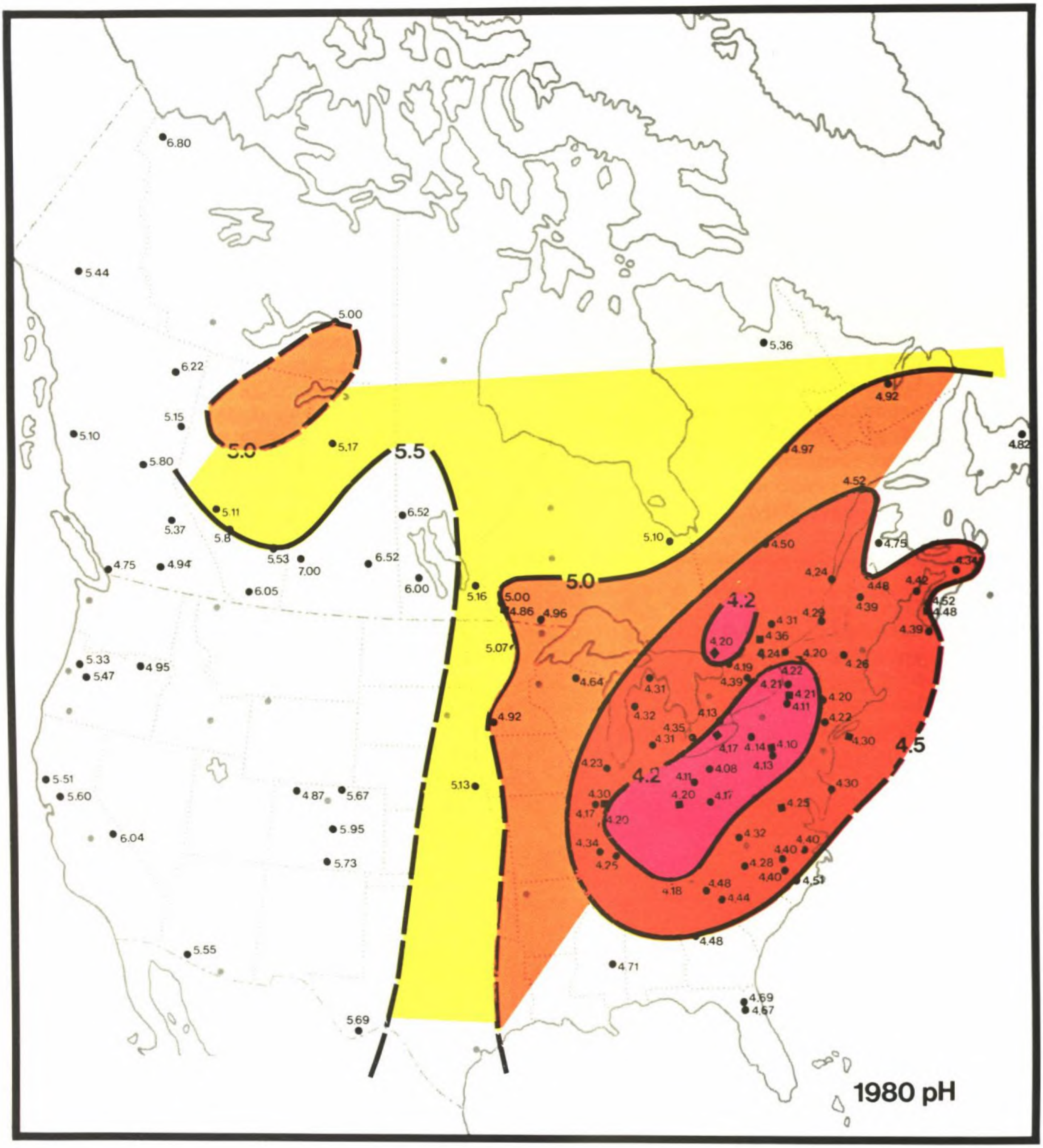
The relative importance of each process (i.e., dry vs. wet deposition), is still being evaluated. Although the results are not fully conclusive, modelling and mean balance studies indicate wet and dry deposition of sulphur compounds are of equal importance in north Europe and North America (Fowler 1980; Haines et al. 1981). Dry deposition seems to be of lesser importance in remote areas. Harvey et al. (1981) conclude that dry deposition is relatively more important than wet deposition 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 acidic deposition 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 amounts of 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 2-4 show large areas of North America which are receiving precipitation with a pH less than 5.6. This results in elevated concentration and deposition of acids to the surface as shown in Figures 2-5 a and b.

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, PAHs 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



Precipitation amount - weighted mean annual pH in North America for the calendar year 1980.

Figure 2-4.

Legend

Canada	**United States**
● CANSAP	● NADP
☐ APN	☐ MAP3S
◆ OME	

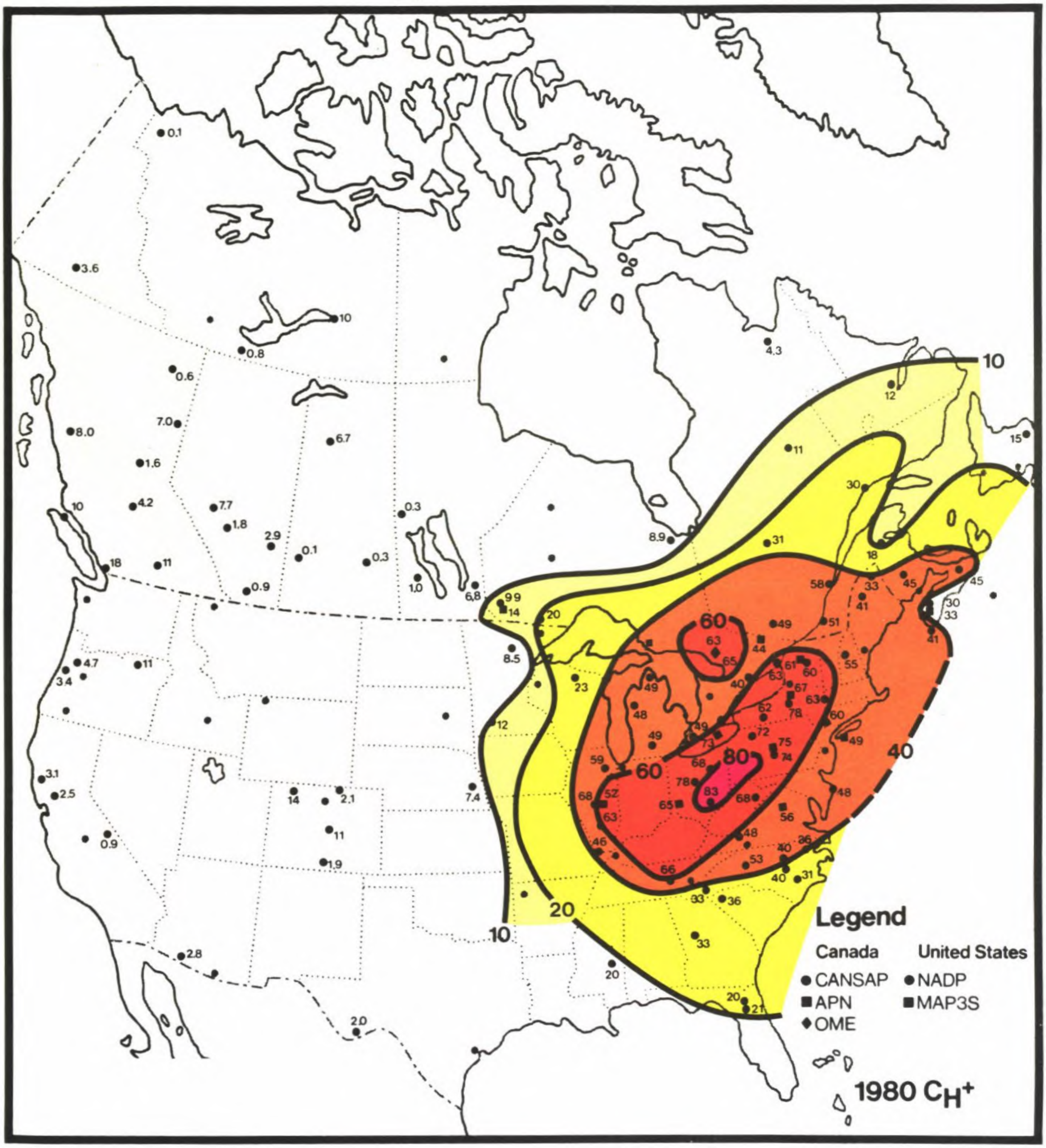
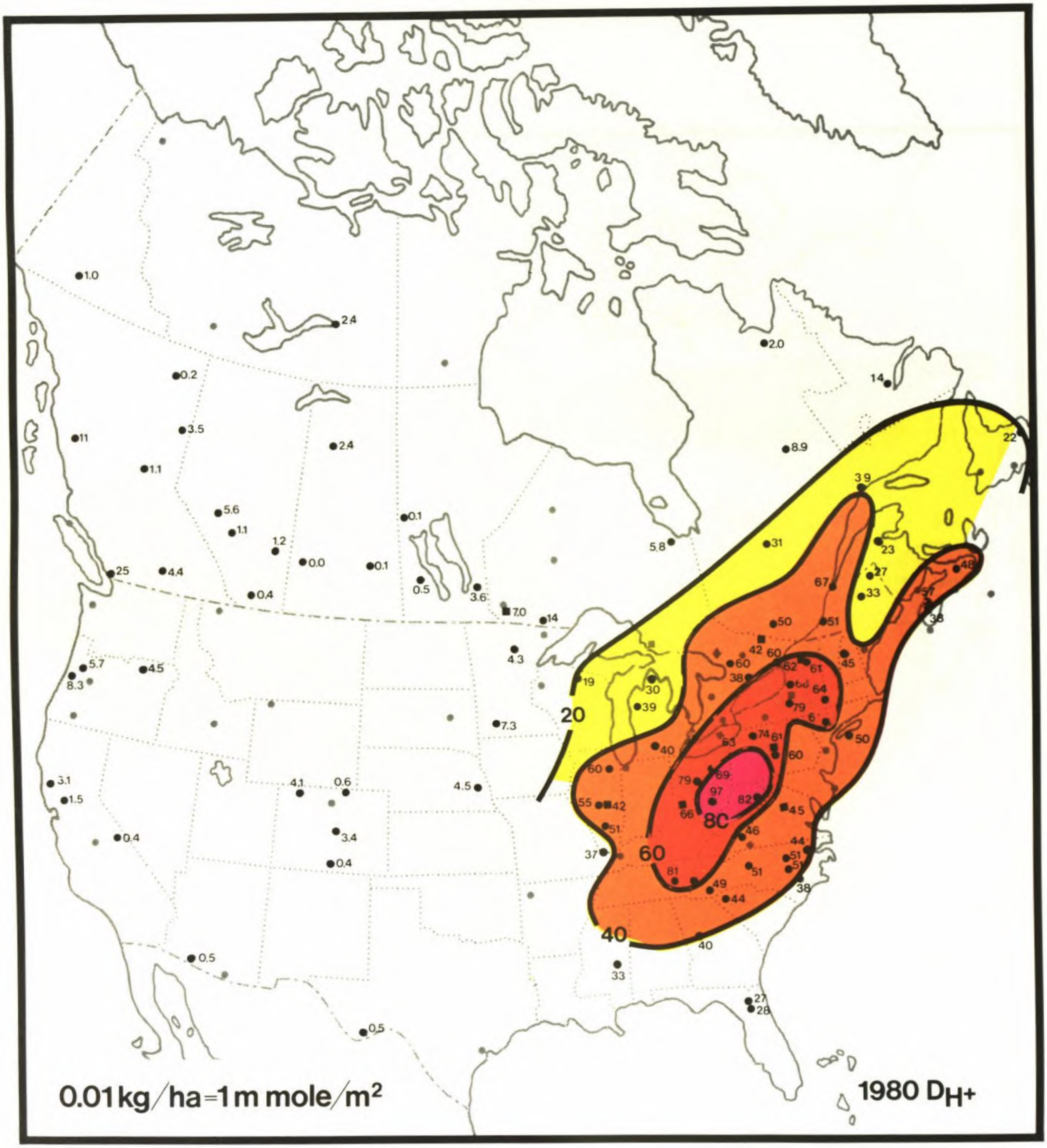


Figure 2-5a. Precipitation amount - weighted mean hydrogen ion concentration in 1980 (μmoles per litre).



Precipitation amount-weighted mean hydrogen ion deposition for 1980 (m moles per square metre).

Figure 2-5b.

Legend

Canada	United States
● CANSAP	● NADP
□ APN	□ MAP3S
◆ OME	

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 4 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 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 2-6, 2-7 and 2-8 illustrate the concentration and deposition patterns of sulphate, ammonium and nitrate ions, respectively. Both sulphate and nitrate ion concentrations are highest in the east with high values also recorded in southern Alberta and Saskatchewan. Table 2-5 defines the conversion factors for ion deposition and concentration.

The percent of normal precipitation for 1980 is shown in Figure 2-9. While most areas received at least 75% of the normal precipitation, others received up to twice as much precipitation as normal.

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)

	ELA[b]	Muskoka-Haliburton[c]	Hubbard Brook[d]	Kejimkujik[a] Park[e]	Sagamore Lake[f]
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

[a] Wet deposition only, ( ) indicating excess sulphate.

[b] Schindler et al. 1976

[c] Scheider et al. 1979

[d] Likens et al. 1977

[e] Kerekes 1980

[f] Johannes and Altwicker 1980

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

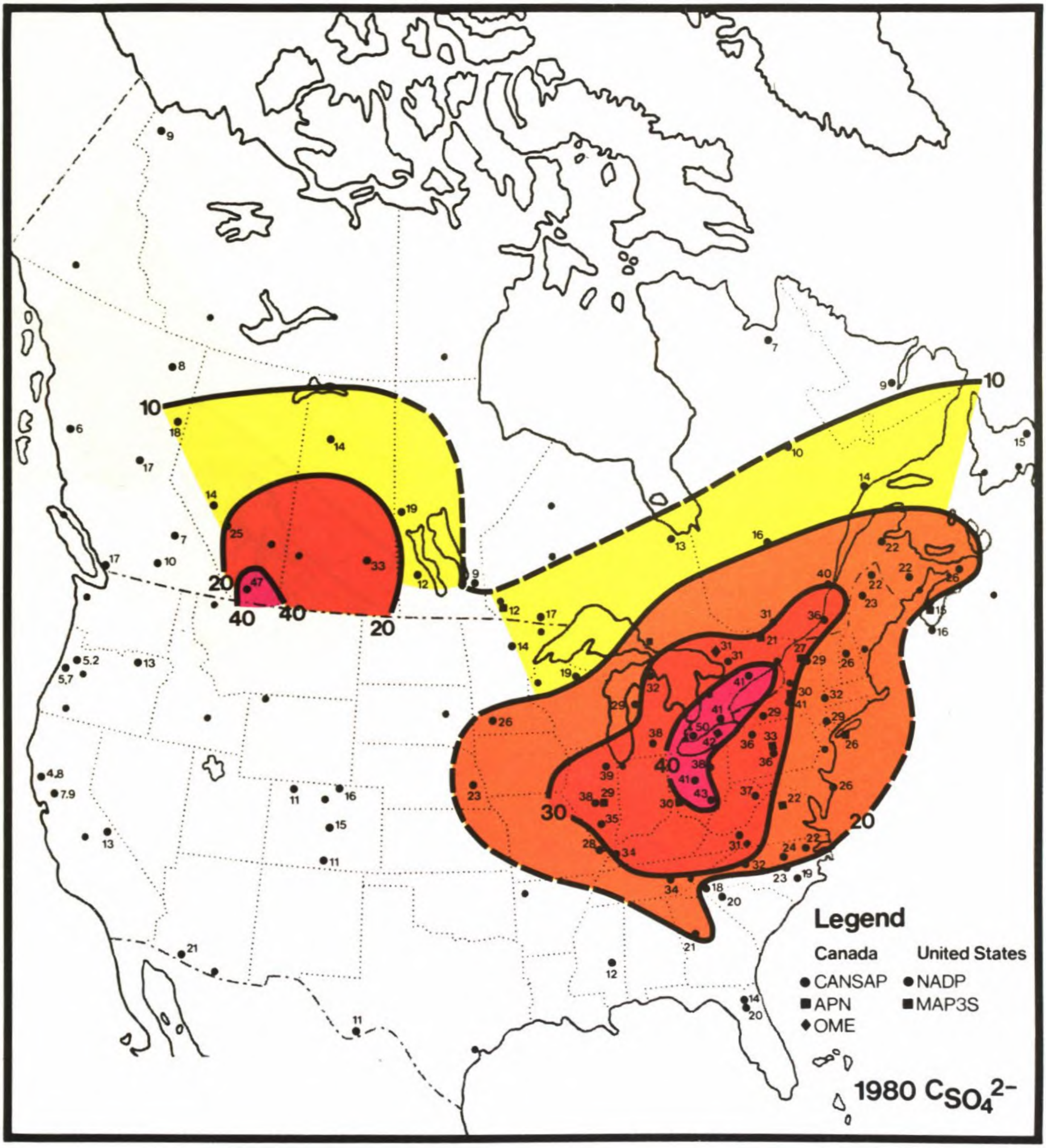
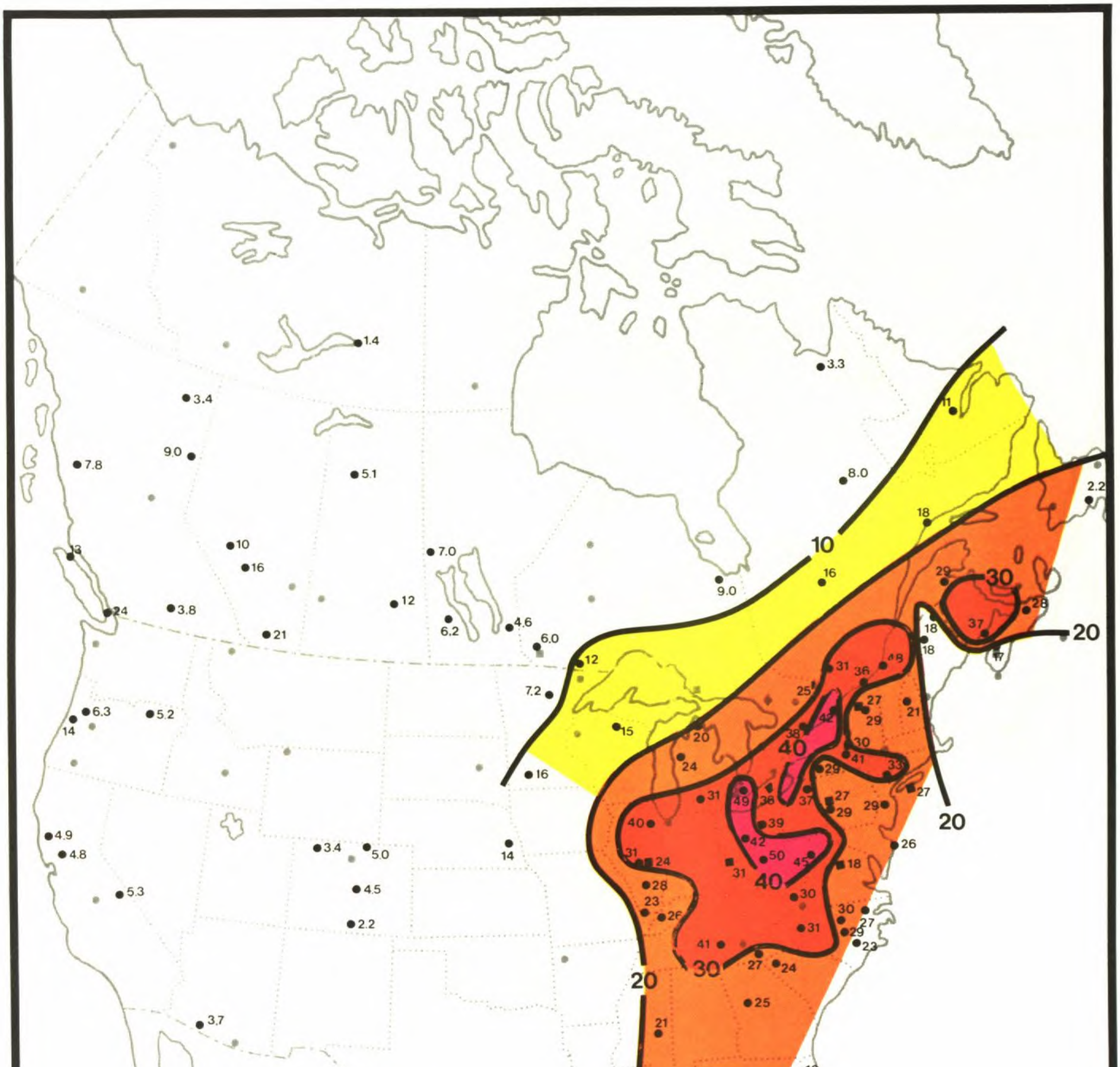


Figure 2-6a. Precipitation amount - weighted mean sulphate ion concentration for 1980 (μmoles per litre).



Precipitation amount - weighted mean sulphate ion deposition for 1980 (m moles per square metre).

Figure 2-6b.

Legend

Canada	United States
● CANSAP	● NADP
☐ APN	☐ MAP3S
♦ OME	

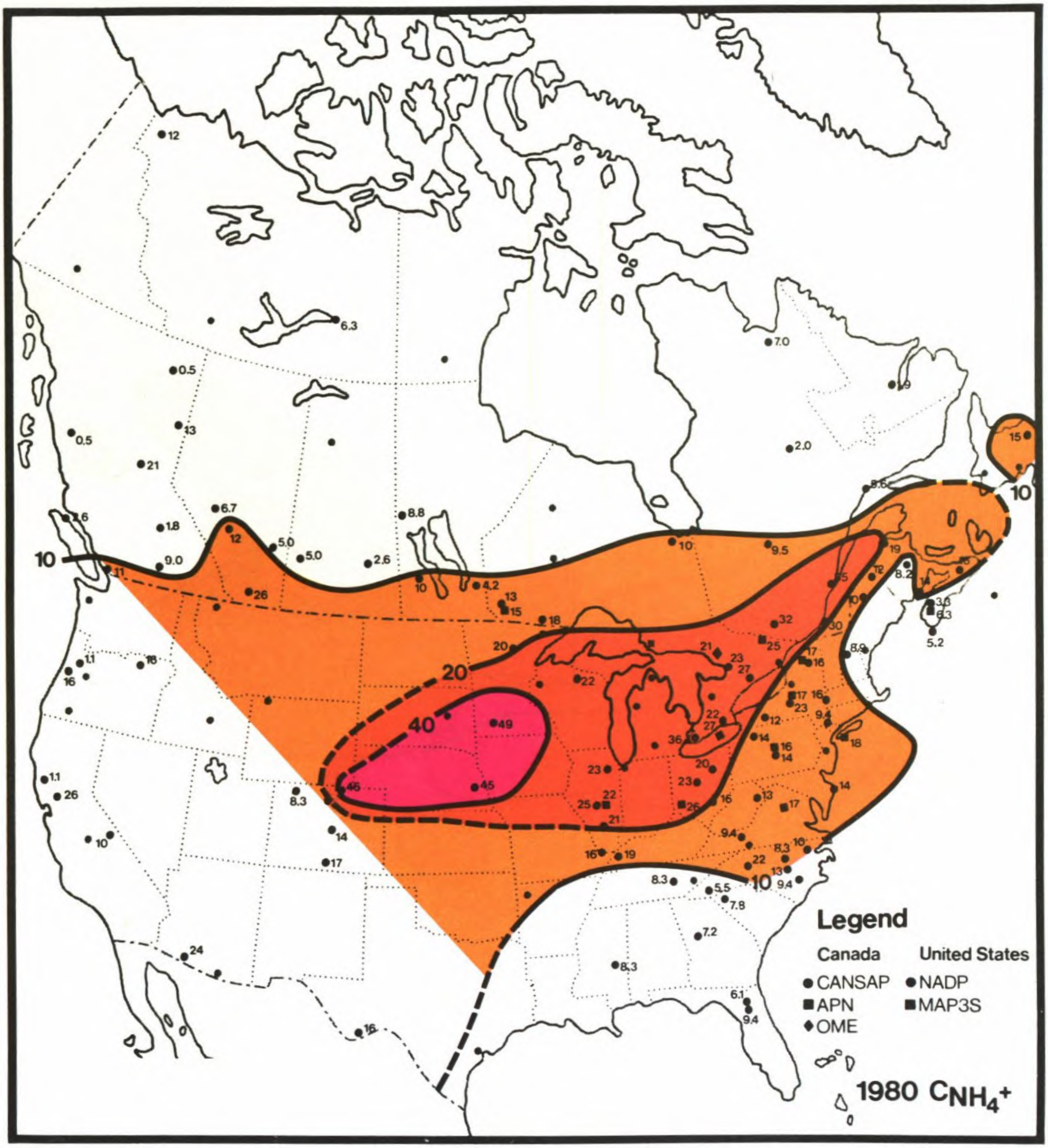
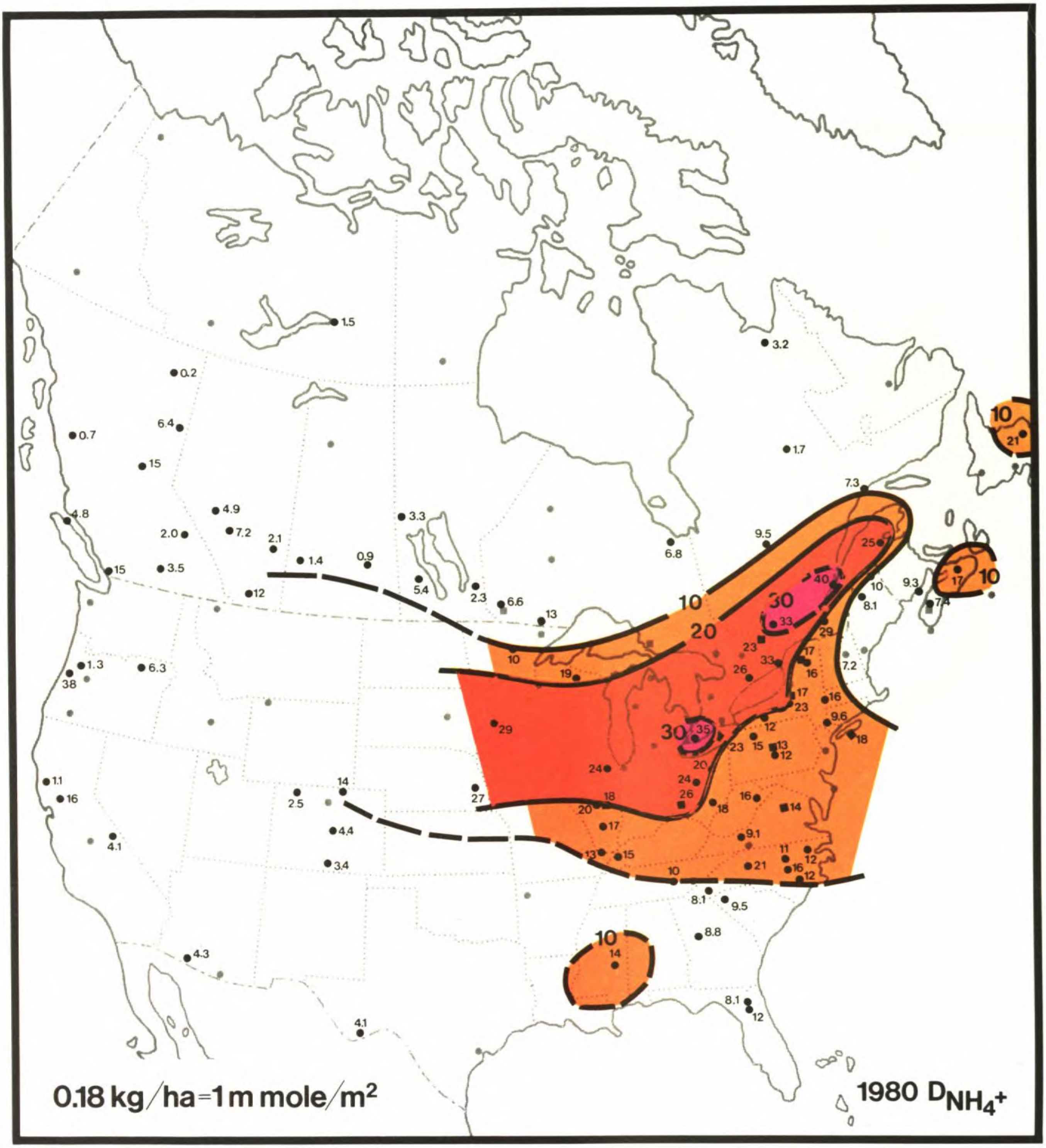


Figure 2-7a. Precipitation amount - weighted mean ammonium ion concentration for 1980 (μmoles per litre).



Precipitation amount - weighted mean ammonium ion deposition for 1980 (m moles per square metre).

Figure 2-7b.

Legend

Canada	**United S**
● CANSAP	● NADP
□ APN	□ MAP3S
◆ OME	

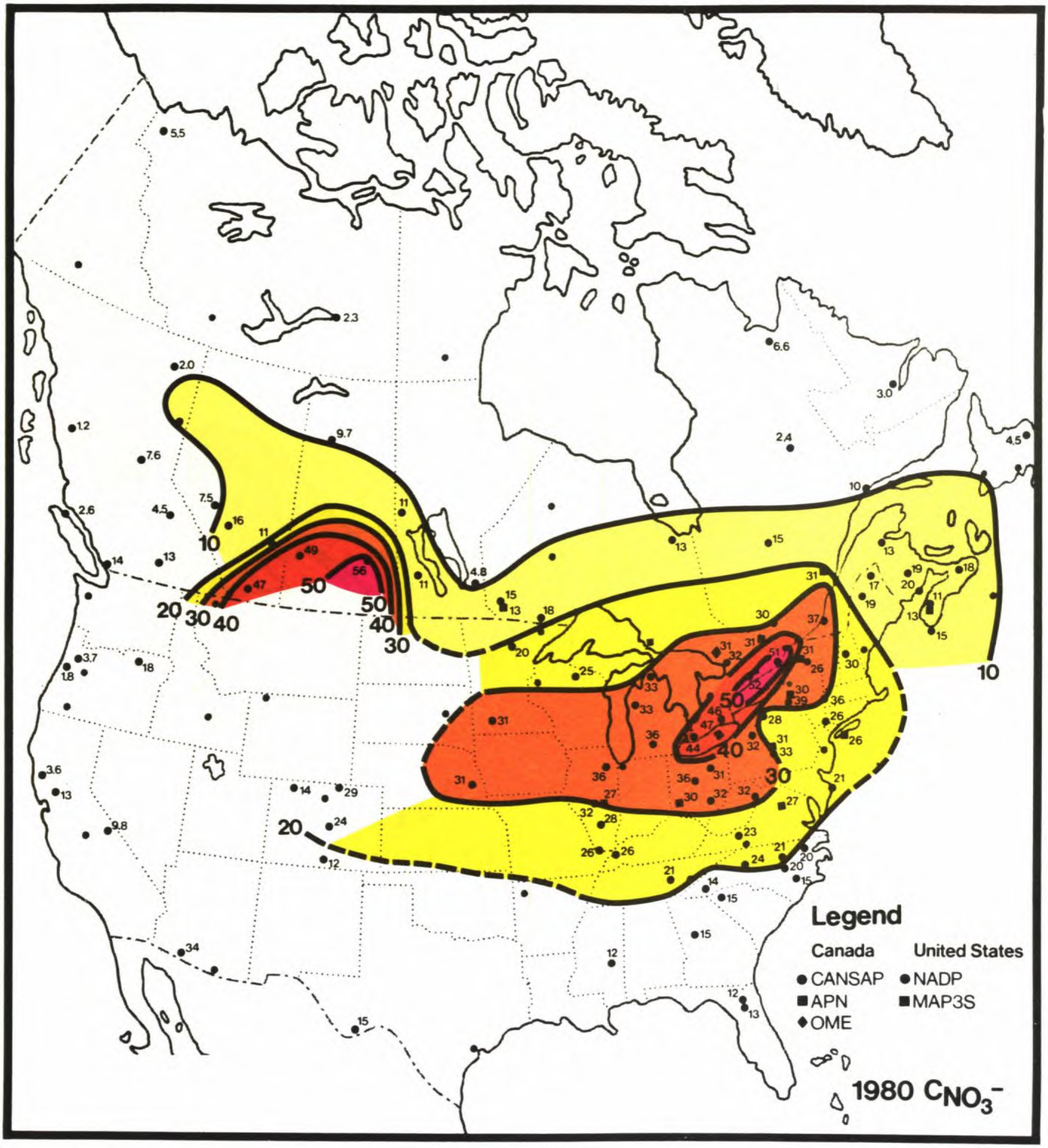
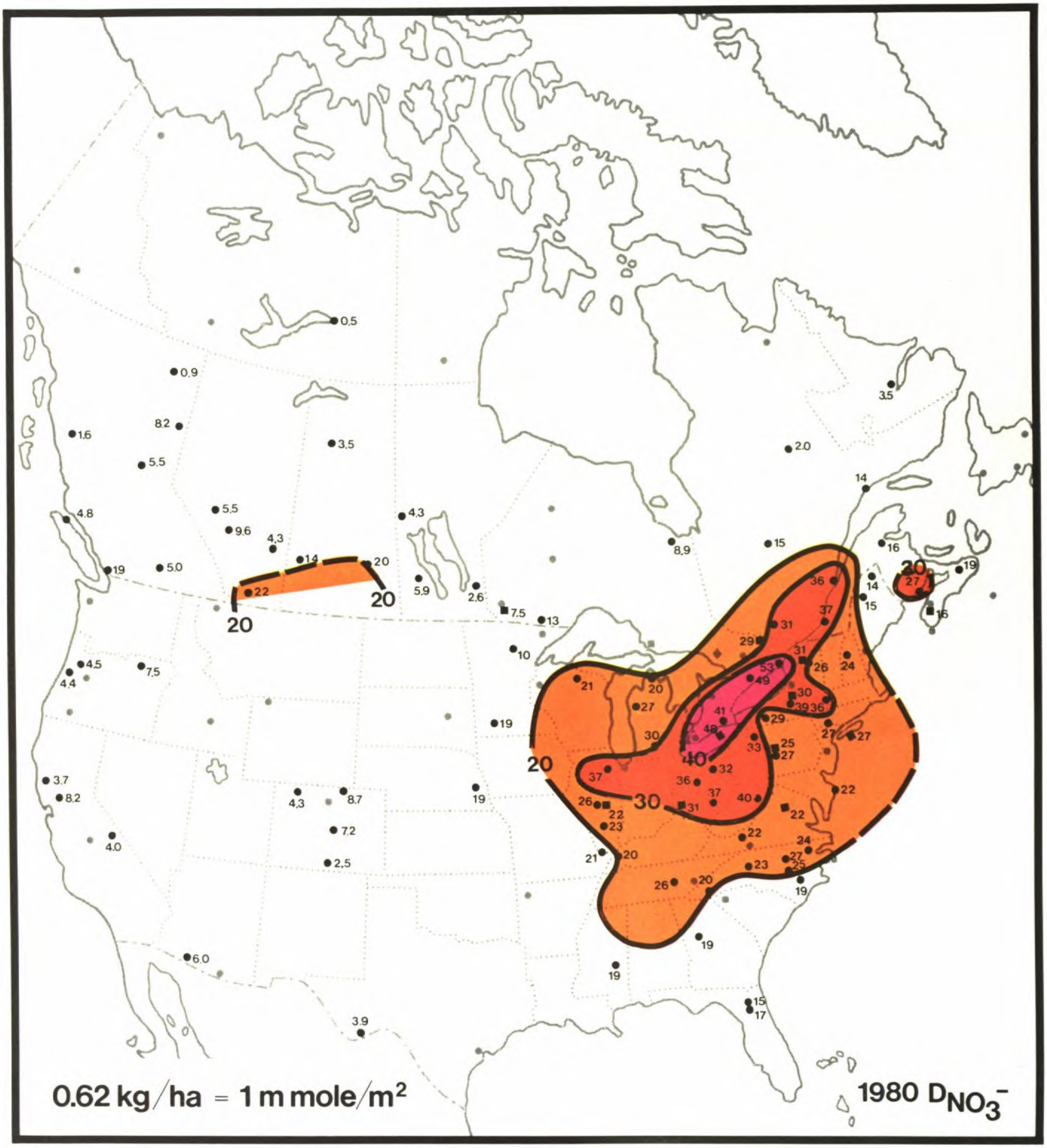


Figure 2-8a. Precipitation amount - weighted mean nitrate ion concentration for 1980 (μmoles per litre).



Precipitation amount - weighted mean nitrate ion deposition for 1980 (m moles per square metre).

Figure 2-8b.

Legend

Canada	United States
● CANSAP	● NADP
☐ APN	☐ MAP3S
◆ OME	

TABLE 2-5. CONVERSION FACTORS FOR CONCENTRATION AND DEPOSITION UNITS

ION	CONCENTRATION mg/L PER μmole/L	DEPOSITION kg/ha PER mmole/m^2
H^+	0.0010	0.010
NH_4^+	0.0180	0.180
Na^+	0.0230	0.230
Ca^{2+}	0.0401	0.401
Mg^{2+}	0.0243	0.243
$SO_4{}^{2-}$	0.0961	0.961
NO_3^-	0.0620	0.620
Cl^-	0.0355	0.355

Example for $SO_4{}^{2-}$ 0.0961 mg/L equal 1 μmole/L

0.961 kg/ha equal 1 mmole/m^2

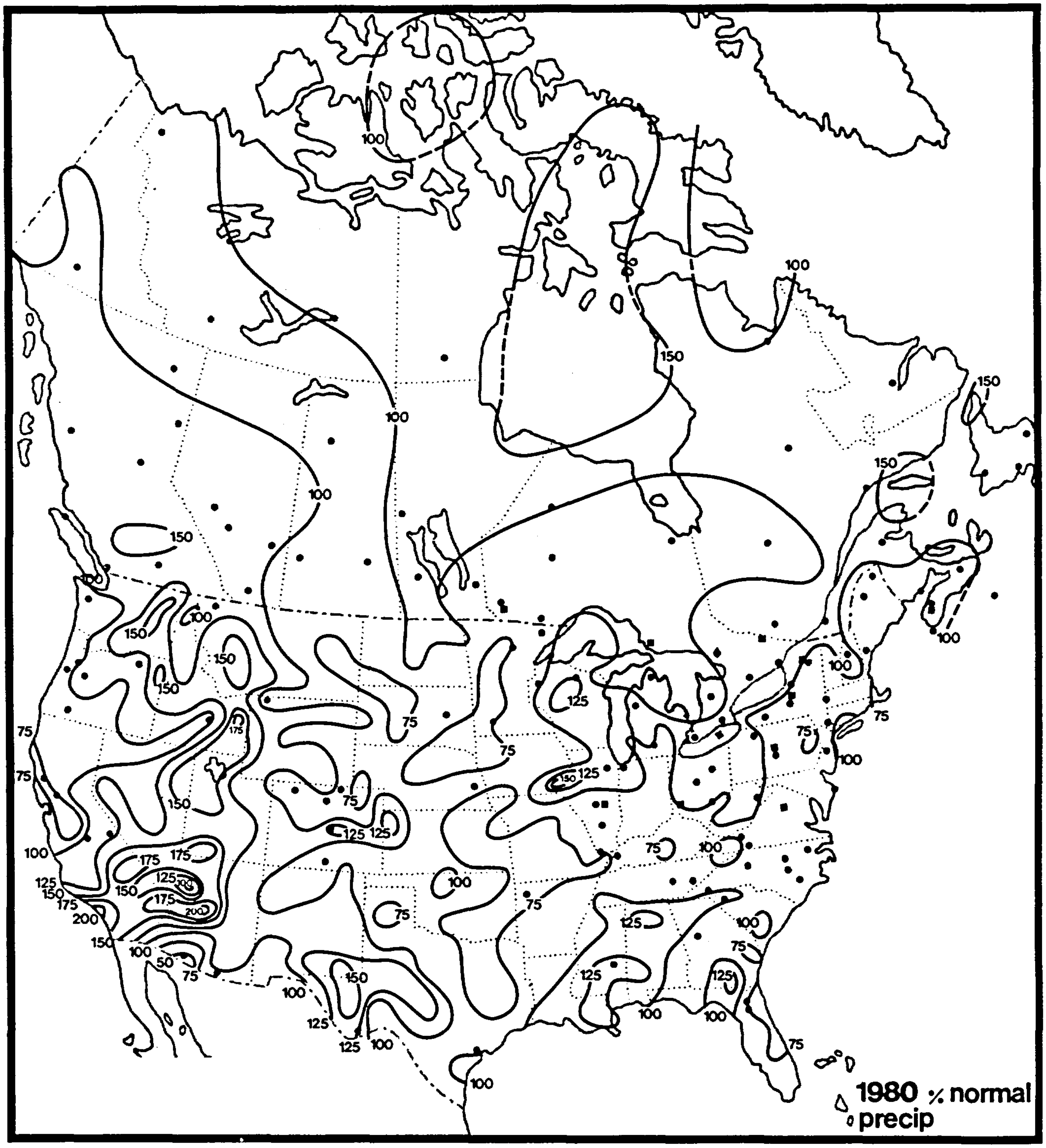


Figure 2-9. Percent of normal precipitation in North America in 1980.

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SECTION 3

AQUATIC EFFECTS

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AQUATIC EFFECTS

3.1 INTRODUCTION

This assessment is structured to address three major questions concerning aquatic effects of acidic and pollutant 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 alterations?
3. What is the geographical distribution and acid-loading tolerance of watersheds of various sensitivities?

Several approaches were used to evaluate these questions. Firstly, emphasis was placed on identifying and substantiating historical (long-term) changes in aquatic systems possibly related to long-range transport 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 that are at risk. Included are detailed documentations of affected aquatic environments, both chemical and biotic components, and definition of time trends for observed changes.

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

Finally, this section focuses on the aquatic ecosystems and biota that are sensitive to acidic deposition. It was, therefore, necessary to define an acid-loading tolerance, to identify regions sensitive to acid inputs, to identify aquatic resources at risk from higher acid-loading levels, 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 the effects of acidic deposition on aquatic ecosystems, it is necessary to examine the fate of ions deposited from the atmosphere, directly on aquatic systems and indirectly through deposition on watersheds. In the latter case deposition may result in geochemical alterations of watersheds. These geochemical alterations must be considered before a complete understanding of chemical inputs to and changes in aquatic ecosystems can be achieved.

3.2.1 Hydrogen Ion (Acid)

Hydrogen ions (acid) (H^+) drive most chemical weathering reactions. They are supplied from both external and internal sources. The major external source is acid supplied by atmospheric deposition (meteorological input). Internal sources are biological and chemical processes occurring within the watershed.

Carbon dioxide (CO_2) in the atmosphere represents a large, but occasionally rate-limited, reservoir of carbonic acid (H_2CO_3). Carbon dioxide contributes to both internal and external sources of hydrogen ions. The major process of chemical weathering is the exchange of protons (H^+) for cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+). The proton source for the weathering process is derived from the external supply (precipitation) and from internal biochemical generation. In a typical calcium carbonate-or silicate-bearing soil or rock, this normal weathering process gives rise to waters having calcium and bicarbonate as the major ionic constituents. (See standard texts on limnology; e.g., Hutchinson [1957] or Wetzel [1975].)

The hydrogen ion cycle within soils is quite complex and not well understood. At the Hubbard Brook Watershed, New Hampshire, the average external net annual input of hydrogen ion equivalents observed over the 1963-74 decade was 86.5 ± 3.3 meq/m^2.yr (milli-equivalents/square metre.year) (Likens et al. 1977b). If this were the only source of H^+ ions at Hubbard Brook and the ecosystem were in a steady state, one might expect this hydrogen ion input to be balanced by hydrogen ion exports plus the net rate at which ionic Ca, Mg, K, Na, and Al are leached from the soil. 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 yield 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 were identified as: (1) nitrogen compounds, particularly NH_4^+; (2) reduced carbon oxidized in the soil; (3) organic acids, such as citric, tartaric, tannic, and oxalic acids, produced by biological activity within the soil; (4) oxidation of small amounts of sulphide minerals in the bedrock; and (5) the uptake of cations (e.g., K^+, Ca^{2+}) by the forest vegetation and the forest floor.

Currently, in eastern North America, the amounts of hydrogen ion being deposited generally are in the range of 50-100 meq/m^2.yr for areas receiving the highest acidic deposition. To neutralize this acid input, a base equivalent of 25-50 kg/ha.yr (kilograms/hectare.year) of calcium carbonate would be required. Carbonate soils can neutralize this amount of acid for an indefinite time with only a small percentage increase in total runoff of calcium and magnesium salts which is a small loss compared to the total stored in the watershed. However, in areas underlain by rocks resistant to weathering and with shallow noncalcareous soils, such as much of the Precambrian Shield region, the amount of salts and alkaline materials normally leached are on the order of 10-100 meq/m^2.yr. External hydrogen ion loadings to these areas are of the same order of magnitude as this leaching rate. When hydrogen ion inputs exceed the levels of available Ca and Mg, other less available metals are leached. For example, some of the acid results in leaching of such cations as aluminum, iron, zinc and manganese. In some cases, hydrogen ion inputs exceed the ability of the soils to fix hydrogen ions and excess hydrogen ions are exported to surface waters.

In most parts of the Precambrian Shield, current levels of hydrogen ions from rainfall are neutralized within the soils of the watersheds during most of the year. Retention (neutralization) of hydrogen ions deposited in bulk deposition has been measured at 88, 94 and 98% on an annual basis, at the Experimental Lakes Area (Ontario), Hubbard Brook (New Hampshire) and Muskoka-Haliburton (Ontario), respectively (Schindler et al. 1976; Likens et al. 1977b; Scheider et al. 1979c). On the other hand, 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 a watershed occurs during a brief period in the spring. This large volume of water, coupled with less opportunity for infiltration and interaction with the soil, has resulted in some cases in "shock level" concentrations of acid exported to streams and surface waters of lakes (Schofield 1981). Hultberg (1977) reported on such shock level pH declines in Swedish lakes and rivers and demonstrated that in some cases these pH declines were associated with fish kills.

The total ionic strength of surface waters is determined largely by the hydrological and geochemical properties of the catchment basin. "Soft" waters, of low ionic strength, occur within basins having chemically resistant and very little readily-exchangeable material, often associated with igneous bedrock or its soil derivatives. "Hard" waters of higher ionic strength are derived from basins having greater amounts of carbonate lithology (see Section 3.5). The amount of cations exported from a basin thus becomes a parameter which, under similar hydrologic and acid-loading conditions, characterizes the basin in an integrated sense. The chemical composition of receiving waters is dependent on the types of weathering reactions within the surrounding watershed. If the weathering has been the result of reactions with CO_2 and carbonic acid, the major ionic constituents in surface waters will be bicarbonate and calcium. When strong acids such as H_2SO_4 are introduced (for example, as acidic deposition) into a bicarbonate-weathering system, the generation of bicarbonate alkalinity may be altered (see Section 3.3). Instead of weathering resulting primarily from reactions with carbonic acid and yielding bicarbonate ions as a major end product:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \tag{1}$$

or

$$\underset{\text{(K-feldspar)}}{3\ KAlSi_3O_8} + 2H_2CO_3 + 12H_2O \rightarrow 2K^+ + 2HCO_3^- + 6H_4SiO_4 + KAl_3Si_3O_{10}(OH)_2 \tag{2}$$

the reaction of sulphuric acid with limestone or other rocks yields sulphate as a major anion:

$$CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO_4{}^{2-} + H_2O + CO_2 \tag{3}$$

Alternatively, the reaction can be considered as a progressive titration of bicarbonate alkalinity.

$$Ca^{2+} + 2HCO_3^- + H_2SO_4 \rightarrow Ca^{2+} + SO_4{}^{2-} + H_2O + 2CO_2 \tag{4}$$

Alkalinity of waters is a measure of the reserve acid neutralizing capacity (ANC) that remains to be titrated to any chosen pH level. Dissolved carbonate species (HCO_3^- and $CO_3{}^{2+}$), if present in sufficient concentrations, react together as a buffering system, tending to retard or limit changes in pH. (See Figure 3-1 [Wetzel 1975] for the relationship of the inorganic carbonate species to pH.) For a monoprotic acid [HA]:

$$\text{alkalinity [ANC]} = [A^-] + [OH^-] - [H^+] \tag{5}$$

For a diprotic acid [H_2A]:

$$\text{alkalinity [ANC]} = [HA^-] + 2[A^{2-}] + [OH^-] - [H^+], \tag{6}$$

where the acids are HA and H_2A, respectively (Stumm and Morgan 1970). The major source of buffering in freshwaters is the carbonate system. Therefore for surface waters:

$$[ANC] = [HCO_3{}^-] + 2[CO_3{}^{2-}] + [OH^-] + [B^-] - [H^+] \tag{7}$$

where ΣB^- is the sum of all titrable bases (Lerman 1978). Thus, the loss of bicarbonate during the H_2SO_4 titration represents a decrease in the buffering capacity of the water (lower alkalinity).

As a result of the above reactions, $SO_4{}^{2-}$ replaces $HCO_3{}^-$ in the ionic balance of outflow waters until the titration endpoint is reached, that is, when all the $HCO_3{}^-$ has been consumed (Kramer 1981). The $HCO_3{}^-$ remaining at any stage above the titration endpoint largely determines the pH or alkalinity of the waters, although organic

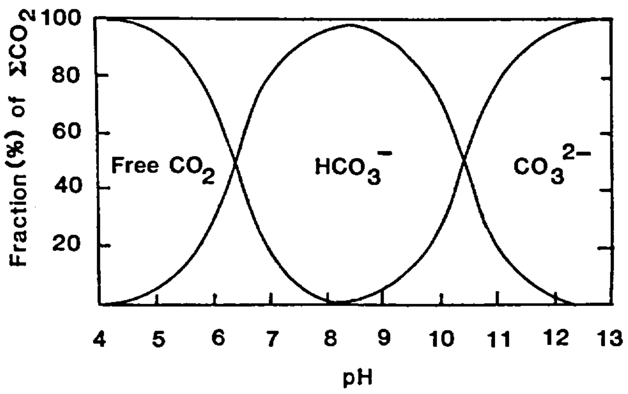


Figure 3-1. Relationship between pH and the relative proportions of inorganic carbon species of CO_2 (H_2CO_3), HCO_3^-, and CO_3^{2-} in solution (from Wetzel 1975).

materials may provide some additional buffering at lower alkalinities (see Section 3.3). Beyond the titration endpoint, large concentrations of hydrogen ion will be present and other buffers such as aluminum or humic materials may also become important in the control of pH of the waters (see Section 3.2.4). Thus, the concentration of cations in surface waters for any given alkalinity reflects a basin's ability to produce cations and may be used as an index of its capacity to neutralize acidic deposition added to the basin.

Henriksen (1980) and Thompson (1982) have used this assumption and the necessity of ionic charge balance to estimate surface water sensitivity or the ability of a basin to respond to an external stress of acidification. Hesslein (1979) has applied similar assumptions and used alkalinity to estimate acid loadings which would be required to produce acidification. Thus, if arbitrary "loading" or acidification stress levels are specified, alkalinity can provide a quantified measure of the sensitivity of a basin to further acidification of waters. For example, HCO_3^- concentrations of 100 to 200 μeq/L, have been identified as approximate levels below which a basin may be considered to be sensitive to acidification (Altshuller and McBean 1979; Glass and Loucks 1980). When the flow rates through a basin are specified, the alkalinity provides a flux or basin yield of reserve ANC. If significant loss of alkalinity has not occurred this equates to the Ca^{2+} or cation flux used in the Cation Denudation Rate (CDR) model of Thompson (1982). Alkalinity (concentration or flux) or CDR therefore provide techniques to estimate quantitatively the capacity of a drainage basin to withstand acid loading (see Sections 3.9.2 and 3.9.3).

Acidification of nonorganic surface waters by external sources of H^+ may thus be a combination of two processes: (1) a retardation of the development of alkalinity in the watershed (Kahl et al. 1982), and (2) a titration (Henriksen 1979) of surface water alkalinity.

The Calcite Saturation Index (CSI), was defined by Conroy et al. (1974) as the undersaturation of waters with respect to $CaCO_3$. As modified by Kramer (1981):

$$CSI = \log K - \log [Ca^{2+}] - \log [HCO_3^-] - pH$$

where $\log K = 2.582 - 0.024t$

t = temperature (°C) and [ ] are concentrations.

The CSI allows for assessment of pH and alkalinity on a single logarithmic scale. Saturation with respect to calcium carbonate gives a value of zero with degree of undersaturation on an increasing positive scale. Kramer (1976) considered values greater than CSI = 3 to indicate waters sensitive to acidification. To date, a quantitative relationship between acidification potential and CSI units has not been developed.

3.2.2 Nitrate and Ammonium Ions

Atmospheric deposition of nitrate is only about one-third to one-half as great on an equivalent basis as the sulphate deposition in eastern North America, but in some areas of the western United States nitrate may represent up to 60% of the annual acid fractions in rainfall (Lewis and Grant 1979; Liljestrand and Morgan 1978).

Nitrogen deposition can result in either acidification or neutralization of surface waters depending on the ionic form. Nitrogen, as nitrate ions (NO_3^-), can be incorporated directly by vegetation resulting in the release of hydroxyl ions (OH^-) into the environment (Figure 3-2). The hydroxyl ions neutralize hydrogen ions and raise the pH of the soil and water. Natural decomposition of nitrogenous plant material releases hydrogen ions, but net annual accumulation of plant tissue dominates in most ecosystems (Bormann and Likens 1979). Hence, net production of neutralizing capacity from nitrate addition is often dominant, especially during warm periods of the seasons (see data from Harvey et al. 1981; Brewer and Goldman 1976). This is particularly significant where forest harvest rather than decomposition removes plant materials, because the neutralizing portion of the cycle is left in the system and a portion of the acidification source (decomposition) is removed.

Ammonium salts and sulphate particulates are present in both dry and wet deposition. Ammonium is a source of hydrogen ions (Figure 3-2) when the nitrogen is utilized by plants. This release of hydrogen ions can be a significant source of acidification in soils and surface waters. Nitrogen is usually in short supply in terrestrial habitats, and is readily incorporated and retained by ecosystems (Reuss 1976) (Table 3-1).

Nitric acid and ammonium salts are stored in snowpack and released as acid components to streams and lakes during spring snowmelt and may, therefore, be partially responsible for the documented episodic increase in acidity in aquatic ecosystems. During the growing season, however, both terrestrial and aquatic vegetation use most of the deposited nitrate and ammonium ions, except for periods of heavy rainfall. Because nitrate ions often occur at higher concentrations in precipitation than do ammonium ions, there is often a net production of alkalinity.

3.2.3 Sulphate

Sulphur, like nitrogen, is an essential plant nutrient and the incorporation of sulphate into vegetation releases hydroxyl ions (Figure 3-3). As opposed to nitrogen, sulphur in soil is usually in adequate supply for plant growth. Additions of sulphur may not be entirely incorporated into living tissue. Sulphate ions can also be absorbed by soils and reduced by bacterial action. This reaction consumes acid and raises the pH of the soil-water environment.

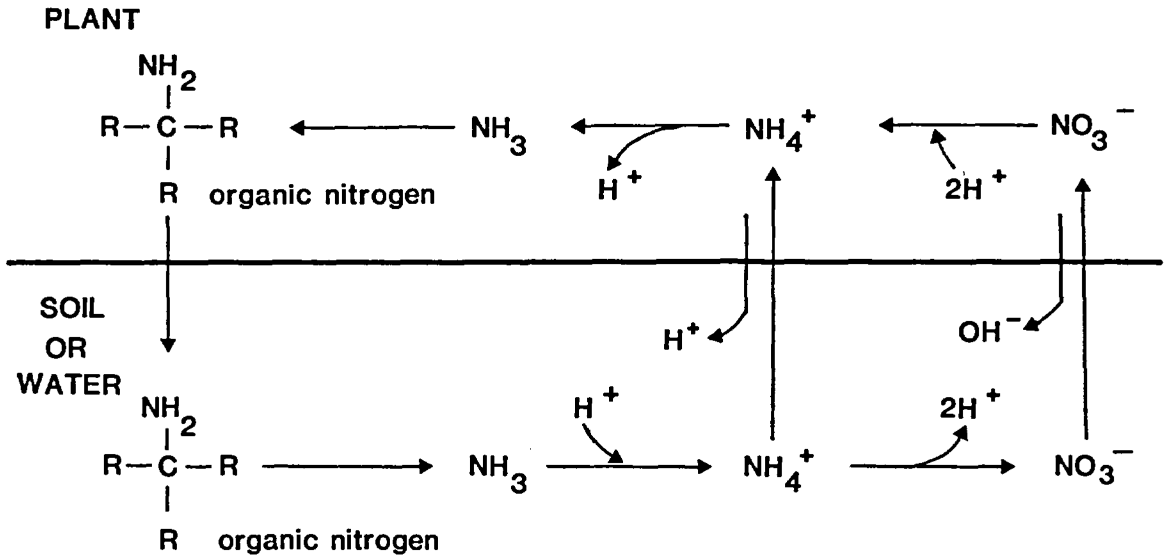


Figure 3-2. Simplified nitrogen cycle showing chemical changes caused by plant and soil processes (from Reuss 1976).

TABLE 3-1. THE RETENTION OF NITRATE, AMMONIUM ION AND TOTAL NITROGEN BY FORESTED WATERSHEDS IN SEVEN CALIBRATED WATERSHED STUDIES

	% Retention in the watershed on an annual basis						
Substance	ELA[a] Ontario	Muskoka-Haliburton[b] Ontario	Hubbard Brook[c] New Hampshire	Kejimkujik Park[d] Nova Scotia	Sagamore Lake[e] New York	Woods Lake[e] New York	Panther Lake[e] New York
NO_3^-	-	75	15	99	43	70	15
NH_4^+	-	95	89	98	90	90	90
Total Nitrogen	81-90	-	-	-	-	-	-

[a] Schindler et al. 1976.

[b] Scheider et al. 1979c.

[c] Likens et al. 1977b.

[d] Kerekes 1980.

[e] Galloway et al. 1980 (figures estimated from published bar graphs).

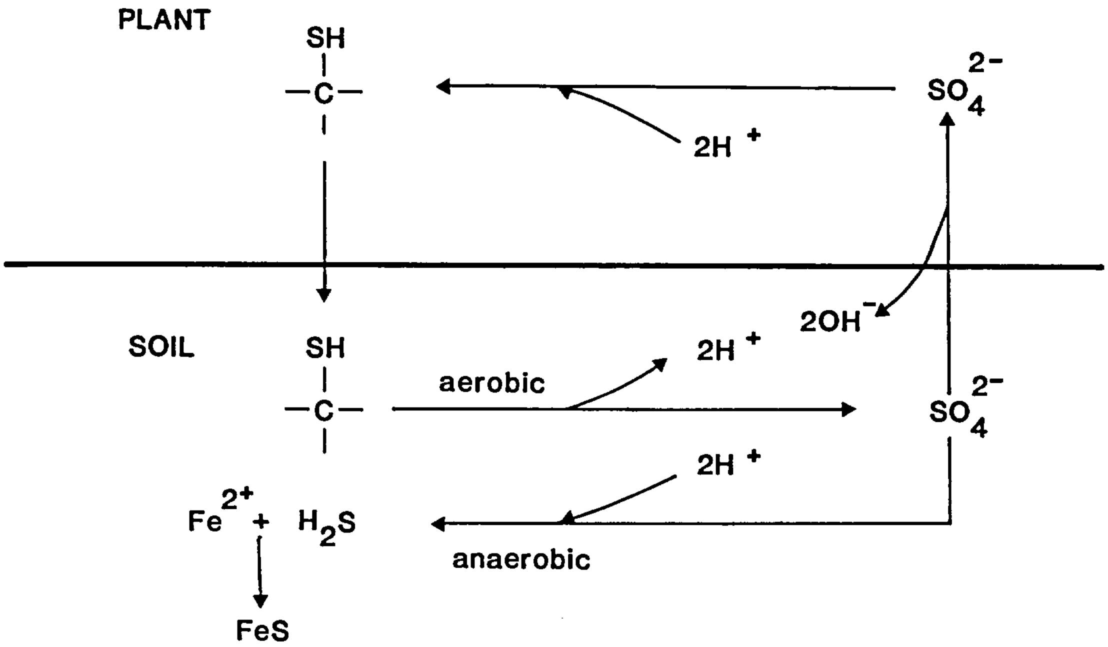


Figure 3-3. Simplified sulphur cycle showing chemical changes caused by plant and soil processes (modified from Reuss 1976).

Sulphide (S^{2-}) can subsequently be oxidized back to sulphate, resulting in the production of hydrogen ions.

In spite of these possible reactions in granites and related rock types, much of the SO_2 and SO_4^{2-} deposited in acidic deposition is not retained. Sulphate is leached out of soils and is often the anion balancing the presence of H^+ and other cations in surface and shallow ground waters. The amount of SO_4^{2-} in runoff from the Shield areas is very close to the amount deposited in precipitation. At the Experimental Lakes Area (ELA) in Ontario, Schindler et al. (1976) found the atmospheric SO_4^{2-} input measured in bulk precipitation and the SO_4^{2-} export in the runoff were in balance. Likens et al. (1977b) found 67% of the total input in runoff at Hubbard Brook, New Hampshire. Kerekes (1980) reported that outputs of sulphate were about 80% of the annual inputs for the Lower Mersey River system in Nova Scotia. In the Adirondack Mountains of New York, Galloway et al. (1980b) observed that sulphate inputs and outputs were in balance for two lake/watershed systems, while for a third watershed some accumulation of sulphur may be occurring within the terrestrial system. In some cases, the SO_4^{2-} in surface waters is greater than the total input measured in precipitation and the difference may be due to sulphur inputs in dry deposition (see Section 3.6.1).

Although little sulphate is retained in granitic watersheds, in certain kinds of soils, such as are common in the southeastern U.S., a large portion of sulphate inputs may be retained in the soil by soil adsorption processes (Johnson et al. 1980). This will have the very important effect of retarding the movement of cations, including H^+, from the soil to aquatic systems. (See Section 4.4.2 for further discussion.)

3.2.4 Aluminum and Other Metals

Surveys of waters in regions affected by acidic deposition indicate elevated levels of aluminum (Al), cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni) and/or zinc (Zn) in many acidic lakes and streams (Almer et al. 1978; Beamish 1974; Conroy et al. 1976; Henriksen and Wright 1978; Schofield 1976b). These increased concentrations of metals may result from either increased atmospheric loading (associated with or independent of acidic deposition) or increased metal solubility caused by increasing surface water acidity. Elevated concentrations of Cd, Cu, Pb, and Ni are probably derived from increased atmospheric deposition. For these metals, deposition and concentrations significantly above background levels occur principally in lakes and streams in relatively close proximity to pollutant sources (e.g., Sudbury region of Ontario; Conroy et al. 1976). Although increased atmospheric loadings of these metals may occur in conjunction with acidic deposition, acidic deposition and acidification of surface waters are not direct causative factors. On the other hand, increased concentrations of Al, Mn, and Zn can occur without increased atmospheric metal loadings. For example, addition of acid to limnocorrals in the Experimental Lake Area, Ontario, produced substantial increases in lake water concentrations of Al, Mn, Zn, and Fe at pH levels 6 and 5 (Schindler 1980). Elevated concentrations of these metals result from an increase in solubility at lower pH levels (Stumm and Morgan 1970) and their mobilization from the surrounding watershed and lake and stream sediments (Galloway et al. 1980a). Elevated concentrations of Al, Mn, and Zn in acidic waters are for the most part, a direct consequence of atmospheric deposition and acidification.

Discussions of the effects of acidic deposition on geochemical cycling of metals have focused on aluminum. One of the effects of soil acidification is the mobilization of aluminum. The solubility of this metal is pH dependent, with a minimum solubility at about pH 6 (May et al. 1979; Stumm and Morgan 1970) (Figure 3-4). Several reports have documented elevated aluminum concentrations in acidic surface waters (Figure 3-5) (Cronan and Schofield 1979; Dickson 1978; Driscoll et al. 1980; Richard 1982; Wright and Gjessing 1976; Wright et al. 1980), and in effluent from lysimeters in soils treated with acid solutions (Abrahamsen et al. 1977; Dickson 1978). 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; Herrmann and Baron 1980). Elevated aluminum concentrations in streams 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 (Driscoll 1980b; Seip et al. 1980).

The mechanism supplying Al^{3+} to soil water, and therefore to shallow interflow water, is the dissolution of aluminum minerals or exchange reactions on soil organic matter. Norton (1976) and Reuss (1976) suggest the following as an explanation of weathering reactions for aluminum minerals:

$$Al_2Si_2O_5(OH)_4 + 6H^+ \rightleftharpoons 2Al^{3+} + 2H_4SiO_4 + H_2O$$

$$Al(OH)_3 + H^+ \rightleftharpoons Al(OH)_2^+ + H_2O$$

$$Al(OH)_2^+ + H^+ \rightleftharpoons Al(OH)^{2+} + H_2O$$

$$Al(OH)^{2+} + H^+ \rightleftharpoons Al^{3+} + H_2O$$

These reactions are likely to occur in watersheds where there are no carbonates to consume H^+. In such instances, the reactions above become the primary buffering mechanism (N.M. Johnson 1979; Kramer 1976). The pH at which this buffering occurs is around 4.5-5.0 (Johannessen 1980). Henriksen (1980) has shown that lakes with pH 4.6-4.8 have a higher pH than expected from a theoretical titration

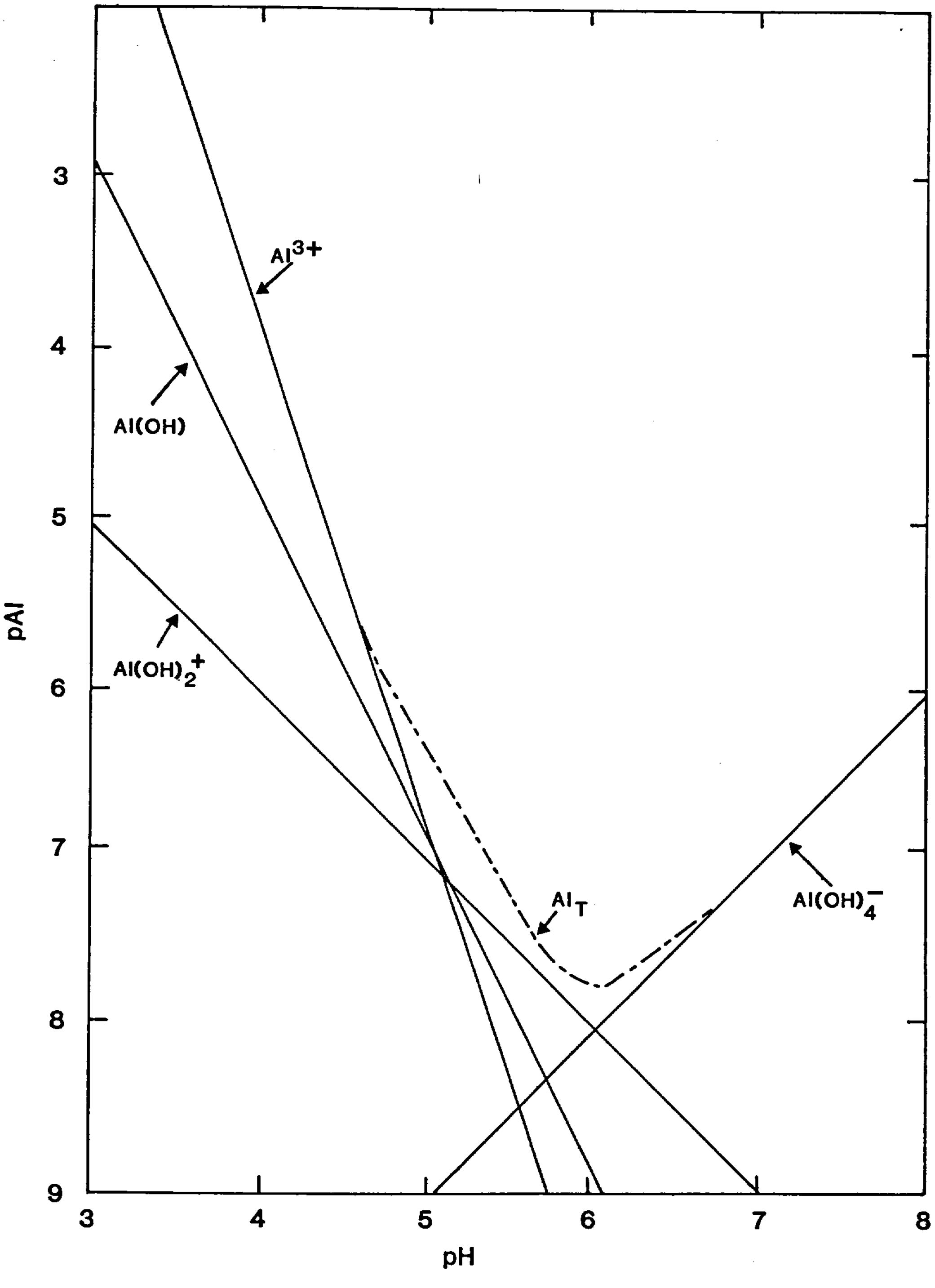


Figure 3-4. Aqueous aluminum in equilibrium with gibbsite (after May et al. 1979).

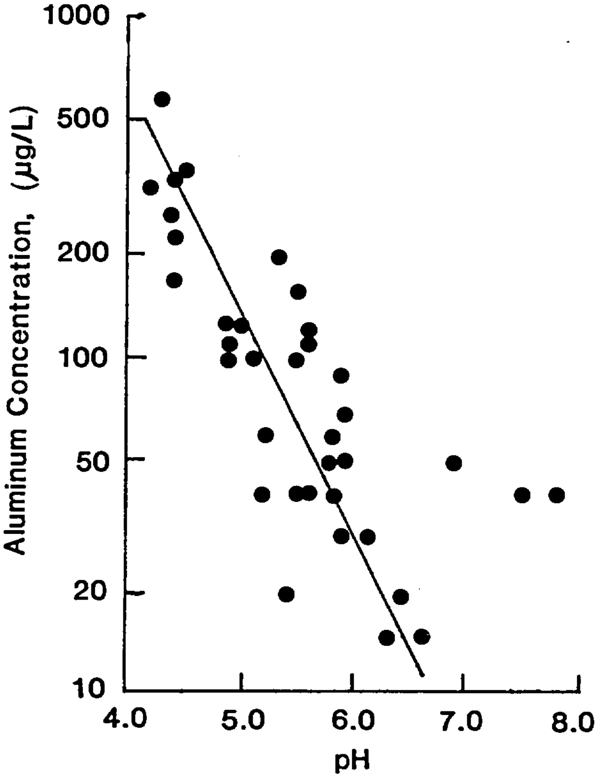


Figure 3-5. Relationship of observed stream concentrations of aluminum to the pH of surface water (modified from Wright and Gjessing 1976).

curved based only on bicarbonate buffering, and that the extra buffering can be explained by the presence of aluminum.

In aquatic systems, aluminum forms a variety of complexes with water and its constituents, including hydroxide, fluoride, silicate, organic matter, and sulphate (Driscoll et al. 1980). In surface waters of the Adirondack Region of New York, Driscoll (1980b) found aluminum-organic complexes were the predominant monomeric aluminum form (average = 44%). Concentration increased linearly with total organic carbon content. Aluminum-fluoride complexes were the most abundant inorganic form (average = 29% of the total monomeric Al), with concentrations increasing with decreasing pH, although their formation was generally limited by fluoride concentration.

3.3 NATURAL ORGANIC ACIDS IN SOFT WATERS

Surface and ground waters can have low pH values or become acidified as a result of natural processes including:

1) natural chemical weathering of pyrite and other sulphide-rich rocks (Herrmann and Baron 1980; Huckabee et al. 1975);

2) net oxidation of reduced organic material due to aerobic biological decay (Likens et al. 1969);

3) oxidation of reduced inorganic material following a lowering of water tables, lake levels, with subsequent exposure to oxygen (Urquhart and Gore 1973);

4) strong cation exchange, especially by *Sphagnum sp.*, with subsequent release of H^+ (Clymo 1967); and

5) production of organic acids which are dissociated in the pH range 3 to 6 (Oliver and Slawych 1982).

Natural acidification due to chemical weathering (process 1) is usually identifiable because of local geologic conditions (e.g., bedrock geology and Fe-rich secondary soil and sediment mineralization). Processes 2 and 3 are not steady-state phenomena and can generally be related to mechanical disturbances in the watershed or meteorological changes. Process 4, common in humid temperate or sub-arctic climates, is normally distinguishable by analysis of the local hydrology, vegetational studies, and the presence of coloured (humic) waters (related to process 5).

A major portion of the dissolved organic carbon in natural waters is organic acids, especially humic and fulvic acids. These acids are produced (process 5) by microbial degradation of plant and animal matter. They are poorly characterized in terms of chemical and physical properties but serve two important functions. They display acidic properties and contribute significantly to acidity in some organic-rich waters. Secondly, these organic compounds chelate various metals that: (1) increase total metal solubility, and (2) may decrease the concentration of biologically available metals (Reuter and Perdue 1977).

The relationship between colour (Platinum units) and dissolved organic carbon (DOC) has been evaluated by several workers (e.g., Juday and Birge 1933) and the relationship between DOC and organic acid has been evaluated empirically by Thurman and Malcom (1981). The extent of dissociation of the acid can be estimated by methods developed by Oliver and Slawych (1982). Thus, the organic anion concentration can be estimated with a knowledge of DOC and pH, both commonly made measurements. Alternatively, the organic anion concentration can also be estimated based on a complete chemical analysis (cations and anions) using an ion balance approach.

Many bogs and organic rich soils have undiluted water pH values in the range of 3.5 to 4.5 due to high concentrations of DOC and associated acidity. The high H^+ concentration is not totally balanced by SO_4^{2-}, NO_3^- Cl^-, or HCO_3^- and the pH is clearly determined largely by organic acid production and cation exchange (Clymo 1967).

The synoptic surveys of acidic clearwater lakes (Dickson 1980; Haines 1981b; Haines and Akielaszek 1982; Norton et al. 1981a; Wright and Henriksen 1978; among others) have concentrated on lakes that have relatively low or no water colour, and therefore having low DOC, low organic acid content, and low organic anion concentrations. Ion balances are achieved largely using only H^+, major cations and sulphate for lakes with pHs below about 5.5 where HCO_3^- becomes relatively unimportant.

Natural soil processes in well-drained terrain may produce considerable acidity due to soil respiration (which raises dissolved CO_2 and carbonic acid concentrations) and biological breakdown of organic material to produce organic acids and chelators. Water percolating through the soil profile may commonly have pH levels lowered to near 4.0 in the organic horizons. As these solutions descend further, acidity is consumed by inorganic reactions including mineral weathering and desorption of cations. Additionally, organic compounds precipitate with increasing pH and/or oxidize to CO_2 and H_2O. The result is that acidic soil solutions commonly have their pH raised from about 4.0 to 5.5-6.5 within a few vertical meters of travel (Cronan 1982). Should these solutions emerge as surface water, the pH would be elevated, "nonacidic", and HCO_3^- would be a major charge balancing anion, along with sulphate. However, if soils are shallow and unreactive, solutions may reach streams prior to effective neutralization (A.H. Johnson 1979) and prior to the development of the maximum allowable HCO_3^- alkalinity. The addition of excess acidity (as H_2SO_4 or $(NH_4)_2\ SO_4$) to soil waters decreases the pH of soil solutions further (even for soils with pH values originally around 4). As a result, given the same flow path, a smaller proportion of the acidity will be consumed. Therefore, surface water emerges with a lower pH, lower alkalinity, and possibly elevated concentrations of cations due to accelerated cationic leaching (Abrahamsen 1980). A number of processes may ameliorate the impact of increased acid loading, the most important of which are net uptake of NO_3^- by plants (Reuss 1976) and SO_4^{2-} adsorption by soils (Johnson et al. 1980).

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 (Driscoll 1980a; Wilson 1979), 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 underestimation of alkalinity when the usual acidimetric determination method is used (Driscoll 1980a). In addition, these substances can influence the bioavailability of acid-leached cations such as Al, Mn, Fe and Zn by acting as chelators.

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 (Dillon and Rigler 1975; Oglesby 1977a, 1977b; Reckhow 1979; Vollenweider 1975).
>
> "Common reasons for the use of this approach include:
>
> (a) the relative importance of 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 compounds 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."
> (Dillon et al. 1982)

Ionic balances of watersheds have been used as a means of quantifying net basin chemical fluxes (Figure 3-6). This approach is being used to evaluate the effects of acidic deposition on element budgets. Several studies have been underway since the early 1960s. One of the earliest studies and the longest continuous record (1963-present) is

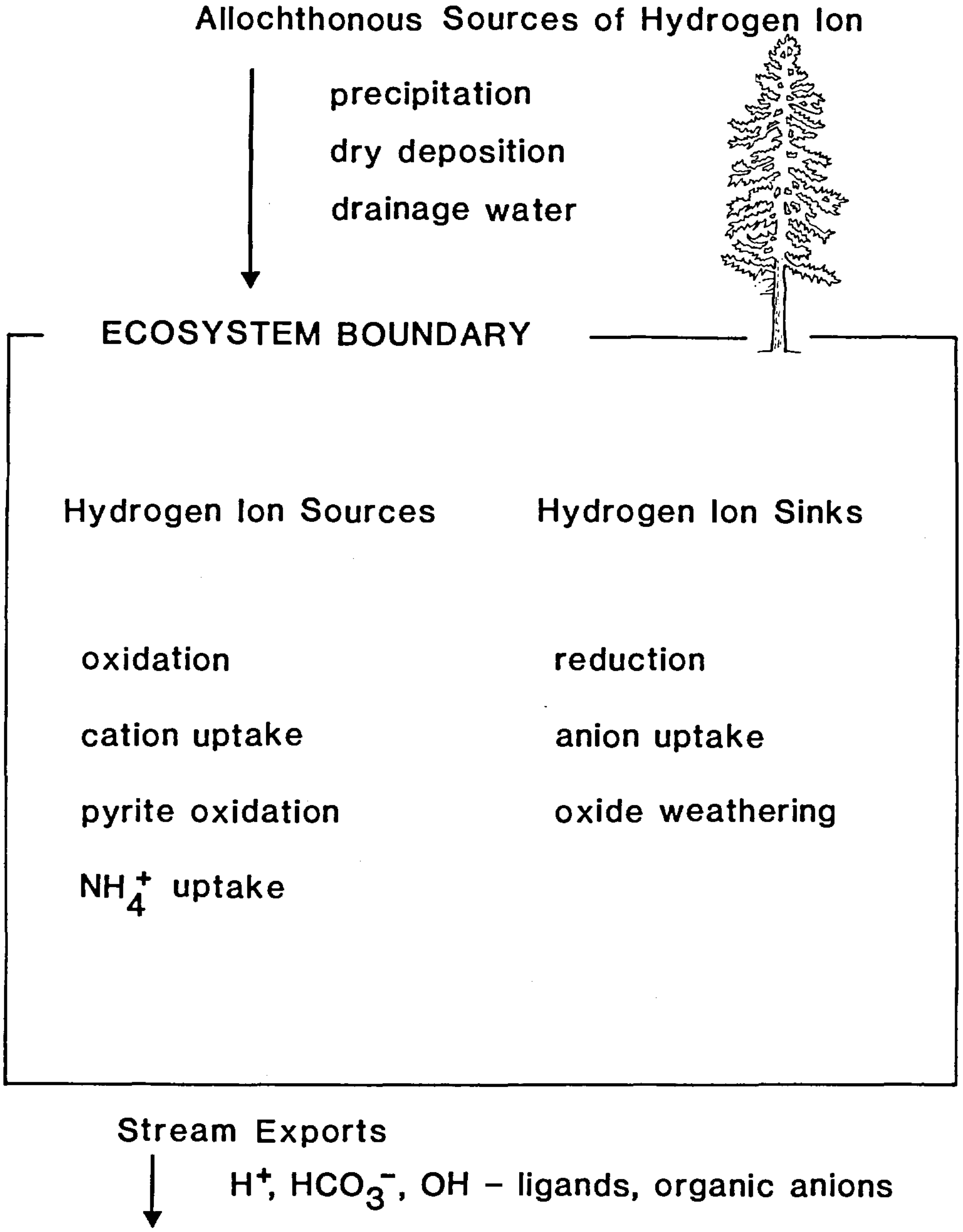


Figure 3-6. Schematic representation of the hydrogen ion cycle (Driscoll 1980a).

from Hubbard Brook, New Hampshire, summarized by Likens et al. (1977a).

3.4.1 Element Budgets at Hubbard Brook, New Hampshire

The ionic composition of bulk precipitation at the Hubbard Brook ecosystem is essentially characterized by acids, such as H_2SO_4 and HNO_3. 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, nitrate, and bicarbonate species. The chemical and biological reactions of hydrogen ion, nitrate, ammonium, and sulphate are very important in driving displacement and weathering reactions.

Observed trends and annual ion budgets for 11 years at Hubbard Brook demonstrate the influence of atmospheric inputs on surface water quality. High rates of H^+, NO_3^-, and SO_4^{2-} inputs were observed throughout the period. The average annual weighted pH of precipitation from 1964-65 through 1973-74 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 average exceeded a pH of 5.0. Fluctuations in hydrogen ion deposition can be explained in large part by the fluctuation in total precipitation. Concentrations for SO_4^{2-} and NH_4^+ varied from year to year, but showed no statistically significant time-trends for the period. In contrast, annual weighted NO_3^- concentrations were about 2.3-fold greater in 1971-74 than they were in 1955-56 (Likens et al. 1977b).

From 1964 to 1970, there was a general downward trend in the percentage sulphate contribution to the total anion equivalents (Figure 3-7). During the period 1970-77, the rate of decline decreased or perhaps the trend even reversed. The proportion of nitrate to the total anion equivalents has increased throughout the period. Two conclusions were drawn: (1) nitric acid was of increasing importance in precipitation at Hubbard Brook (Likens et al. 1976), and (2) the average annual change in nitrate was somewhat smaller after 1970, apparently due to slower increases in nitrate concentration relative to sulphate in precipitation. The proportion of hydrogen ion to the total cations increased throughout the period even though the total equivalent concentration of cations decreased (Likens et al. 1980).

The Hubbard Brook study site is an isolated headwater catchment. As a result, the influx of chemicals is limited principally 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. (1977b) were, therefore,

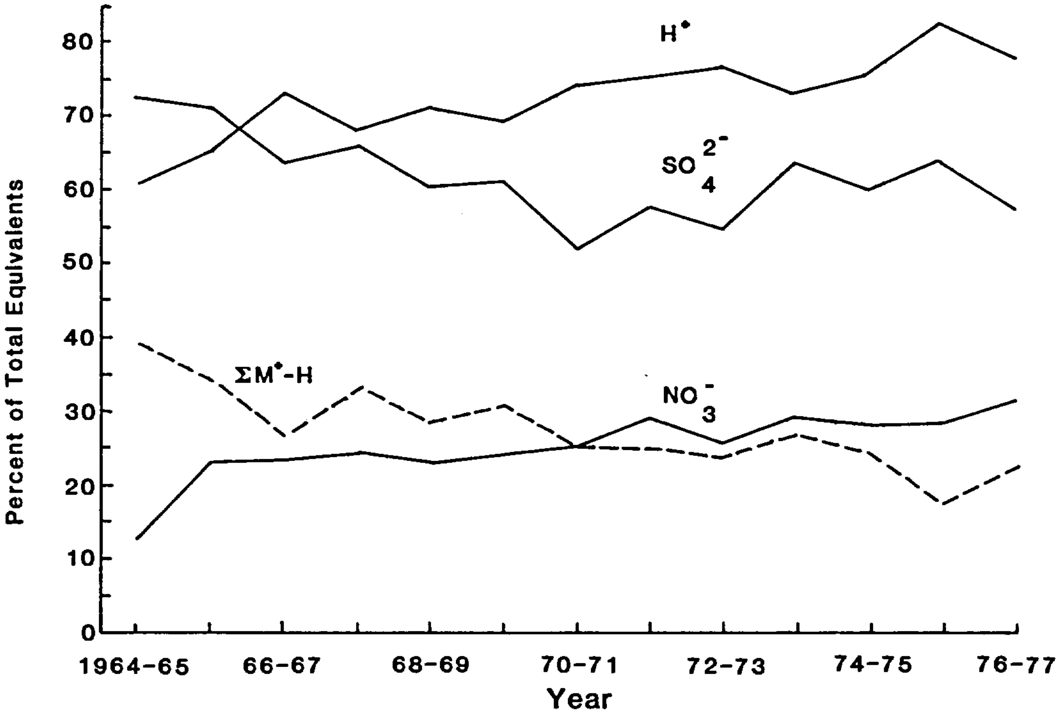


Figure 3-7. Percent of ionic composition of precipitation for the Hubbard Brook Experimental Forest during 1964 to 1977. ΣM^+ is sum of all cations (Likens et al. 1980).

able to estimate with reasonable accuracy the mean annual budgets for most of the major ions (Table 3-2). Over the long term, there was considerable variation. However, calcium, magnesium, potassium, sodium, sulphate, aluminum, and dissolved silica budgets indicated net annual losses. Net annual gains of ammonium, hydrogen ion, and phosphate occurred in these undisturbed, accreting watershed ecosystems. Nitrate and chloride budgets indicated a net accumulation in all but 3 of the 11 years of study.

Overall, during 1963-74 there was an annual net loss of total dissolved inorganic substances from the experimental watersheds amounting to 74.7 kg/ha.yr. The average net output of dissolved inorganic substances minus dissolved silica (1963-1974) was 38.4 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 1964-65, the driest year of the study. The largest net losses of dissolved inorganic substances occurred during the wettest year, 1973-74 (139.7 kg/ha).

Likens et al. (1977b) also noted the complexity of computation of the long-term cationic denudation rate in the Hubbard Brook ecosystem because of the need to consider accumulations in living and dead biomass. The net accretion of biomass should be viewed as 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 concluded that: (1) cations stored within the biomass must be included in calculations of contemporary weathering; (2) the rate of storage is a consequence of the current state of forest succession and changes with time; and (3) the existence of the forest and its state of development must be included in geological estimates of weathering.

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, the 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 at Hubbard Brook (Figure 3-8).

TABLE 3-2. ANNUAL BUDGETS OF BULK PRECIPITATION INPUTS AND STREAM-WATER OUTPUTS OF DISSOLVED SUBSTANCES FOR UNDISTURBED WATERSHEDS WITHIN THE HUBBARD BROOK EXPERIMENT FOREST (Likens et al. 1977b)

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	Annual mean kg/ha
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	a	a	a	a	a	a	a	a	a	a	a	a	a
Output	1.6c	1.2	1.7	1.9	2.1	2.2	2.2	1.8[c]	1.7[c]	2.3[c]	3.2[c]	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[c]	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[c]	0.27	0.92	0.45	0.24	0.16	0.51	0.23	0.05	0.18	0.42	3.7	0.34
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[c]	0.76	0.85	1.05	0.96	0.85	0.93	1.18	0.97	1.08	1.14	10.62	0.96
Output	0.08[c]	0.06[c]	0.05	0.07	0.06	0.09	0.09	0.14	0.13	0.16	0.20	1.13	0.10
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	0.86
SULPHATE													
Input	33.7b	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	42.7b	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	-14.8
NITRATE													
Input	12.8[c]	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[c]	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[d]													
Input	a	a	a	a	a	a	a	a	a	a	a	a	a
Output	6.2[b]	4.6[b]	6.2	9.4	9.6	7.0	6.0	7.1[b]	6.6[b]	9.0[b]	12.5[b]	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

[a] Not measured, but trace quantities.

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

[c] Calculated from weighted concentration for 1964-1966 times precipitation for 1963-1964.

Based on annual concentration of 0.50 mg/1 (Juang and Johnson 1967).

[d] Watershed 4 only.

HUBBARD BROOK HYDROGEN ION BUDGET

Allochthonous	inputs
Precipitation	+ 960
Dry Deposition	+ 362

Weathering Reactions		Net Accumulation in Forest Floor and Forest Biomass	
Ca	- 1055	Ca	+ 475
Mg	- 288	Mg	+ 74
Na	- 252	Na	+ 7
K	- 182	K	+ 156
S	+ 25	S	- 125
Al	- 211	Fe	+ 103
Fe	- 78	NO_3^-	- 47
P	+ 83	NH_4^+	+ 144
		P	- 90
TOTAL	- 1957		+ 697

Stream Exports

Stream pH (H^+)	-100
Stream Alkalinity (HCO_3^-)	+126
Discrepancy in Charge Balance (organic anions, hydroxide ligands)	+ 26

SUMMARY

Hydrogen Ion Sources	+ 2541
Hydrogen Ion Sinks	- 2428
Budget Discrepancy	+ 113

Figure 3-8. Hydrogen ion budget (meq/m^2.yr) for Hubbard Brook Experimental Forest (Driscoll and Likens in press).

3.4.2 Element Budgets in Canada

The calibrated watershed technique for measuring rates of movement of elements has also been used in Canada and results have been summarized by Harvey et al. (1981):

> "Input-output budgets (mass balances) for major ions are being measured at a number of locations in Canada as described in Table 3-7 [Table 3-3 this report]. In all cases, mass balance measurements have excluded possible contributions via subsurface flow, although the evidence available for these lakes suggests that these contributions are negligible (Schultz 1951). Net exports of Ca^{2+}, Mg^{2+} and K^+ are shown in Table 3-8 [Table 3-4 this report] for Canadian 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. No Canadian information on inputs and outputs of aluminum was found. Nicolson (1977) reported only output of major ions from 12 watersheds in the Experimental Lakes Area, northwestern Ontario; input by precipitation to the nearby Rawson Lake watershed (Schindler et al. 1976) was used to calculate a net export for these 12 watersheds."

Harvey et al. (1981) drew attention to several main observations. With one exception, Clear Lake, all of the watersheds studied had a net output of the major cations ($Ca^{2+} + Mg^{2+} + Na^+ + K^+$). The net export of $Ca^{2+} + Mg^{2+}$ dominated the ion budgets particularly in the watersheds in British Columbia which contain some calcareous till. The study sites in British Columbia received a larger amount of precipitation (260 to 450 cm/yr) a factor which may increase the export of cations. Potassium export is low in all cases reflecting the biological demand for this element in the watersheds. In all cases there is a net accumulation of $NH_4^+ + NO_3^-$ in the watersheds.

The export of cations from ELA and Rawson Lake watersheds on the Precambrian shield in Western Ontario was about 30-40% of the export from the Hay Lake watersheds in the Muskoka-Haliburton area. The corresponding H^+ inputs were 5-10 times greater at Harp Lake, also in Muskoka-Haliburton.

More sulphate was exported from the watersheds than entered via wet or bulk deposition. In some cases (Rawson Lake and Jamieson Creek) the differences may be within experimental error, and in some cases the input may be underestimated due to dry deposition and canopy effects.

TABLE 3-3. DESCRIPTION OF WATERSHEDS IN CANADA UTILIZED FOR MASS BALANCE STUDIES (Harvey et al. 1981)

Study Location	A (km^2)	Annual ppt. (cm)	DESCRIPTION OF WATERSHED 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, grandodiorite	4 yr published, 5 yr 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 (Harvey et al. 1981)

	Net export (meq/m^2.yr)									Input of H^+
Watershed	Ca^{2+}	Mg^{2+}	Na^+	K^+	ΣM	NH_4 as N	NO_3^- as N	HCO_3^-	SO_4^{2-} as S	(meq/m^2.yr)
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]	24.0	18.0	3.4	82.0	-0.9	-0.8	-	38.8	est. 7-10
	17.7[b]	16.4	11.1	0.5	45.7					
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.

> "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 watersheds, the opposite situation is observed. In view of these contradictory observations, the mechanisms for cation export in this area is uncertain. 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 H^+ loading of 7-10 $meq/m^2.yr$ in precipitation may account for 20% of the net cation export. On the other hand, in southern Ontario where the cation export is ~3 times greater than in northwestern Ontario, 50% 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 four-fold increase in net output of cations."

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

Land use practices within watersheds have been suggested as an influence on acidification (Henderson et al. 1980; Likens et al. 1978; Rosenqvist et al. 1980). Henderson et al. (1980) have summarized results from watersheds at Hubbard Brook (New Hampshire), Fernow (West Virginia), and Coweeta (North Carolina) which were experimentally manipulated through a series of forest cutting practices (Table 3-5). The work was designed to estimate changes in streamflow concentrations of cations, particularly the potential effects of H^+ concentrations. At Hubbard Brook, after felling of all vegetation and herbicide treatments for three successive years, nitrogen discharges into stream flow increased by 245.9 kg/ha.yr. Export of dissolved Ca^{2+} and K^+ increased by 65.2 and 28.7 kg/ha.yr respectively compared to a control watershed (Bormann et al. 1974). Increased acidity from biomass decomposition amounted to 69.9 x 10^3 μeq/ha.yr of H^+. This additional acidity is presumed to have been a major contributor to the accelerated 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 produced significantly less effect on soil leaching rates. Organic matter decomposition was about 5% of that of the total vegetation removal (500 kg/ha.yr versus 10,500 kg/ha.yr). Subsequently, internal H^+ production was also less, as was resultant cation leaching than in the deforestation experiment discussed above (Likens et al. 1977a).

Commercial clear-cutting at the Fernow watershed generated fewer H^+ equivalents possibly because only economic biomass was removed,

TABLE 3-5. SUMMARY OF TOTAL CATION RELEASE, HYDROGEN ION PRODUCTION, AND THE CATION RELEASE RATIO FOR THREE MANIPULATED WATERSHED STUDIES (Henderson et al. 1980)

	H^+ produced (eq/ha)	Total cation release (eq/ha)	$\frac{\text{Cation release}}{H^+ \text{ produced}}$ (eq/eq H^+)
Hubbard Brook, New Hampshire			
Deforested	69,960	6,850	0.10
Strip-cut	8,400	390	0.05
Fernow, West Virginia			
Clear-cut	960	170	0.18
Fertilization	55,710	2,420	0.04
Coweeta, North Carolina			
Clear-cut and cable-logged	360	50	0.14

reducing overall decomposition rates and resultant H^+ formation (Henderson et al. 1980). 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 10-fold increase in stripping of calcium ions occurred, plus a 6-fold increase in magnesium, a 50% increase in potassium leaching, and a 3.6-fold increase in sodium ion denudation (Henderson et al. 1980.)

The possibility of changes in land use causing acidification of surface waters, rather than atmospheric inputs of acid, has been explored in great detail by 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. The greatest number of lakes from which fish populations have been lost occurred in areas without farming activity. Although it is well documented that land use changes affect the quality of runoff, including pH, these reports conclude that the large scale acidification of lakes in Scandinavia is apparently not due to land use changes.

In Canada, all of the surface waters which have elevated excess sulphate occur only in areas which have high atmospheric deposition of sulphate (Figure 2-6b). Land use changes, such as logging, have taken place in many areas, including those areas which do not have excess sulphate in surface waters (see Section 3.6.1). All of the surface waters sampled in Northeastern North America that have experienced loss of alkalinity also have elevated excess sulphate concentrations. In areas with less acidic deposition, loss of alkalinity in surface waters has not been observed. These observations indicate that loss of alkalinity from surface waters is associated with increased sulphates resulting from atmospheric deposition rather than land use changes.

Wright et al. (1980) summarized their observations as follows: "Acidified lakes often barren of fish are found in southern Norway, southern Sweden, southwestern Scotland, the Adirondack Mountains, New York, and southeastern Ontario. These areas have in common granitic or other highly siliceous types of bedrock, soft- and poorly-buffered surface waters and markedly acidic precipitation (average pH below 4.5)."

A recent USGS report (Peters et al. 1981) provided a 14-year data analysis of precipitation in New York state (nine stations) and stream chemistry. "Statistical analyses of chemical data from several streams throughout New York yielded little evidence of temporal trends resulting from acid precipitation, except in the Adirondack mountains, where the soils lack significant buffering capacity. In most areas of the state, chemical contributions from urbanization and farming, as well as the neutralizing effect of carbonate soils, conceal whatever effects acid precipitation may have on chemical quality of streams." (Peters et al. 1981)

In summary, the experiments concerning different forest and vegetation-removal practices showed wide variation in the short-term (less than five years) patterns of H^+ produced and cation releases. A survey of European information on land use changes found no evidence that land use changes had an important role in acidification of water or impact on fish populations. Therefore, we conclude that although land use changes can affect the quality of runoff and loss of alkalinity in surface waters, land use changes do not appear to have a major impact on alkalinity nor pH changes in surface waters, with the exception of some waters affected by mine drainage.

3.5 AQUATIC ECOSYSTEMS SENSITIVE TO ACIDIC DEPOSITION

The roles of soils, bedrock and vegetation in regulating surface water chemistry must be considered when assessing the sensitivity of aquatic ecosystems to acidic deposition. The geochemical properties of a watershed provide the primary controls determining surface water alkalinity. Sensitivity evaluations can be based on parameters such as lake and stream alkalinity or calcite saturation index. These parameters do not necessarily reflect the long term capacity of watersheds to buffer or neutralize acidic deposition. Ideally, aquatic and terrestrial data should be evaluated in combination. Unfortunately, the present data base is not sufficient to do so for all of eastern North America. Data on terrestrial systems (especially soils and bedrock) are more readily available. Therefore, terrestrial data have been used to identify areas likely to contain potentially sensitive aquatic ecosystems for all of eastern North America. The mapping of such areas is based on an estimation of the capacity or potential of the terrestrial system within an area to reduce the acidity of incoming atmospheric deposition. To identify aquatic regimes already acidified and those most susceptible, in terms of present levels of acidic deposition, it will be necessary to compare terrestrial-based mapping with aquatic chemistry data and regional deposition maps of SO_4^{2-} in precipitation (Section 3.9).

3.5.1 Mapping of Watershed Sensitivity for Eastern North America

Cowell et al. (1981) considered a number of characteristics of terrestrial environments to be essential for the assessment of aquatic sensitivity (Table 3-6). Important factors include soil chemistry, soil depth, drainage, landform relief, vegetation type and bedrock geology. Each of these factors plays a significant role in ameliorating the effects of acidic deposition. It is important to evalute as many factors as practical in order to derive an overall assessment for any area. Single factor assessments can be

TABLE 3-6. TERRESTRIAL FACTORS AND ASSOCIATED CRITERIA FOR DETERMINING THE POTENTIAL OF TERRESTRIAL ECOSYSTEMS TO REDUCE THE ACIDITY OF ATMOSPHERIC DEPOSITION (modified after Cowell et al. 1981)

TERRESTRIAL FACTORS	POTENTIAL TO REDUCE ACIDITY OF ATMOSPHERIC DEPOSITION		
	HIGH	MODERATE	LOW
Soil Chemistry			
I) Exchangeable Bases Surrogates:	> 15 meq/100g	6 to 15 meq/100g	< 6 meq/100g
(a) Family Particle Size and pH in water	clayey, > pH 5.0	clayey, pH 4.5 to 5.0	clayey, < pH 4.5
	loamy, > pH 5.5	loamy, pH 5.0 to 5.5	loamy, < pH 5.0
	all calcareous soils	sandy, > pH 5.5	sandy, < pH 5.5
(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)
(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 content	______________	low sulphate adsorption: high organic matter AND/OR low Al_2O_3 and/or Fe_2O_3 + Fe_3O_4 content
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%)	discontinuous to sparse (20 to 60%)	sparse to barren (< 20%)
Underlying Material			
I) Parent Material	carbonate bearing	noncarbonate bearing	noncarbonate bearing
II) Bedrock Material	limestone, dolomite, and metamorphic equivalents, calcareous clastic rocks, carbonate rocks interbedded with noncarbonate rocks	volcanic rocks, shales, greywackes, sandstones, ultramafic rocks, gabbro, mudstone, metaequivalents	granite, granite gneiss, orthoquartzite, syenite

misleading, especially in areas where soil mineralogy differs from underlying bedrock lithology such as glacially-derived soils and old, deeply weathered soils over limestone (such as in United States, south of the glacial limit).

In both the U.S. and Canadian mapping, soils and bedrock are the primary factors assessed. It is assumed that resultant lake or stream water chemistry will reflect the combined interaction of the varying soil and bedrock characteristics on acidic deposition. Surface and shallow groundwater flow conditions are assumed to best characterize the surface water regime. Groundwater residence times and deep groundwater circulation were not considered.

Certain types of vegetation, especially broad-leaved deciduous trees, are capable of reducing acidity of intercepted precipitation (Fairfax and Lepp 1975, 1976). The nature of chemical modifications by vegetation species, however, is not yet fully understood. Therefore, the effect of vegetation type and cover on aquatic system sensitivity has not been included in this analysis.

Lucas and Cowell (1982) have mapped the potential of soils and bedrock to reduce acidity of atmospheric deposition across eastern Canada (east of Manitoba). A similar study has been carried out by Olson et al. (1982) for the eastern U.S. The mapping was coordinated in order to produce a comparable basis for evaluation. Although the conceptual framework is similar, data availability and quality varied considerably both between and within countries.

The maps of eastern Canada and the eastern United States presented here combine bedrock, soil and certain other factors (Table 3-7) in order to interpret the potential ability of terrestrial ecosystems to reduce acidity. A low potential implies that acidic deposition could reach aquatic systems with little neutralization. Many of the low potential ecosystems are naturally acid and may contribute a high capability to acidify incoming precipitation because of organic acids, especially in areas receiving low inputs of mineral acids. High potential areas would generally be capable of reducing acidity such that impacts to aquatic systems would be minimal.

Specific factors used in the mapping for both Canada and the United States are listed in Table 3-7. The assessment of relative potential to reduce acidity may be inferred from Table 3-6. The methodologies for combining and weighting the variables shown in Table 3-7 are discussed below.

The map of eastern Canada (Figure 3-9 in map folio) is presented at the compilation scale of 1:1,000,000. The U.S. map (Figure 3-10 in map folio) is shown at 1:5,000,000.

TABLE 3-7. TERRESTRIAL FACTORS AND ASSOCIATED DATA BASES UTILIZED FOR THE INTERPRETATION OF THE POTENTIAL TO REDUCE ACIDITY OF ATMOSPHERIC DEPOSITION (After Lucas and Cowell 1982; Olson et al. 1982)

TERRESTRIAL FACTORS/SURROGATES	DATA SOURCES[a]
<u>EASTERN CANADA</u>	
1) Soil Chemistry	
Surrogates: i) Texture (sand, loam or clay) - Quebec, the Maritimes and Newfoundland/Labrador, northern Ontario	Ecodistrict Data Base (Environment Canada 1981a, b, c)
ii) Depth to Carbonate (high, low or no lime) - Ontario	Ontario Land Inventory (MNR 1977)
iii) Glacial Landforms - northwestern Ontario	Pala and Boissonneau 1979
iv) Organic Soils (≥50% of mapping unit)	Ecodistricts (Environment Canada 1981a, b, c) and Ontario Land Inventory (MNR 1977)
2) Soil Depth - shallow (25 cm to 1 m) - deep (>1 m)	Ecodistricts (Environment Canada 1981a, b, c) and Ontario Land Inventory (MNR 1977)
3) Bedrock Geology - type	Shilts et al. 1981
- % exposed (<25 cm deep)	Ecodistricts (Environment Canada 1981a, b, c) and Ontario Land Inventory (MNR 1977)

TABLE 3-7. CONTINUED

TERRESTRIAL FACTORS/SURROGATES	DATA SOURCES[a]
EASTERN UNITED STATES	
1) Soil Chemistry	
i) mean soil order pH (in distilled water)	Soil Map (USGS 1970)
ii) SO_4^{2-} adsorption (assumed for Ultisols only)	Johnson et al. 1980
2) Elevation - landform	Hammond's Landform Map (USGS 1970)
- 2000 ft a.s.l	Topographic Map (USGS 1970)
3) Bedrock Geology - type	Hendrey et al. 1980; Norton 1982
4) Land Use - urban areas	1977 National Resource Inventory (USDA 1978)
- cultivated (managed) soils	1978 Census of Agriculture (USDC 1979)

[a] All U.S. data sources listed have been compiled within the Geoecology Data Base (Olson et al. 1980).

3.5.1.1 Eastern Canada

The map of Eastern Canada (Figure 3-9) was prepared from several data sources (Table 3-7). Quebec, the Maritimes and Newfoundland-Labrador were interpreted using the Ecodistrict Data Base (Environment Canada 1981 a, b, c) described in Cowell et al. (1981) and the bedrock sensitivity evaluation of Shilts et al. (1981). In northeastern Ontario, north of 50°N latitude, Ecodistricts were used in combination with the Ontario bedrock geology maps (Ontario Ministry of Natural Resources, Maps 2198 and 2200). In northwestern Ontario, the recent physiographic mapping of Pala and Boissonneau (1979), and bedrock geology mapping (Ontario Ministry of Natural Resources, Maps 2199 and 2201) provided the basis for interpretations north of 52°N. Interpretations for the area to the south are based on Shilts et al. (1981) and the Ontario Land Inventory (OLI) (OMNR 1977; also described in Richards et al. 1979). The OLI was originally generated at 1:250,000. As much information as possible has been retained in the 1:1,000,000 scale mapping presented here. This partially accounts for the apparent variation in map detail.

A cautionary point regarding the use of the Ecodistrict data base in Quebec, the Maritimes and Newfoundland-Labrador must be emphasized. The Ecodistrict delineations are based on a series of biophysical factors including geology and soils. However, the units are not based solely on these two factors. In an attempt to isolate the critical geological factor in sensitivity assessment, the bedrock sensitivity evaluation compiled by Shilts et al. (1981) was superimposed directly on the Ecodistrict map south of 52°N latitude. As no similar map is available for soils for eastern Canada and, with the premise that the ecodistricts delineate major soil characteristics the Ecodistrict base is assumed as the soil base for the combined map. Because of this assumption, for the resultant subdivisions of ecodistricts, the soils data represent the dominant characteristics as described for the original ecodistrict and not the more site specific combined units. However, the Shilts et al. (1981) interpretation was used primarily to improve the resolution in areas where carbonate predominated or where soils were thin and discontinuous and the bedrock sensitivity was most important in the overall evaluation.

In assessing map units, each factor in Table 3-7 is assigned a high, moderate or low potential to reduce acidity of atmospheric deposition independently (except percent bedrock exposure). Dominant factors were then combined and weighted in order to derive an overall rating for the map units. Subdominant characteristics were not considered. Specific combinations of the factors mapped as high, low or moderate potential for reducing acidity are identified in Table 3-8. This table shows 74 classes (of which 65 actually occur) which have been grouped into high, low and moderate potentials to reduce acidity. In addition there are 10 classes representing terrain dominated by organic deposits for which no specific interpretation has been made.

TABLE 3-8. TERRESTRIAL CHARACTERISTICS OF AREAS HAVING HIGH, MODERATE AND LOW POTENTIAL TO REDUCE ACIDITY FOR EASTERN CANADA (after Lucas and Cowell 1982)

	TERRAIN DESCRIPTION					MAP AREA	
	Polygon Classification	Soil Depth[a]	Soil Texture[b]	Bedrock Lithology[c]	% Bedrock Outcropping[d]	km^2	% of Eastern Canada
HIGH POTENTIAL TO REDUCE ACIDITY	H1a	deep	clay	Type 1	0-49	78,890	2.51
	H1b	deep	loam	Type 1	0-49	65,960	2.10
	H1c	deep	sand	Type 1	0-49	8,105	0.26
	H1d	deep	clay	Type 1	50-99	N/A	N/A
	H1e	deep	loam	Type 1	50-99	1,004	0.03
	H1f	deep	sand	Type 1	50-99	109	<0.01
	H1g	shallow	clay	Type 1	0-49	7,989	0.25
	H1h	shallow	loam	Type 1	0-49	5,305	0.17
	H1i	shallow	sand	Type 1	0-49	8,959	0.29
	H1j	shallow	clay, loam or sand	Type 1	50-99	1,405	0.04
	H1k	bare		Type 1	100	N/A	N/A
	H2a	shallow	clay	Type 2	0-49	4,317	0.14
	H2b	shallow	clay	Type 3	0-49	5,467	0.17
	H3a	deep	clay	Type 2	0-49	20,567	0.66
	H3b	deep	clay	Type 3	0-49	65,470	2.09
	H3c	deep	clay	Type 4	0-49	101,420	3.23
MODERATE POTENTIAL TO REDUCE ACIDITY	M1a	deep	clay	Type 2	50-74	7,104	0.23
	M1b	deep	clay	Type 3	50-74	N/A	N/A
	M1c	deep	loam	Type 2	50-74	83	<0.01
	M1d	deep	loam	Type 3	50-74	5,543	0.18
	M1e	deep	sand	Type 2	50-74	N/A	N/A
	M1f	deep	sand	Type 3	50-74	9,615	0.31
	M1g	deep	clay	Type 2	75-99	N/A	N/A
	M1h	deep	clay	Type 3	75-99	N/A	N/A
	M1i	deep	loam	Type 2	75-99	2,325	0.07
	M1j	deep	loam	Type 3	75-99	489	0.02
	M1k	deep	sand	Type 2	75-99	N/A	N/A
	M1l	deep	sand	Type 3	75-99	N/A	N/A
	M1m	shallow	clay	Type 2	50-74	N/A	N/A
	M1n	shallow	clay	Type 3	50-74	1,038	0.03
	M1o	shallow	loam	Type 2	50-74	3,114	0.10
	M1p	shallow	loam	Type 3	50-74	740	0.02
	M1q	shallow	sand	Type 2	50-74	48	<0.01
	M1r	shallow	sand	Type 3	50-74	14,345	0.46
	M1s	shallow	clay, loam or sand	Type 2	75-99	374	0.01
	M1t	shallow	clay, loam or sand	Type 3	75-99	2,218	0.07
	M1u	bare		Type 2	100	415	0.01
	M1v	bare		Type 3	100	14	<0.01

TABLE 3-8. CONTINUED

	TERRAIN DESCRIPTION					MAP AREA	
	Polygon Classification	Soil Depth[a]	Soil Texture[b]	Bedrock Lithology[c]	% Bedrock Outcropping[d]	km^2	% of Eastern Canada
MODERATE POTENTIAL TO REDUCE ACIDITY	M2a	deep	clay	Type 4	50-74	82	< 0.01
	M2b	shallow	clay	Type 4	50-74	982	0.03
	M3	shallow	loam	Type 4	0-49	60,388	1.93
	M4a	shallow	sand	Type 2	0-49	15,234	0.49
	M4b	shallow	sand	Type 3	0-49	202,167	6.44
	M5	shallow	clay	Type 4	0-49	13,776	0.44
	M6a	shallow	loam	Type 2	0-49	14,155	0.45
	M6b	shallow	loam	Type 3	0-49	51,297	1.64
	M7a	deep	loam	Type 2	0-49	35,546	1.13
	M7b	deep	loam	Type 3	0-49	104,406	3.33
	M7c	deep	loam	Type 4	0-49	64,804	2.07
LOW POTENTIAL TO REDUCE ACIDITY	L1a	deep	clay	Type 4	75-99		
	L1b	deep	loam	Type 4	75-99	3,322	0.11
	L1c	deep	sand	Type 4	75-99	6,538	0.21
	L1d	shallow	clay, loam or sand	Type 4	75-99	80,800	2.58
	L1e	bare		Type 4	100	10,405	0.33
	L2a	deep	loam	Type 4	50-74	47,460	1.51
	L2b	deep	sand	Type 4	50-74	2,150	0.07
	L2c	shallow	loam	Type 4	50-74	11,905	0.38
	L2d	shallow	sand	Type 4	50-74	156,862	5.00
	L3	shallow	sand	Type 4	0-49	527,190	16.80
	L4a	deep	sand	Type 2	0-49	15,595	0.50
	L4b	deep	sand	Type 3	0-49	161,509	5.15
	L4c	deep	sand	Type 4	0-49	676,252	21.55
ORGANIC TERRAIN[e]	O1a		organics	Type 1	0-50	205,748	6.56
	O1b		organics	Type 2	0-50	40,426	1.29
	O1c		organics	Type 3	0-50	52,949	1.70
	O1d		organics	Type 4	0-50	142,200	4.53

TABLE 3-8. CONTINUED

	TERRAIN DESCRIPTION					MAP AREA	
	Polygon Classification	Soil Depth[a]	Soil Texture[b]	Bedrock Lithology[c]	% Bedrock Outcropping[d]	km^2	% of Eastern Canada
ORGANIC TERRAIN[e]	02a		organics	Type 1	51-74	34	< 0.01
	02b		organics	Type 2	51-74	N/A	N/A
	02c		organics	Type 3	51-74	207	< 0.01
	02d		organics	Type 4	51-74	377	0.01
	03a		organics	Type 1	75-99	48	0.01
	03b		organics	Type 2	75-99	N/A	N/A
	03c		organics	Type 3	75-99	55	< 0.01
	03d		organics	Type 4	75-99	327	0.01

[a] Soil depth is defined as follows:
deep - >1 m average soil thickness
shallow - 25 cm - 1 m average soil thickness
bare - <25 cm average soil thickness

[b] Soil texture is used to interpret soil sensitivity for most of eastern Canada. In Ontario where depth to carbonate information is available, the following corresponding classes were used:
clay - high or very high lime
loam - moderate and low lime
sand - low base or no lime

[c] Bedrock sensitivity classes were defined by Shilts et al. (1981) on the basis of lithology. Specifically:
Type 1 - Limestone, marble, dolomite
Type 2 - Carbonate-rich siliceous sedimentary: shale, limestone; non-calcareous siliceous with carbonate interbeds: shale, siltstone, dolomite; quartzose sandstone with carbonates
Type 3 - Ultramafic rocks, serpentine, noncalcareous siliceous sedimentary rocks: black shale, slate, chert; gabbro, anorthosite: gabbro, diorite; basaltic and associated sedimentary: mafic volcanic rocks.
Type 4 - Granite, gneiss, quartzose sandstone, syenitic and associated alkalic rocks.

[d] Average bedrock outcropping within each map unit is shown as a percent of map unit.

[e] Organic materials are the dominant soil constituent wherever organics are indicated.

These are areas of high natural acidity which contribute organic acids to enclosing watersheds.

Percent bedrock exposure and soil depth were key parameters for weighting the relative contribution between bedrock type and soil chemistry. Generally, the emphasis was on the bedrock capacity to reduce acidity where bedrock exposure was greater than 50% of an area. If soils were deep (greater than 1 m) and occurred in more than 50% of the map unit, then soil chemistry was emphasized. Soil and bedrock potentials to reduce acidity in map units having combinations of shallow soils and bedrock exposures less than 75% were either averaged or assigned the highest potential. Soil chemistry was interpreted using texture and depth to carbonate because of the nature of the data bases. However, in comparing these with the smaller-scale Soil Map of Canada (Clayton et al. 1977) there appears to be a good correlation with soil order. Hence, sand or no lime soils are dominantly acid Podzols (or "Rockland") and clay or high lime soils are dominantly Luvisols and Gleysols. Loam or low lime soils tend to be more varied including Podzolic, Luvisolic and Brunisolic orders.

Map units identified as having a high potential to neutralize acidic deposition are predominantly areas underlain by carbonate bedrock (H1) or areas dominated by deep clay or high lime soils (H3). These each cover approximately 6% (Table 3-8) of the map area represented in Figure 3-9. The former assumes at least some interaction between carbonate-rich bedrock and precipitation prior to entering the aquatic regime. This is probably valid for most of eastern Canada where limestones have either been exposed or buried under carbonate-rich tills by the latest glaciation. In the Hudson Bay Lowland (northernmost Ontario and part of northwestern Quebec) organic deposits blanket the carbonate-rich substrate. Although large streams, rivers and lakes in this region intersect mineral soil, smaller peatland lakes, ponds and streams have naturally soft waters which developed as peat material accumulated over the carbonates. All such organic terrains are considered separately for this reason.

The two dominant combinations of soil and bedrock identified as having a moderate potential to reduce acidity are shallow loam or low lime soils overlying bedrock of moderate (M6) and deep loam or low lime soils (M7). Each of these occupy approximately 7% of eastern Canada. The distribution of all moderate classes is highly variable across eastern Canada.

All five combinations identified as having a low potential are recorded in eastern Canada. In Ontario and Newfoundland-Labrador the dominant class is deep sand (L4). Shallow sands (L3) are frequently found in the more northerly regions, notably in Quebec and Ontario. These two classes are predominately acid Podzols. Areas of high bedrock exposure (L2) are common to shore zones of lakes and northern areas.

Major areas of organic soils overlying noncalcareous bedrock (05b, 05c and 05d) are identified in western New Brunswick, southern Labrador and Newfoundland and in the west central portion of Quebec. Large areas of peatland are identified adjacent to the Hudson Bay Lowland in northwestern Ontario. Throughout central and western Ontario are numerous small pockets of organic soils. These areas are, to varying degrees, undergoing natural organic acidification and hence already contribute low pH, low bicarbonate waters to enclosed watersheds. It is not clear to what degree peatlands and organic groundwater are affected by, or in turn modify, incoming anthropogenic mineral acids.

3.5.1.2 Eastern United States

The potential for terrestrial systems to reduce acidity of atmospheric deposition was determined by combining information on soil chemistry, bedrock geology, terrain characteristics, and land use (Table 3-7). A map covering the eastern 37 states (Figure 3-10) was produced at Oak Ridge National Laboratory to characterize the relative potential for areas to reduce acidity of acidic deposition prior to being transferred to aquatic systems. The analysis utilized available national resource inventories and was interpreted according to the current understanding of mechanisms of transport and alteration of acid inputs in terrestrial systems (Seip 1980). County-level data from the Geoecology Data Base (Olson et al. 1980) were used in the analysis to provide a regional perspective. As more detailed data or new studies are completed, the resolution or interpretation of the map may need to be revised.

Initially, counties that were predominantly (> 50%) urban or agricultural were excluded from the analysis. Management and land use practices (liming, fertilizing, etc.) in these areas would tend to dominate modifications resulting from acidic deposition. The 1977 National Resource Inventory (USDA 1978) was used to define land in urban built-up areas and transportation corridors. The 1978 Census of Agriculture (USDC 1979) provided data on cropland. This resulted in 1,648 of the 2,660 counties in the east being included in the analysis. They contained predominantly forest, range, or pasture.

Rapid surface runoff of precipitation or snowmelt can preclude significant interaction with soils or bedrock. Steep areas with greater than 160 m of relief and elevation greater than 600 m based on Hammond's landform map (USGS 1970) and a general topographic map (USGS 1970) were identified as areas in which topography dominated the movement of rainfall to streams and lakes.

Counties covered by 50% or more of soil types with a surface pH of less than 5.0 were assigned a low potential to reduce the acidity of incoming precipitation. However, it should be noted that these soils are naturally acid and could contribute natural acidity to aquatic ecosystems. Criteria for natural acid generation in the soil are lacking and thus it is not known how significantly acidic deposition adds to the natural acidification in areas with low soil pH (see Section 3.5.2). Thus, the interpretation of all areas having a low potential to reduce acidity as being highly sensitive ignores natural acidity contributions.

Chemical and physical soil characteristics employed in the analysis represent average values for the A horizon (upper 20-25 cm) for the 82 great soil groups occurring in the eastern United States. These values were obtained from published literature (Klopatek et al. 1980). The great soil groups were combined to estimate values for the 195 soil mapping units identified (USGS 1970) in the east. Although the exact proportions of great soil groups within map units are not readily available, the dominant great soil group was given a weighting factor of 0.66 to calculate average map unit values. Proportions of soil mapping units within counties were estimated from the 1:7,500,000 scale soil map of the United States (USGS 1970).

Sulphate adsorption capacity of soils provides additional neutralization of acidic water infiltrating the soil. Sulphate adsorption prevents H^+ transport and can increase soil cation exchange capacity (see Section 4.5 on soil sensitivity mapping). Ultisols generally have high sulphate adsorption capacity, although few studies have determined the current status of adsorption capacity in existing Ultisols, such as occur extensively in the southern United States (Johnson et al. 1980). Counties containing 50% or more Ultisols were identified on Figure 3-10 as having high potential to reduce acidity.

Bedrock influence was based on the occurrence of type 1 (low to no ability to neutralize acidic inputs) and type 2 (medium to low ability to neutralize acidic inputs) bedrock as defined and mapped by Hendrey et al. (1980). Counties having 50% or more area in type 1 and 2 were defined as having low potential to reduce the acidity of acidic deposition which comes in contact with bedrock. These are also designated sensitive. The remaining counties were generally dominated by type 4 (greater ability to neutralize acid inputs) with a high potential to neutralize acid water coming in contact with bedrock. Such areas are often called insensitive to acid rain.

The influence of these factors on the ability of the watersheds to neutralize acid inputs was evaluated on a county by county basis. Although counties are generally uniform in size in the eastern United States, some of the larger counties occur along the Canada-United States border in Maine and Minnesota. For each factor, 50% or greater of land surface area was used as dominance criterion to classify counties. Therefore, significant areas can exist within counties that differ from the final designated classification. Thus, Figure 3-10 displays the broad regional patterns but evaluation of an individual county requires more detailed analysis to determine the extent and coincidence of the various factors within that county. The analysis identified the dominant factor(s) in each county that would determine if a county had relatively low, moderate or high potential to reduce the acidity of acidic deposition. The moderate class would both be between the extremes in reducing acidity and also may be more variable, that is, within a moderate county, there may be both areas of low and high of sensitivities.

Seven classes were used to describe the combinations that occurred (Table 3-9) with the agricultural/urban areas shown as blank on the map (Figure 3-10). The factors in each class and the assignment of low, moderate or high potential are defined in Table 3-8. Classes 3, 4 and 6 are combinations of soils and bedrock having opposite potentials for reducing acidity. In these areas, the soil depth and other terrain characteristics (such as glaciation or soil pans) will determine whether soil or bedrock properties dominate. Class 3 consists of low pH soils overlaying bedrock with high ability to neutralize acid. In the south these soils are generally very thick and bedrock would be an insignificant factor. However, in northern glaciated areas, the thin, porous soils would probably result in a high potential to reduce acidity of precipitation through the interaction with the bedrock.

3.5.2 Aquatic - Terrestrial Relationships

The maps shown in Figures 3-9 and 3-10 identify areas of low, moderate or high potential to ameliorate the impact of acidic deposition on aquatic regimes. Map units having the lowest capacity to reduce the acidity of atmospheric deposition should not be interpreted as representing the total land area with acidified lakes and streams in eastern North America. These are the areas where acidification would theoretically be most pronounced provided the input of anthropogenic acids add significantly to natural acid production or, in the case of bedrock dominated systems, exceeded the acid neutralizing capacity of the strata. In order to determine which aquatic ecosystems are already acidified, detailed water chemistry data are necessary (Section 3.6). However, as noted earlier, soil and bedrock information provides the best indication of the long term capacity of watersheds to buffer acidic deposition.

Many questions remain as to how the dilute acid in precipitation can be transported through terrestrial systems without being dominated by organic/soil buffering mechanisms. Current knowledge of terrestrial-aquatic transport fail to account mechanistically for the large changes in surface water pH attributed to acidic deposition. However, lake and stream acidification effects are observed in watersheds where soils are present (Section 3.9). These changes are through mechanisms not now fully understood. Such mechanisms probably relate to rapid drainage through soil macropores as represented by root channels, voids surrounding coarse fragments (such as common in glacially-deposited soils) and other routes. Thus at this stage sensitivity criteria are hypothetical (e.g., soil texture). The maps presented in this section should not be

TABLE 3-9. CHARACTERISTICS OF MAP CLASSES FOR THE EASTERN UNITED STATES AS TO THE POTENTIAL TO REDUCE ACIDITY OF ACIDIC DEPOSITION (Olson et al. 1982)

Class	Potential to Reduce Acidity	No. of Counties	Characteristics
1	Low	72	Steep slopes, high relief, high elevation
2	Low	89	Low soil pH, sensitive bedrock
3	Low-High	114	Low soil pH, nonsensitive bedrock
4	Moderate	291	Low soil pH, sensitive bedrock, sulphate adsorption
5	High	326	Low soil pH, nonsensitive bedrock, sulphate adsorption
6	Moderate	241	High soil pH, sensitive bedrock
7	High	515	High soil pH, nonsensitive bedrock

considered strictly as sensitivity maps. They are objective representations of soil and bedrock characteristics as provided by available data bases. Map units are identified by their "potentials" to reduce acidity based on one interpretation of the criteria. The criteria are plainly visible if anyone should desire some other interpretation or sensitivity assessment. The application of these maps for surface water sensitivity interpretation can, at present, only be tested using emprically based surface water acidification data (Section 3.9).

Low pH soils (eastern U.S.) and acid podzolic soils (eastern Canada) are representative of much of the area identified in Figures 3-9 and 3-10 as having the lowest potential to reduce the acidity of rainfall. According to Wiklander (1973/74) as reported in Seip (1980) as soil pH decreases below 5.0 there is an increasing probability that streams and lakes within a watershed will receive acid and aluminum associated with anion inputs from the terrestrial systems due to increased acidic sulphate deposition. Because these soils generally have low quantities of basic cations (e.g., Ca^{2+}, Mg^{2+}) a significant portion of the increased cation concentration required to balance the increased sulphate input must be H^+ and Al (Johnson and Olson in press). Because these soils are naturally acid, they are also the ones most likely to contribute natural acidity to surface waters (Rosenqvist 1978). Such soils do indeed have the lowest potential to reduce acidity of rainfall, but they also have the potential to acidify incoming rainfall in areas where low acidic deposition occurs (Johnson 1981; Johnson and Cole 1977). Thus, the question of acidic deposition effect is one of quantity, that is, to what extent does acidic or sulphate deposition via the mobile anion mechanism described by Seip (1980) contribute to the natural acidity of waters from such soils?

Aquatic ecosystems most sensitive to acidification and Al mobility, therefore, are those areas identified as having a limited ability to reduce acidity. They may also receive significant inputs of anthropogenic acids. What constitutes a "significant input" can only be determined at present by monitoring surface water chemistry in areas undergoing acidification. It should then be possible to extrapolate these results to other areas by comparing watershed characteristics such as bedrock, soils, proportion of open water to watershed area and vegetation. This would need to be carried out at a more detailed level than the present mapping. However, the maps in Figures 3-9 and 3-10, in combination with acidic deposition maps, illustrate the distribution of the areas within which efforts need to be concentrated in eastern North America.

Groundwaters and surface waters which cross areas of differing capacity to reduce acidity would reflect the chemistry of the most reactive bedrock or soils upstream from any sample point (Hendrey et al. 1980). Thus, both local and regional hydrological and hydrogeological conditions need to be assessed when comparing measured aquatic chemistry with potential of areas to reduce acidity.

It is also important to consider the topographic position of streams and lakes within watersheds. Generally, the most susceptible aquatic resources are those in the headwater portion of watersheds, or in small enclosed watersheds. During spring snowmelt runoff reaches surface waters with little or no contact with soils or bedrock, resulting in episodic pH declines. This effect may occur even in watersheds that are not very sensitive to long-term acidification.

3.5.3 Geochemical Changes Due to Acidic Precipitation

Nearly all precipitation is processed terrestrially before becoming surface water. Thus, changes in soil chemistry might be expected as a result of atmospheric deposition of acids and metals. Many geochemical changes in soils are difficult to measure directly, due to large reserves of elements, and due to complex ecology. However, changes in outputs of soil and groundwaters from stressed systems may be manifested as changes in surface water chemistry. In dilute waters such as found in the Adirondacks and New England, any change should be readily observed, if historical data cover the time interval of change.

Acidification rate (or lack of) is in part a function of relative maturity of the water in question. Low order streams and small headwater ponds will reveal acidification effects before major streams, rivers and lakes (Haines 1981b). Johnson and Reynolds (1977) examined the chemistry of headwater streams in New Hampshire and Vermont. These streams ranged from pH 5.0 to 7.8. Streams situated in sensitive bedrock such as granite or quartz monzonite ranged from pH 5.0 to 6.8. Total dissolved solids were generally very low (12-30 ppm), lower than TDS for many waters in areas that are not experiencing acidic precipitation. Similar results are reported for Hubbard Brook (Likens et al. 1977a). The implication is that cation denudation in New England is relatively low, in spite of acidic precipitation (Johnson et al. 1972, 1981). Studies by Schofield (1982) and Johnson et al. (1972) concur that it is not possible to conclude that increases in weathering (or increases in dissolved load) have occurred in areas receiving acidic deposition.

While major cations are generally low in sensitive terrain, trace metals such as Zn, Mn, Al and Cu have been shown to be elevated in acidified systems (Norton et al. 1981b; Schofield 1982). This increase is a function of the solubility relationships for the metals, as well as atmospheric inputs of heavy metals (Galloway et al. 1980a). Continued inputs of acids may alter soil pH regimes, and result in mobilization of metals into ground- and surface-waters (Burns et al. 1981; Johnston et al. 1981; Kahl and Norton 1982). Aluminum mobilization may neutralize acids, as suggested by N.M. Johnson (1979), but once mobilization has occurred, Al species may buffer acidic waters at low pH (about pH 4.9), much like the carbonate buffer system, but at a lower pH. Once acidified, recovery of waters with high concentrations of Al may be hindered by these Al hydrolysis reactions.

Atmospheric inputs of Pb and Zn can be demonstrated in organic soils in New England. In Massachusetts, Siccama et al. (1980) report that Pb is accumulating in the forest floor at a rate of 30 $mg/m^2.yr$. No increase was reported for Zn, but Zn is much more mobile than Pb. Benninger et al. (1975) estimate that the retention time for Pb at Hubbard Brook Experimental Forest (HBEF) is nearly 5,000 years: thus Pb is largely being retained terrestrially. Other studies have reported concentrations of Pb and Zn above background in the northeast U.S. (Kahl and Norton 1982; Lazrus et al. 1970; Reiners et al. 1975; Schlesinger and Reiners 1974). Hanson et al. (1982) found a gradient of Pb in sub-alpine litter, suggesting that Pb was more concentrated in litter (and therefore in precipitation) in southwest New England, than in northeast New England or the Gaspé Peninsula. Concentrations of these metals may be hundreds of times those found in underlying inorganic soils (Kahl and Norton 1982).

The study by Johnson and Reynolds (1977) did not reveal any markedly acidic streams in New Hampshire or Vermont (low pH = 5.0). Burns et al. (1981) also report nonacidic headwater streams in New Hampshire (mean pH 6.1). However, they conclude that significant acidification has occurred since the 1930s, based on historical colorimetric data. They report that their colorimetry data agreed with their pH meter data. Regardless of the validity of time trend comparison, they also conclude that alkalinity to total base cation ratios are 0.2-0.5 in New England. This indicates that some chemical weathering is occurring through the reaction with strong acids, rather than by carbonic acid, with implications for surface alkalinities in the future. Similar findings have been presented by Cronan et al. (1978) for New Hampshire sub-alpine soils, where sulphuric acid, instead of carbonic or organic acids, is supplying most of the hydrogen ion for weathering reactions. The net result is a replacement of HCO_3^- by SO_4^{2-} as the dominant anion inwaters of the Adirondacks and New England. This replacement is complete in very acidic waters, and may be used as an estimate of acidification when only partial replacement by sulphate has occurred (Henriksen 1979). Schofield (1982) reports an apparent, although not significant, increase in SO_4^{2-} in Adirondack lakes during the past 15 years, although the validity of the comparison between methods is unknown.

3.6 ALTERATIONS OF SURFACE WATER QUALITY

The chemistry of surface water is an integrative measure of precipitation inputs and watershed influences. Altered precipitation inputs may cause biogeochemical changes and account for differences in regional water chemistry. The available data are discussed below as three topics: the present chemistry of aquatic systems; evidence of time-trends in water quality measures; and the patterns of seasonal or episodic variations in water quality.

3.6.1 Present Chemistry of Aquatic Systems

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. As a result, the normal relationship between the dominant cations, calcium and magnesium, and alkalinity is altered. Although these lakes are not necessarily acidic, the alkalinity will be less than predicted, from the sum of calcium plus magnesium (Henriksen 1980).

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 4-3 [Figure 3-11 this report]. 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 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 ... 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 [solid] line in Figure 3-11 may be an indication of the extent of acidification; lakes found below zero alkalinity [the hatched line] 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 4-4 [Figure 3-12 this report]; 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. .....

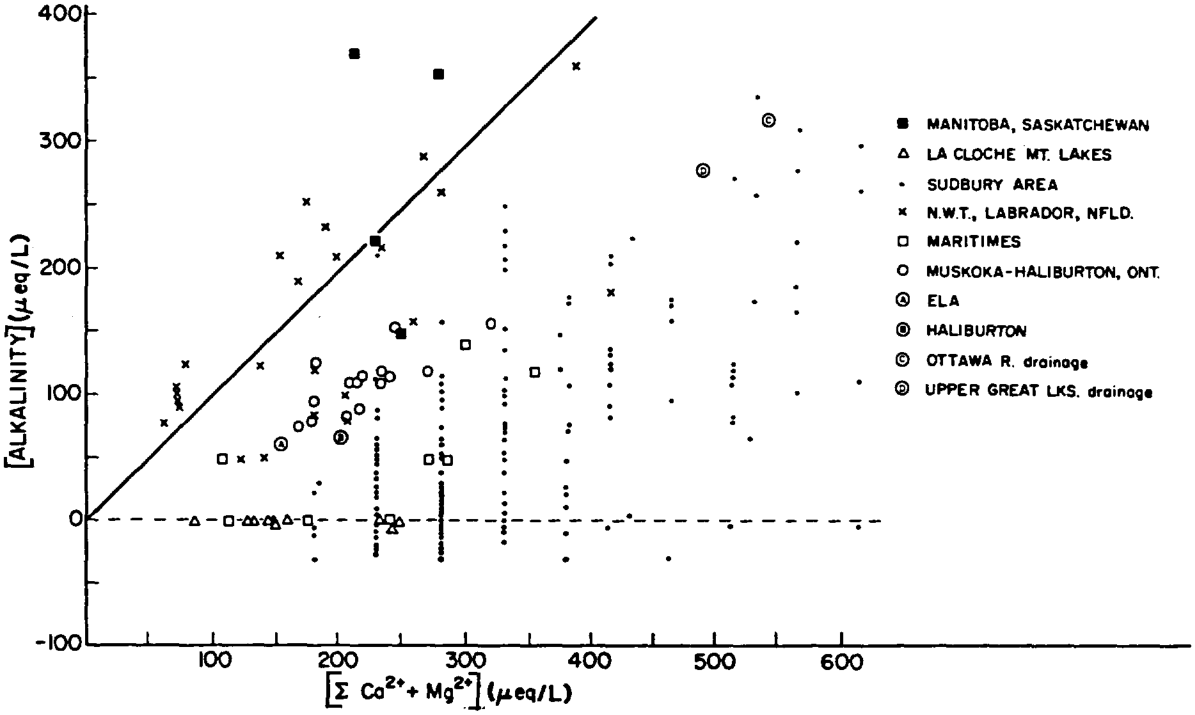


Figure 3-11. Total concentration of calcium plus magnesium with respect to alkalinity for lakes in Canada. Average concentrations for groups of lakes are shown as letters. Individual lake data are shown as symbols. Maritime lakes are not corrected for seasalt contribution. Solid line represents theoretical relationship for lakes unaffected by acidic deposition (see text for explanation and data sources). The scatter of data is due partly to the various techniques used to measure alkalinity (modified from Harvey et al. 1981).

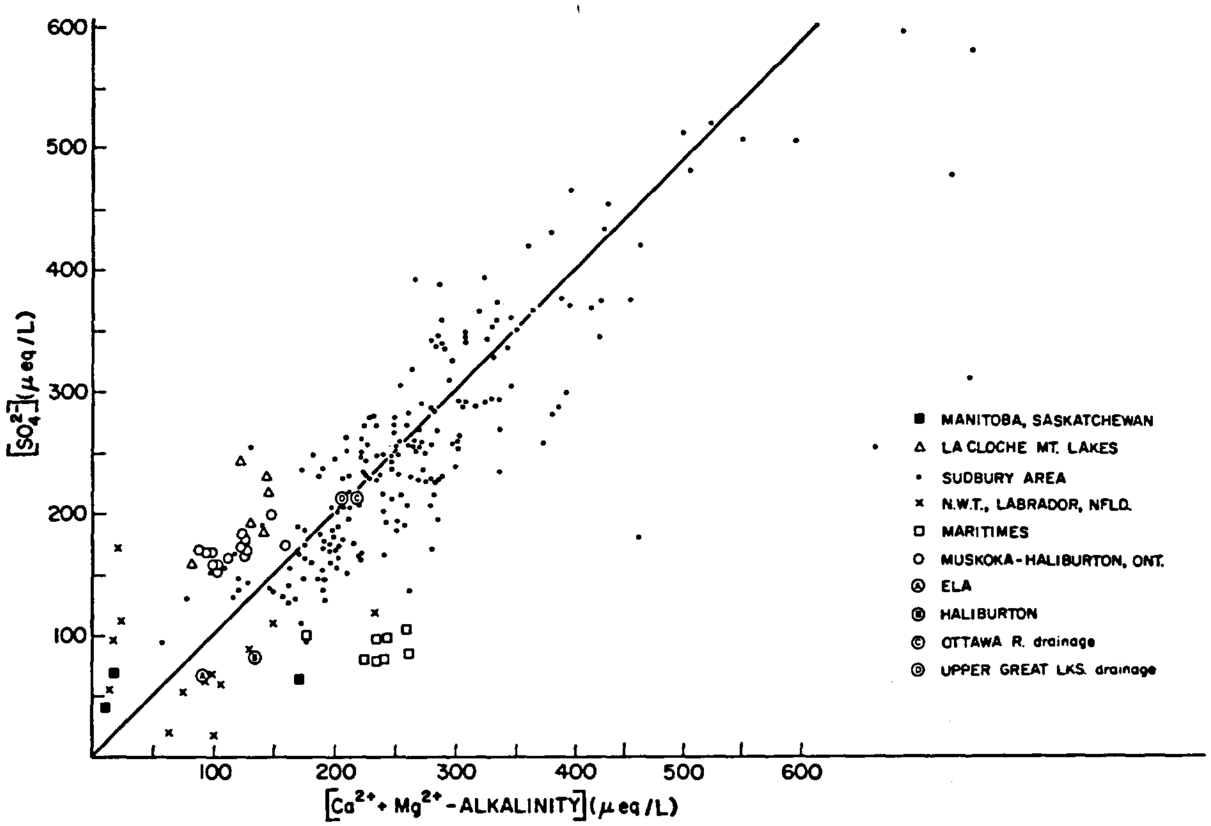


Figure 3-12. $[Ca^{2+} + Mg^{2+}$ - alkalinity$]$ vs. $[SO_4^{2-}]$ for lakes in Canada. Solid line represents theoretical relationship for $[Ca^{2+} + Mg^{2+}]$ not derived from carbonic acid weathering reactions (modified from Harvey et al. 1981).

> 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."

In a study of the most recent available data for lakes in Quebec, Bobée et al. (1982) have shown that a similar relationship between [Ca^{2+} + Mg^{2+}] - [alkalinity] and [SO_4^{2-}] exists on the southern slope of the Canadian Shield in Quebec. Figure 3-13 shows the different hydrographic regions sampled and Figure 3-14 shows the sulphate versus [Ca] + [Mg] - alkalinity relationship for six of the regions. The highest sulphate concentrations and greatest alkalinity deficiencies were observed in the southwest part of the province (Region 04). The concentrations of sulphate and the alkalinity deficits decrease to the north and east. In Region 10, sulphate concentrations average about 30 μeq/L and the alkalinity values were equal to or slightly greater than the calcium plus magnesium values indicating no alkalinity deficit. This supports the hypothesis of atmospherically deposited sulphur being a major influence on lake chemistry.

Current data on pH, alkalinity, sulphate, and other chemical variables are available for surface waters in a wide variety of climatic, geological and biological conditions in eastern North America. These data give an idea of the current chemistry 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. This approach was used by Thompson and Hutton (1982) for lakes in Canada from ELA (Experimental Lakes Area, Kenora, Ontario) eastward to Labrador and Newfoundland (Figure 3-15). The formal names of the lake regions, data sources, and the range of latitude and longitude including the sampled lakes are shown on Table 3-10. Concentrations of sulphate, and of excess sulphate near the coast, were multiplied by the basin runoff of water, obtained from hydrographic records of the basins or were approximated from hydrographic charts (Fisheries and Environment Canada 1978) to determine the sulphate flux or specific yield of sulphate for each basin in units of mass per unit area per year. Lakes used for this comparison exclude those where geological sources and direct industrial or municipal discharges of sulphur to the water body were obvious. Therefore, Thompson and Hutton (1982) assumed that the primary source of the basin sulphate yield was atmospheric. As a test of this assumption they compared the values of sulphate flux with the estimated atmospheric loading of sulphate in

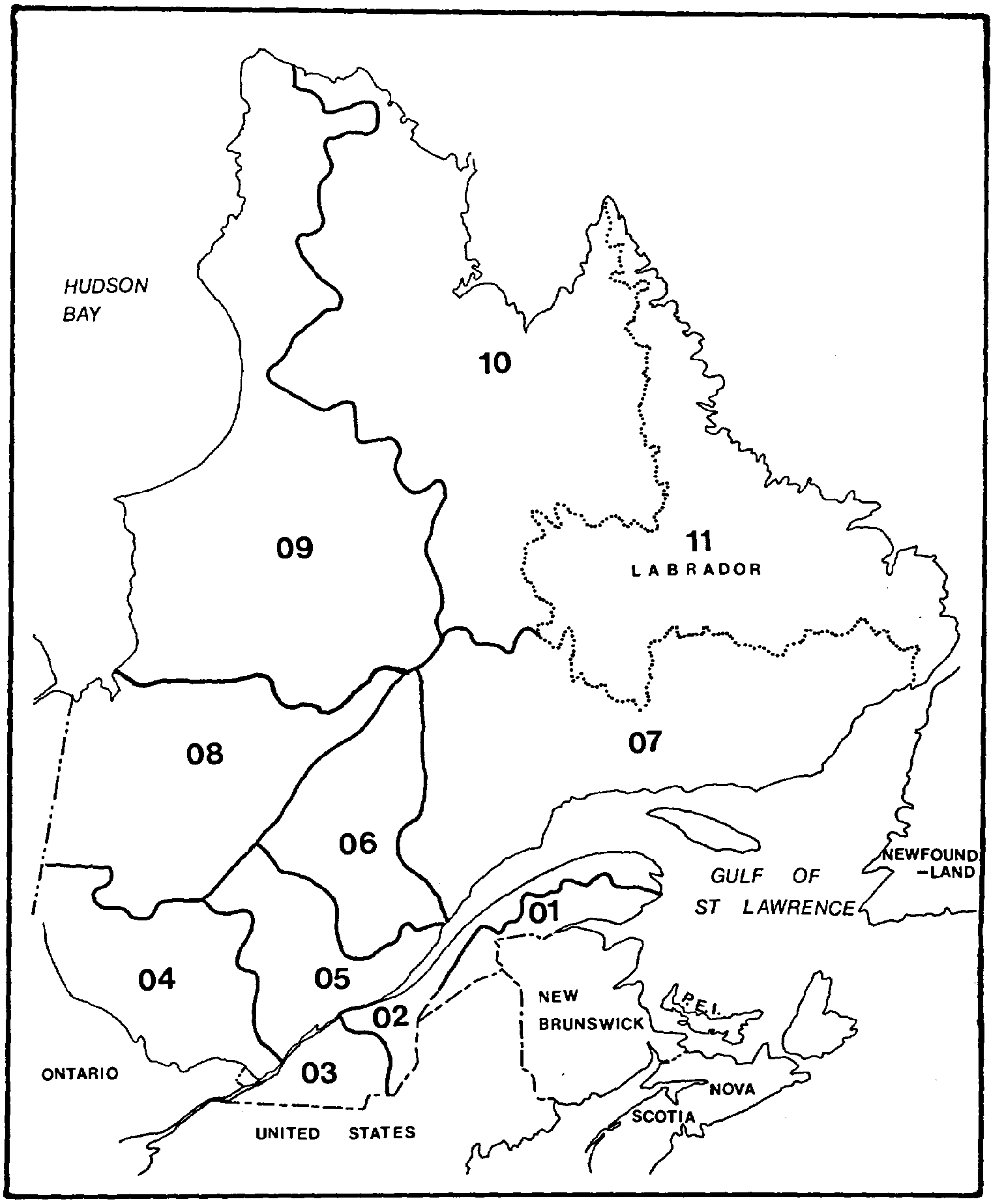


Figure 3-13. Hydrographic Regions of Quebec (Bobée et al. 1982).

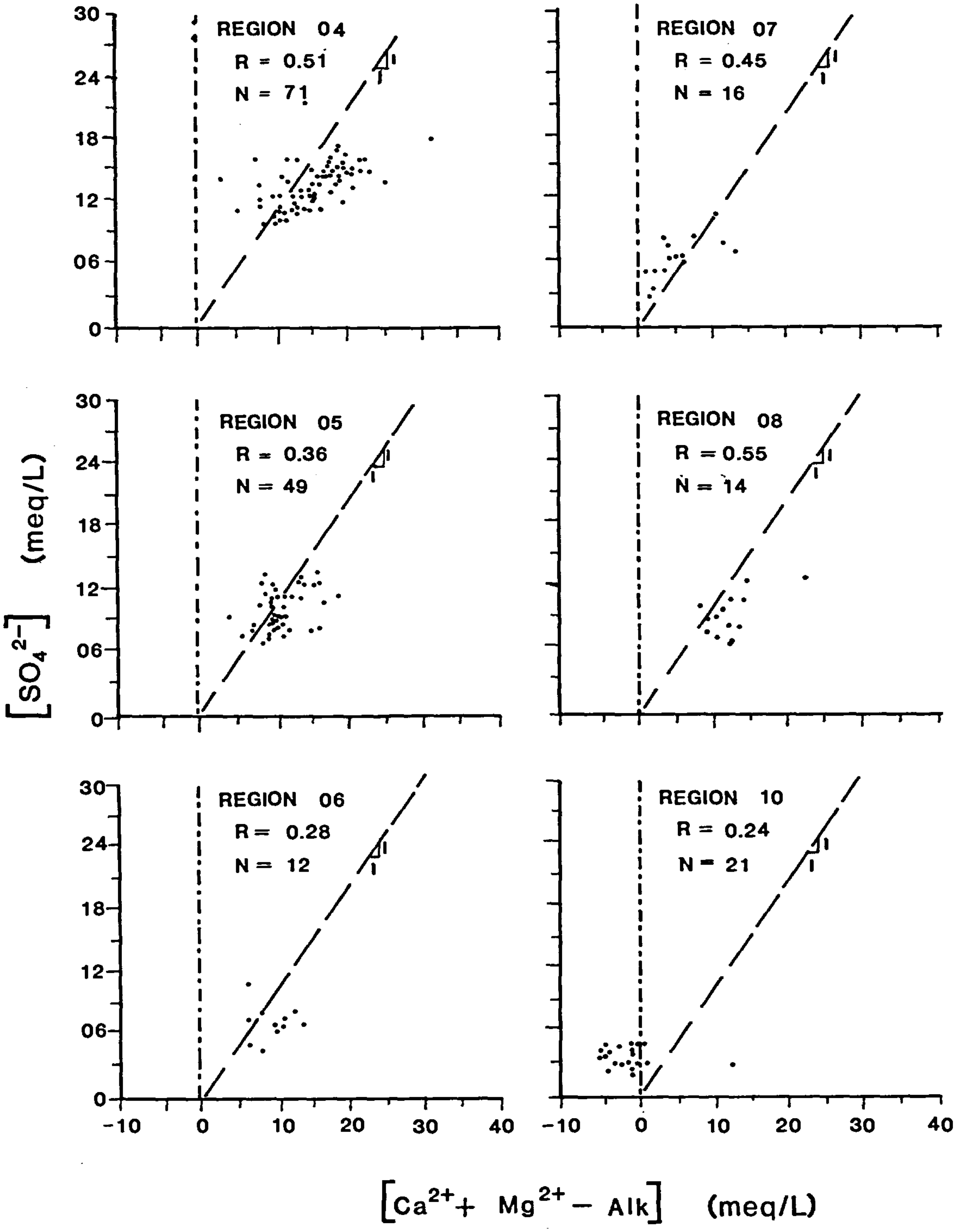


Figure 3-14. Sulphate as a function of [calcium + magnesium - alkalinity] for lakes in Quebec in the hydrographic regions given in Figure 3-13 (Bobée et al. 1982).

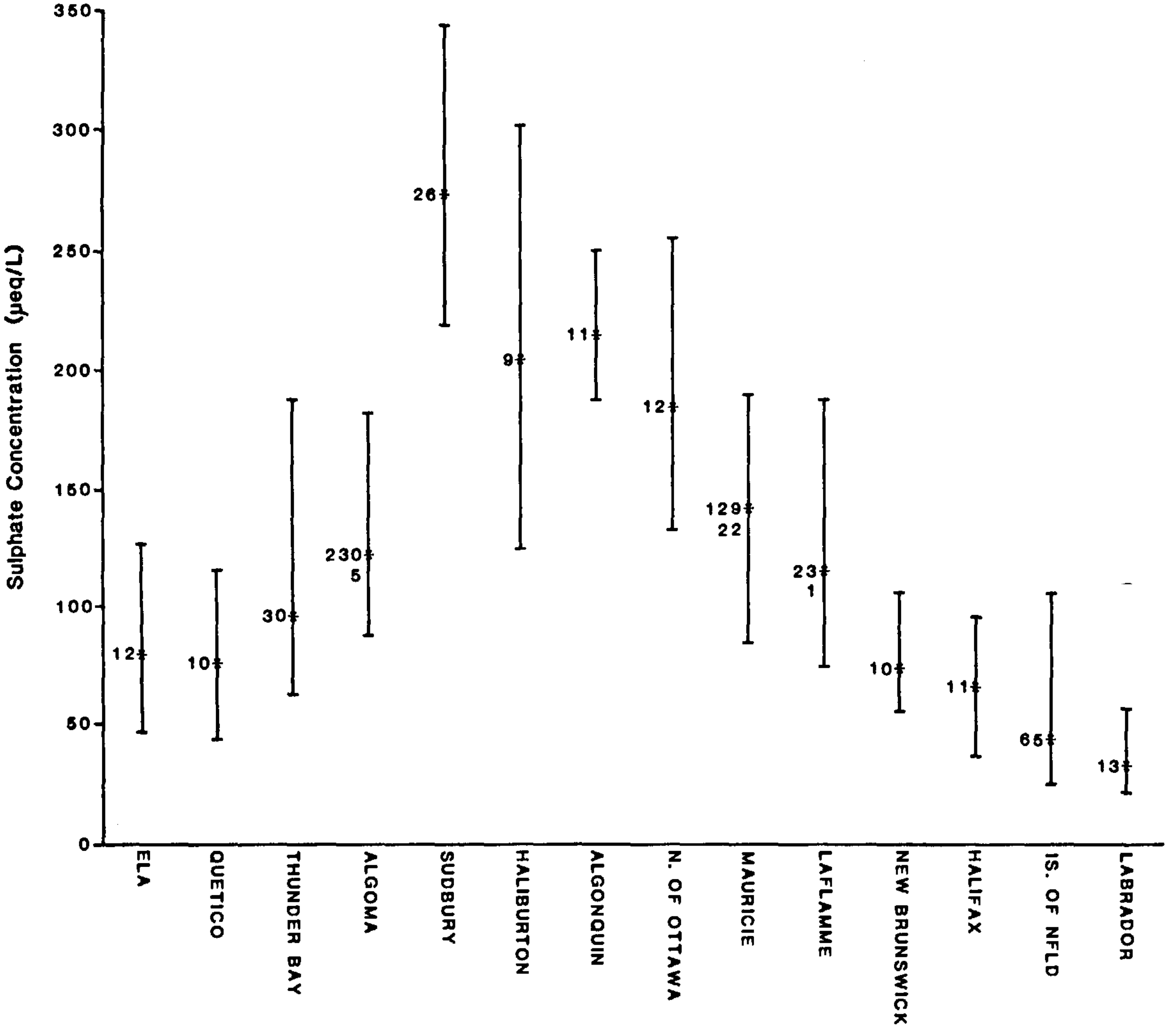


Figure 3-15. Mean (*) and range of SO_4^{2-} concentrations and excess concentrations in Canadian lakes on an approximately west to east axis. The numbers to the left of the means are the number of samples; where there are two numbers, the lower is the number of lakes (Thompson and Hutton 1982).

TABLE 3-10. FORMAL NAMES, LOCATIONS, LAKE DATA SOURCES AND THE LABORATORIES THAT ANALYZED THE SAMPLES FOR THE DATA SHOWN IN FIGURE 3-14 (from Thompson and Hutton 1982)

Lake Data Sets and Sources	Laboratory	Latitude	Longitude
Experimental Lakes Area, Kenora Ontario, Beamish et al. 1976	Freshwater Institute, Winnipeg	49°35' - 49°45'	93°35' - 93°45'
Quetico - Lac des Mille Lacs Fisheries Assessment Unit Lakes Ontario Ministry of the Environment, Northwestern Region	Ontario Ministry of the Environment, Thunder Bay Regional Laboratory	48°00' - 49°00'	90°00' - 92°30'
Thunder Bay Area Lakes, T. Marshall, Ontario Ministry of Natural Resources	Ontario Ministry of the Environment, Thunder Bay Regional Laboratory	48°40' - 49°10'	89°00' - 89°30'
Turkey Lakes, Algoma District, Ontario. D. Jeffries, National Water Research Institute	Environment Canada, Great Lakes Forestry Service, Sault Ste. Marie	47°02' - 47°04'	84°23' - 84°25'
Sudbury District Lake Trout Lakes, J. Gunn, Ontario Ministry of Natural Resources	Ontario Ministry of the Environment Laboratories at Dorset and Rexdale	46°30' - 47°20'	80°30' - 82°00'
Haliburton Highlands Fisheries Assessment Unit Lakes, D. Loftus, Ontario Ministry of Natural Resources	Ontario Ministry of the Environment Laboratories at Dorset and Rexdale	44°40' - 45°20'	78°00' - 79°10'
Algonquin Fisheries Assessment Unit Lakes, F. Hicks, Ontario Ministry of Natural Resources	Ontario Ministry of the Environment Laboratories at Dorset and Rexdale	45°25' - 46°00'	77°45' - 78°55'
Lakes in Quebec, north of Ottawa, Quebec Ministere de l'Environnement	Quebec, Ministere de l'Environnement, Ste. Foy	45°40' - 46°03'	75°37' - 76°07'
Lakes in Parc National de la Mauricie, R. Lemieux, Environment Canada, Quebec Region	Environment Canada, Water Quality Branch, Longueuil	46°45' - 46°54'	72°50' - 73°07'
Lac Laflamme, R. Lemieux, Environment Canada, Quebec Region	Environment Canada, Water Quality Branch, Longueuil	47°19'30"	71°07'30"
Lakes in southern New Brunswick, Peterson (1980)	Environment Canada, Water Quality Branch, Moncton	45°10' - 45°21'	66°18' - 67°04'
Lakes near Halifax, T. Clair, Environment Canada, Atlantic Region	Environment Canada, Water Quality Branch, Moncton	44°38' - 45°00'	63°42' - 64°22'
Headwater lakes on the island of Newfoundland, Clair 1981a	Environment Canada, Water Quality Branch, Moncton	47°40' - 50°	53° - 59°
Labrador lakes, Clair 1981b	Environment Canada, Water Quality Branch, Moncton	52°15' - 54°30'	58°20' - 66°15'

precipitation for the different areas studied. The estimated atmospheric excess sulphate deposition rates in precipitation (flux per unit area per year) in units comparable to the basin specific yield as well as the range of estimated deposition for 1977-80 were obtained from measurements or interpolation of measurements from the CANSAP precipitation network (Barrie and Sirois 1982). These values are shown on Figure 3-15 for direct comparison to the basin-specific yield of surface waters. Also shown on Figure 3-16 are dry deposition of sulphate calculated from measurements of sulphur oxides in air at four Air Pollution Network (APN) stations (ELA, Long Point on Lake Erie, Chalk River, Ontario and Kejimkujik National Park, Nova Scotia (Barrie 1982).

The agreement between the estimated deposition and basin specific yield of sulphate is generally good but shows greater yield than deposition in the areas of highest yield (i.e., the region between Thunder Bay, Ontario and Halifax, Nova Scotia). This deficiency of sulphate measured in precipitation as compared to basin yield of sulphate may, at least in part, be due to dry deposition of sulphate and sulphur dioxide. The dry deposition would be greater in regions nearer to or downwind from industrial sources. There may also be some release of sulphate previously stored in the basin. Contributions from geologic or other sources cannot be entirely dismissed in all cases. However, in these areas the evidence is strong that the atmospheric deposition of sulphate is the primary source of the basin yield of sulphate.

In the province of Quebec there exists a strong south to north gradient of lake sulphate concentrations as illustrated in Figure 3-17 and Figure 3-14. The data were obtained from 256 lakes in the province. The highest observed concentrations are in the southwest portion of the Province, and reach 180 μeq/L. The concentrations decrease gradually toward the north and to the east to values around 30 μeq/L. More than 80% of the lakes have sulphate concentrations higher than 60 μeq/L (Bobée et al. 1982), equivalent to the upper background level for lakes on the Precambrian Shield (Harvey et al. 1981).

Haines and Akielaszek (1982) reviewed available data on surface water pH distributions in sensitive regions. They found that the regions receiving precipitation of lower pH had higher percentages of low pH lakes (Table 3-11).

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

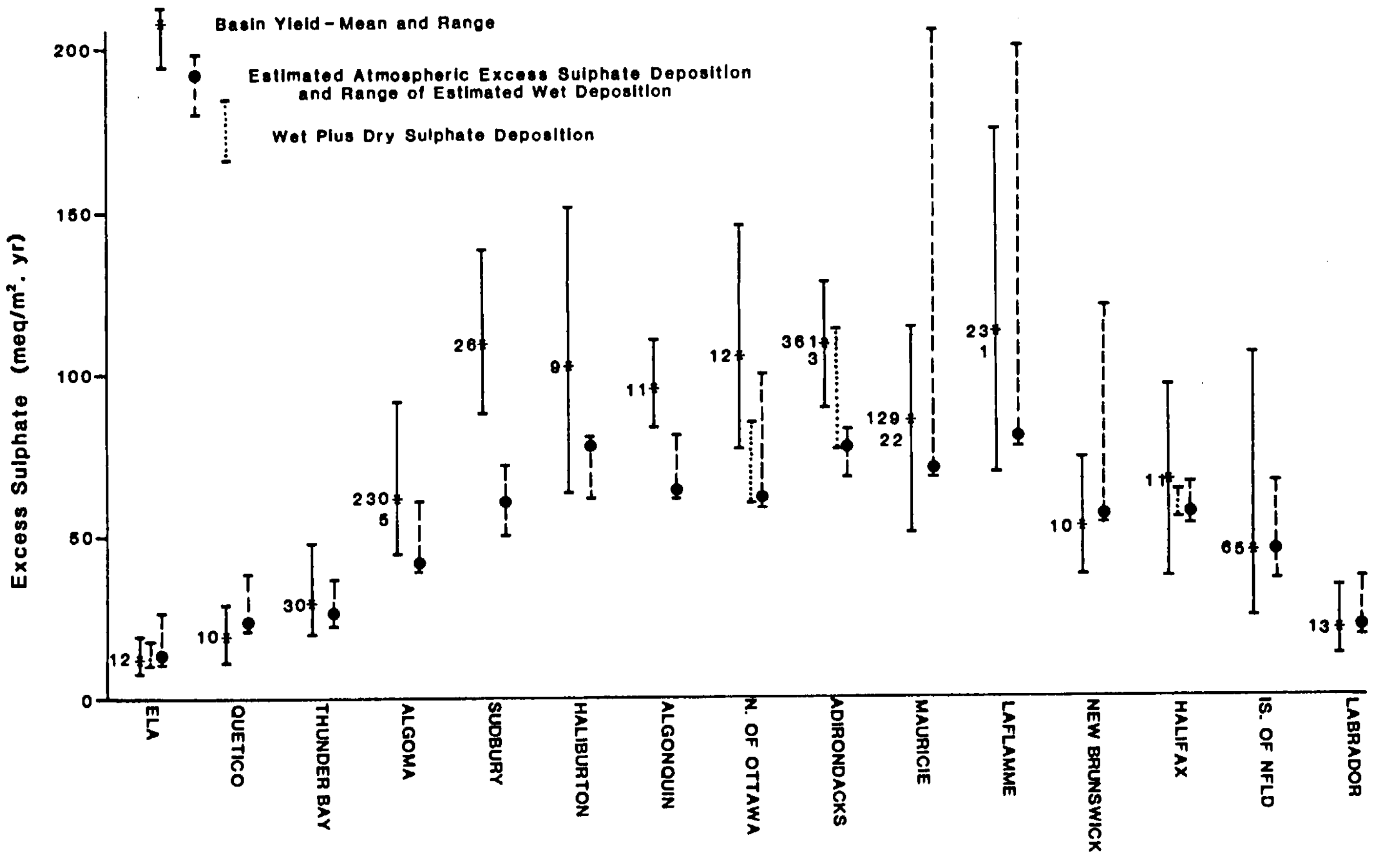


Figure 3-16. Mean and range of basin specific yield of excess sulphate (*) compared with estimated atmospheric excess sulphate deposition (•) in precipitation for 1980 (Thompson and Hutton 1982) and the range of estimated wet deposition for 1977-1980 from the CANSAP precipitation network (Barrie and Sirois 1982). Also shown are wet plus dry deposition of sulphate calculated from 1980 measurements of SO_x in air at four APN stations (Barrie 1982). The Maniwaki wet deposition data have been combined with the Chalk River dry deposition data for purposes of comparison.

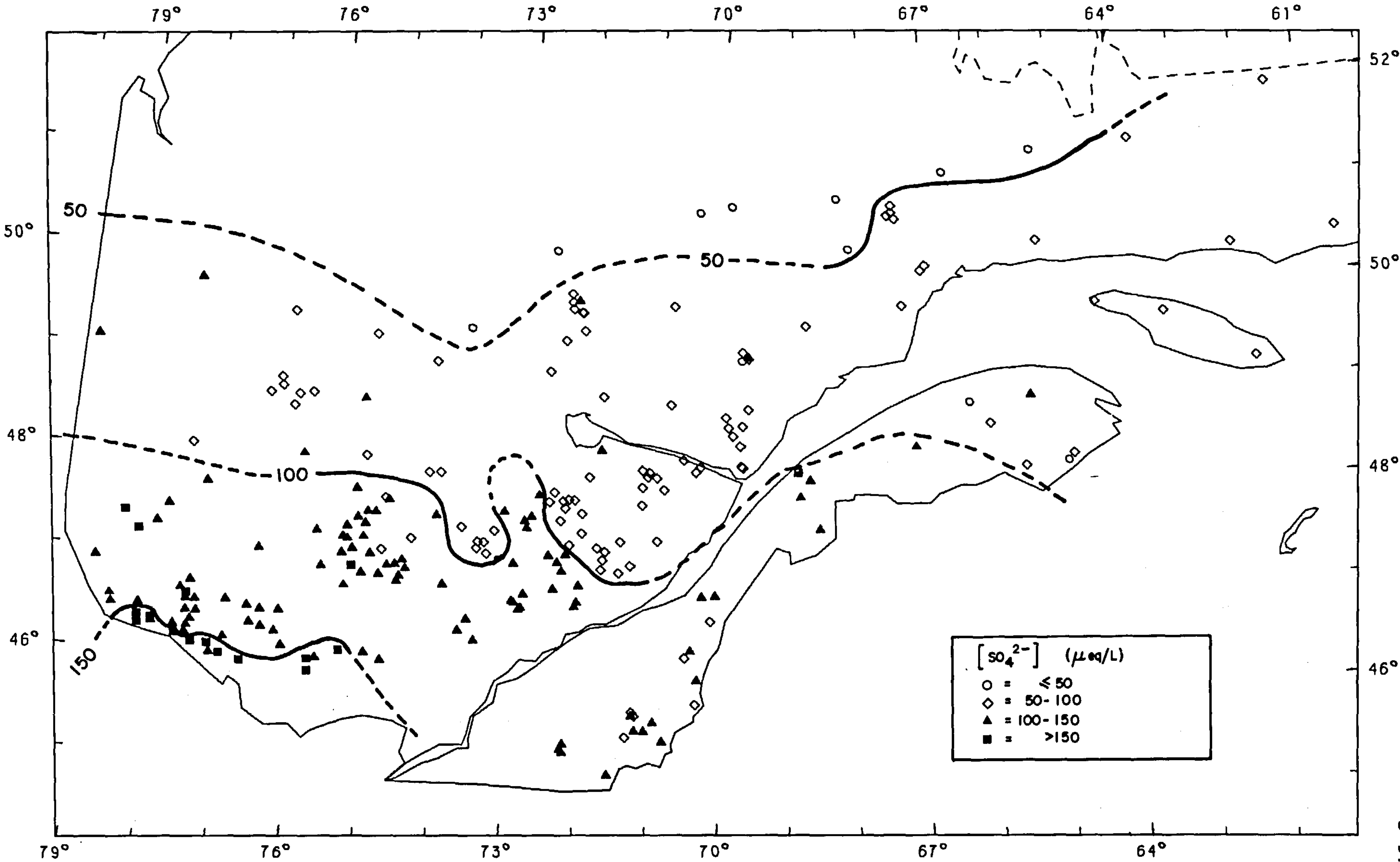


Figure 3-17. Areal distribution of sulphate concentrations in Quebec lakes, summer 1980 (Bobée et al. 1982).

TABLE 3-11. REGIONAL WATER CHEMISTRY SURVEY RESULTS FOR SURFACE WATER pH DISTRIBUTION (Haines and Akielaszek 1982)

LOCATION	NUMBER OF LAKES AND STREAMS	PERCENT IN pH RANGE			REFERENCE
		<5	5-6	>6	
Areas where Precipitation Averages pH 4.6					
New England	226	8	21	71	Haines and Akielaszek 1982
West Sweden	314	36	21	43	Almer et al. 1974
West Sweden	15	27	47	27	Dickson 1975
South Sweden	51	2	20	78	Malmer 1975
South Norway	155	18	38	44	Wright et al. 1977
South Norway	719	64	33	3	Wright and Snekvik 1978
Denmark	14	29	57	14	Rebsdorf 1980
Scotland	72	26	36	38	Wright et al. 1980
Nova Scotia	21	52	24	24	Watt et al. 1979
Quebec	25	12	40	48	Jones et al. 1980
Central Ontario	26	8	58	34	Scheider et al. 1979a
La Cloche Mountains, Ontario	152	28	34	38	Beamish and Harvey 1972
Sudbury, Ontario	150	13	15	72	Conroy et al. 1976
Adirondack Mountains, New York	849	25	30	45	Pfeiffer and Festa 1980
Areas where Precipitation Averages > pH 4.6					
North Norway	77	0	13	87	Wright and Gjessing 1976
Northwest Wisconsin	265	0	6	94	Lillie and Mason 1980
North Minnesota	85	0	0	100	Glass and Loucks 1980

3.6.1.1 Saskatchewan

Measurements of total alkalinity, calcium, magnesium and pH were analyzed for some 300 lakes in Saskatchewan's Precambrian Shield and fringe Shield regions (Liaw and Atton 1981). Concentrations of alkalinity in these lakes varied from 10 to 1740 μeq/L. Forty-four percent of the lakes surveyed had alkalinities of 200 μeq/L or less.

Measurements of lakewater pH, ranged from 5.6 to 8.2, and indicate that, at present, Saskatchewan's Shield lakes are circumneutral. Lakes with pH values between 6.5 and 7.5 accounted for nearly 80% of all lakes investigated. Concentrations of calcium ranged from 7 to 630 μeq/L. About 54% of the lakes surveyed had calcium of 80 μeq/L or less, while 25% had between 80 and 160 μeq/L. Concentrations of magnesium varied from 0 to 130 μeq/L. Approximately 65% of the lakes measured had magnesium concentrations of 24 μeq/L or less, whereas 32% had between 24 and 36 μeq/L. Concentrations of calcium plus magnesium showed a one-to-one relationship to alkalinity (Figure 3-18). This relationship is expected in areas where alkalinity production is by bicarbonate weathering in the absence of strong acids.

3.6.1.2 Ontario

Alkalinity data for 2,624 lakes in Ontario are shown in Table 3-12 (OME 1982). The categories from 1 to 5 indicate decreasing sensitivity to acid deposition. The 48% of the lakes in categories 2 and 3 had some measurable alkalinity less than 200 μeq/L and may be regarded as sensitive to acidic deposition. The spacial distribution of the lakes sampled is shown in Figure 3-19. In Precambrian areas, up to 90% of the lakes are less than 200 μeq/L. Five percent of the lakes had alkalinity values less than zero, i.e., acidified, these lakes are located mainly in the Manitoulin and Sudbury areas which have been subjected to deposition from smelting operations in Sudbury. Scheider et al. (1981) indicate that acidic deposition to the area is substantial. Chan et al. (1980) concluded that much of the deposition is due to long-range transport of acid. The influence of long-range transport is relative to the historic local emissions, with respect to acidifying lakes, cannot be determined.

Data from 16 intensively studied lakes in Muskoka-Haliburton are plotted in Figure 3-20. The average epilimnetic summer pH and the lowest spring pH observed in the surface waters are plotted against the mean summer alkalinity values. The data cover 4 years (1976-1980). Lakes with alkalinity of less than 40 μeq/L experienced pH depressions in surface waters to values less than 5.5. A few streams showed pH values below 4.0 in some cases (Figure 3-21). At Algoma, spring pH values of about 5.0 occur in the surface waters of study lakes with alkalinities less than 40 μeq/L (Scheider 1983).

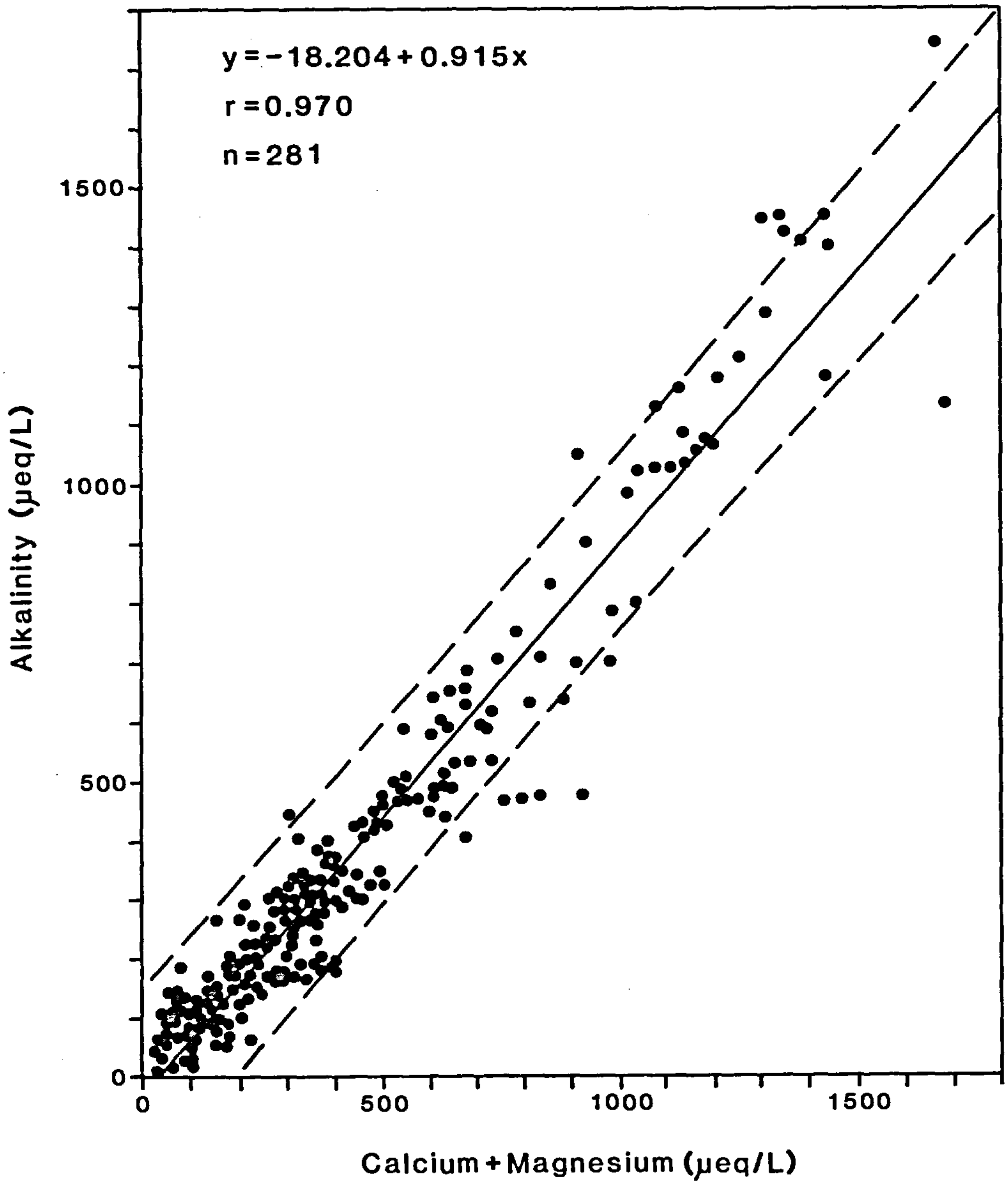


Figure 3-18. Relationship between alkalinity and calcium + magnesium for northern Saskatchewan lakes. Broken lines indicate 95% confidence limits of predicted values (Liaw 1982).

TABLE 3-12. SUMMARY OF THE PERCENTAGE OF LAKES AND STREAMS IN EACH ALKALINITY CLASS BY COUNTY OR DISTRICT FOR ONTARIO (OME 1982)

	County or District	Percentage of Total No. of Lakes in each Alkalinity Class					Total Number of Lakes Evaluated
		1 (≤0 μeq/L)	2 (0-39.9 μeq/L)	3 (40-199 μeq/L)	4 (200-499 μeq/L)	5 (> 500 μeq/L)	
[a]A	[b]Algoma Dist.	4	13	46	20	17	449
B	Bruce Co.	•	•	•	•	100	7
C	[b]Cochrane Dist.	•	1	6	15	78	90
D	Durham Co.	•	•	•	•	100	1
E	Frontenac Co.	•	•	•	10	90	68
F	Grey Co.	•	•	•	•	100	3
G	[b]Haliburton Co.	1	29	43	16	11	197
H	Hastings Co.	•	•	25	15	60	73
I	Huron Co.	•	•	•	•	100	1
J	[b]Kenora Dist.	•	•	12	26	62	116
K	Lanark Co.	•	•	•	•	100	17
L	Leeds Co.	•	•	•	•	100	26
M	Lennox & Addington Co.	•	•	41	12	47	32
N	Manitoulin Dist.	49	30	3	3	15	33
O	Middlesex Co.	•	•	•	•	100	1
P	[b]Muskoka Dist.	1	24	65	3	7	159
Q	[b]Nipissing Dist.	•	10	69	18	3	119
R	Northumberland Co.	•	•	•	•	100	1
S	Ontario Co.	•	•	•	•	100	5
T	[b]Parry Sound Dist.	3	27	62	7	1	180
U	Peel Co.	•	•	•	•	100	1
V	Peterborough Co.	•	3	13	11	73	55
W	Prince Edward Co.	•	•	•	•	100	3
X	[b]Rainy River Dist.	•	3	64	20	13	99
Y	[b]Renfrew Co.	•	3	19	27	51	105
Z	Simcoe Co.	•	•	•	•	100	7
AA	Stormont Co.	•	•	•	•	100	1
BB	[b]Sudbury Dist.	18	23	28	11	20	325
CC	[b]Thunder Bay Dist.	•	3	27	25	45	312
DD	[b]Timiskaming Dist.	14	14	25	21	26	109
EE	Victoria Co.	•	•	•	56	44	27
FF	York Co.	•	•	•	•	100	2

a County/district code for Figure 3-19.

b Counties which are on the Precambrian Shield.

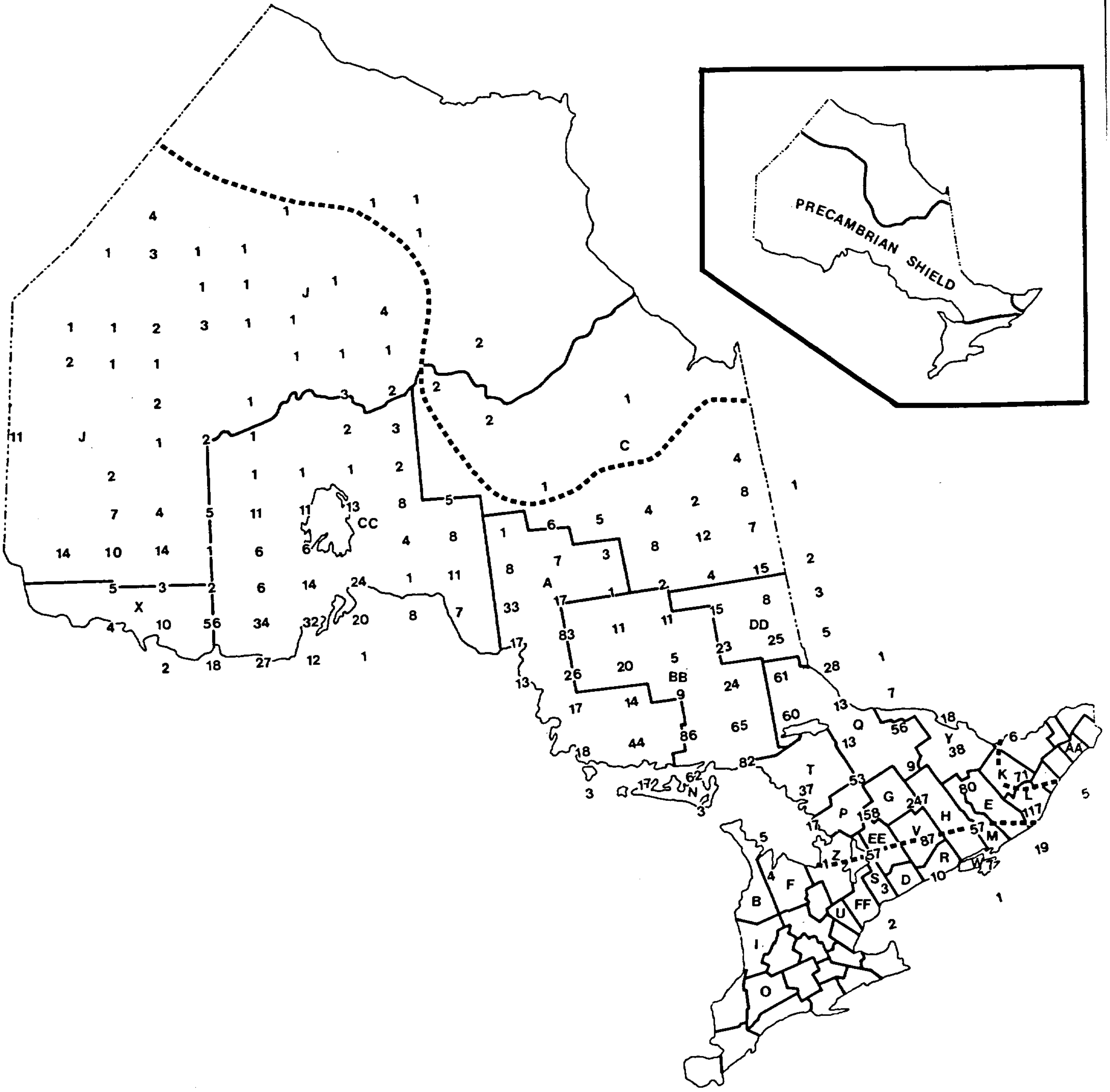


Figure 3-19. Distribution of lakes sampled in Ontario Ministry of the Environment 1981 and 1982 surveys. Numbers indicate number of lakes sampled within each grid cell (1° by .5°) and letters identify county or district as per Table 3-12.

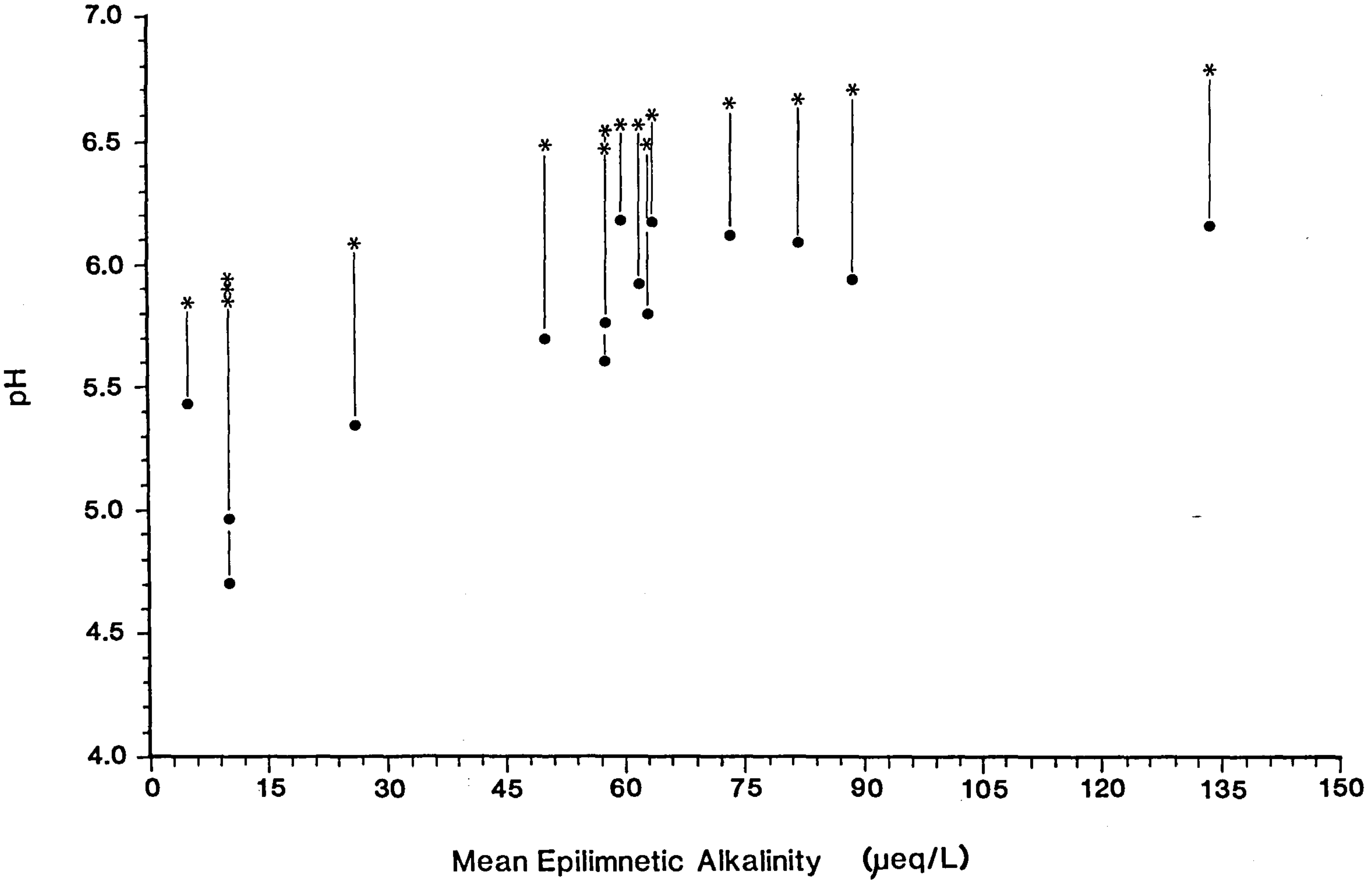


Figure 3-20. Mean summer epilimnetic alkalinity (μeq/L), mean summer epilimnetic pH (*) and minimum surface water pH in spring (●) for 16 lakes in Muskoka-Haliburton (1976-80) (Scheider 1983).

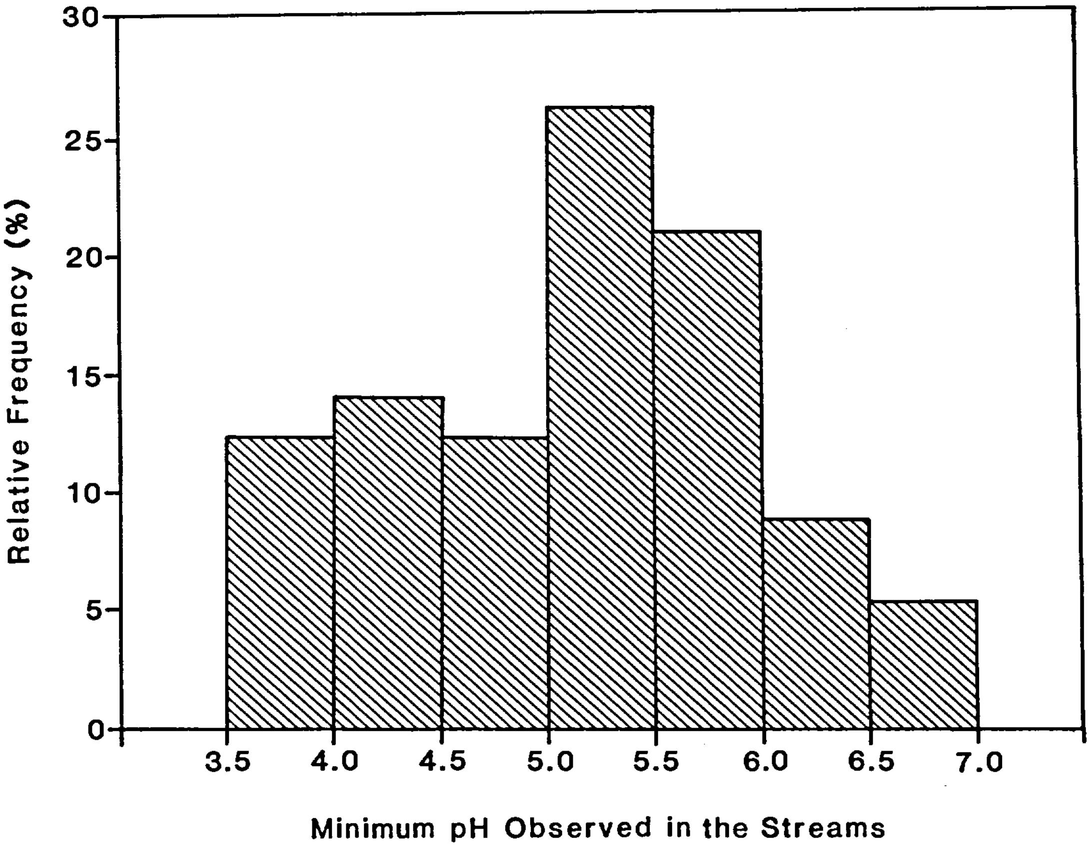


Figure 3-21. Minimum pH values of 57 headwater streams in Muskoka-Haliburton, 1976-80 (Scheider 1983).

3.6.1.3 Quebec

Vast areas of the Province of Quebec are composed of non-calcareous lithology, and glacial transport of materials has 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 and a few other areas are sufficient buffering materials found. A few local occurrences of more adequately buffered waters are found in the Gatineau Lakes, Lake St. Jean, Lake Mistassini, and the Harricana River in northwest Quebec.

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. Examination of the alkalinity and CSI values of the surface waters of the surveyed area gives an indication of sensitivity of waters of Quebec to acidification.

A distribution of calcite saturation index (Conroy et al. 1974) of 181 lakes surveyed during the summer of 1980 (Bobée et al. 1982) is illustrated in Figure 3-22. Values lower than 3 are not very sensitive (15% of the lakes surveyed have a value less than 3.5). Values between 3 and 5 are potentially sensitive (48% of the surveyed lakes have a value between 3.5 and 5.5). Values higher than 5 are extremely sensitive to acidification (37% of lakes of the shield have a value higher than 5.5). The distribution of CSI of surveyed lakes in Quebec, is illustrated in Figure 3-22. It is evident that nearly all waters, other than the St. Lawrence Valley and the Gaspé Regions (Regions 01, 02 and 03, as per Figure 3-13), have CSI equal to or greater than 3 and are, therefore, sensitive to acidification. Surveys of the lakes of Laurentide and La Mauricie Parks appear to indicate a greater sensitivity than do lakes in 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 or pH in the older measurements. The actual sensitivity of lakes in Quebec may, therefore, be even greater than indicated by the older surveys (Ahern and Leclerc 1981; Jones et al. 1980).

Bobée et al. (1982) have shown that 19 of 20 of the lakes sampled on the Precambrian Shield in Quebec south of 50° latitude have alkalinities less than 200 µeq/L, and thus are considered to be sensitive to acidic deposition. For the same region, summer values of pH were below 5.0 for 15% of these lakes, and below 5.5 for 41% (Figure 3-23). The pH frequency distribution has two modes: one between 5.0 and 5.5 and one from 6.0 to 6.5. In a lake with only carbonate species to buffer the water, a pH value of 5.5 indicates that the lake can have rather large pH fluctuations.

> "The importance of the sulphate anion in the lakes of the Canadian Shield (in Quebec) appears clear upon examination of the relationship between bicarbonate and sulphate.

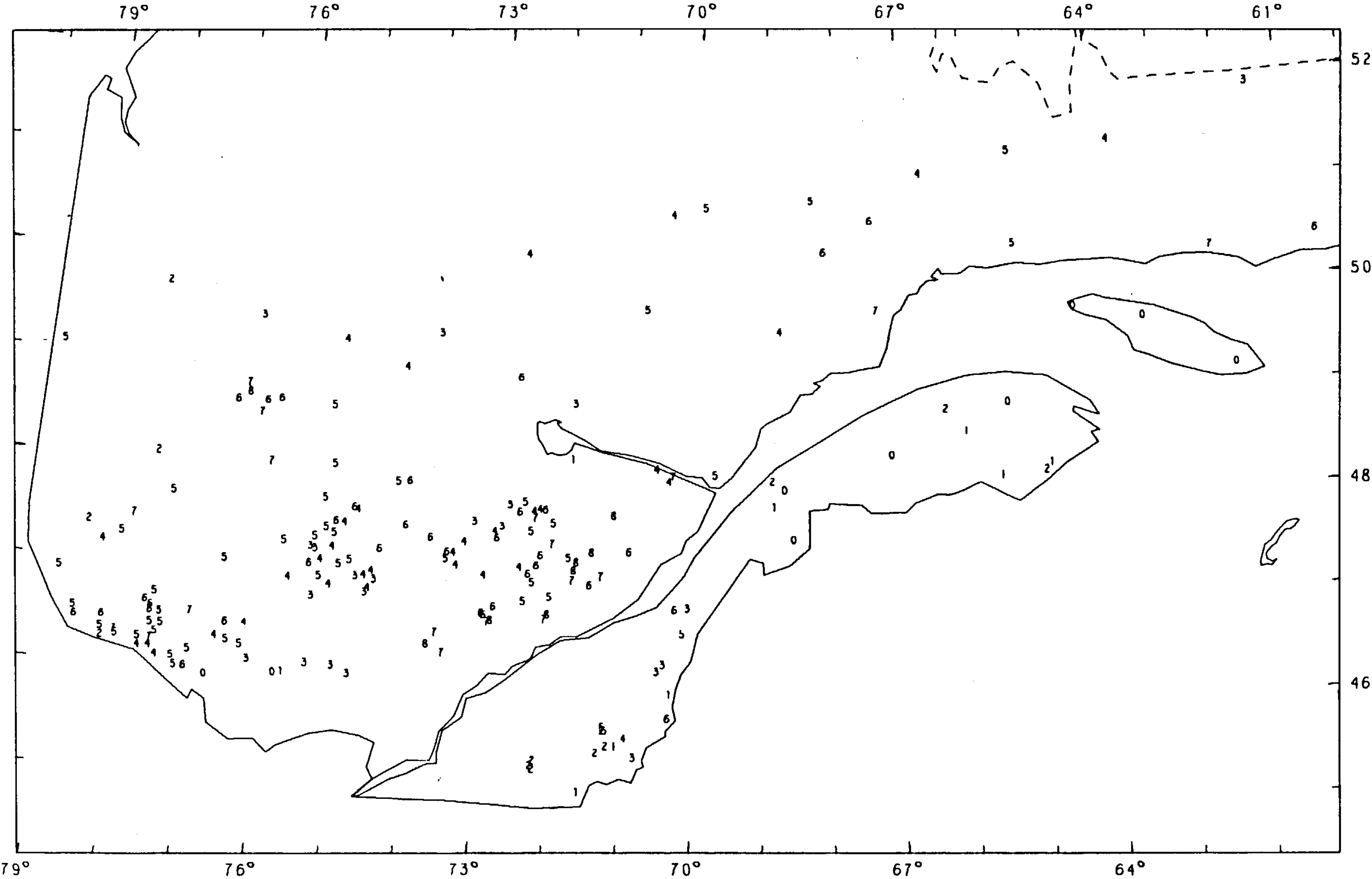


Figure 3-22. Calcite saturation indices for 181 lakes in southern Quebec, summer 1980 (Bobée et al. 1982).

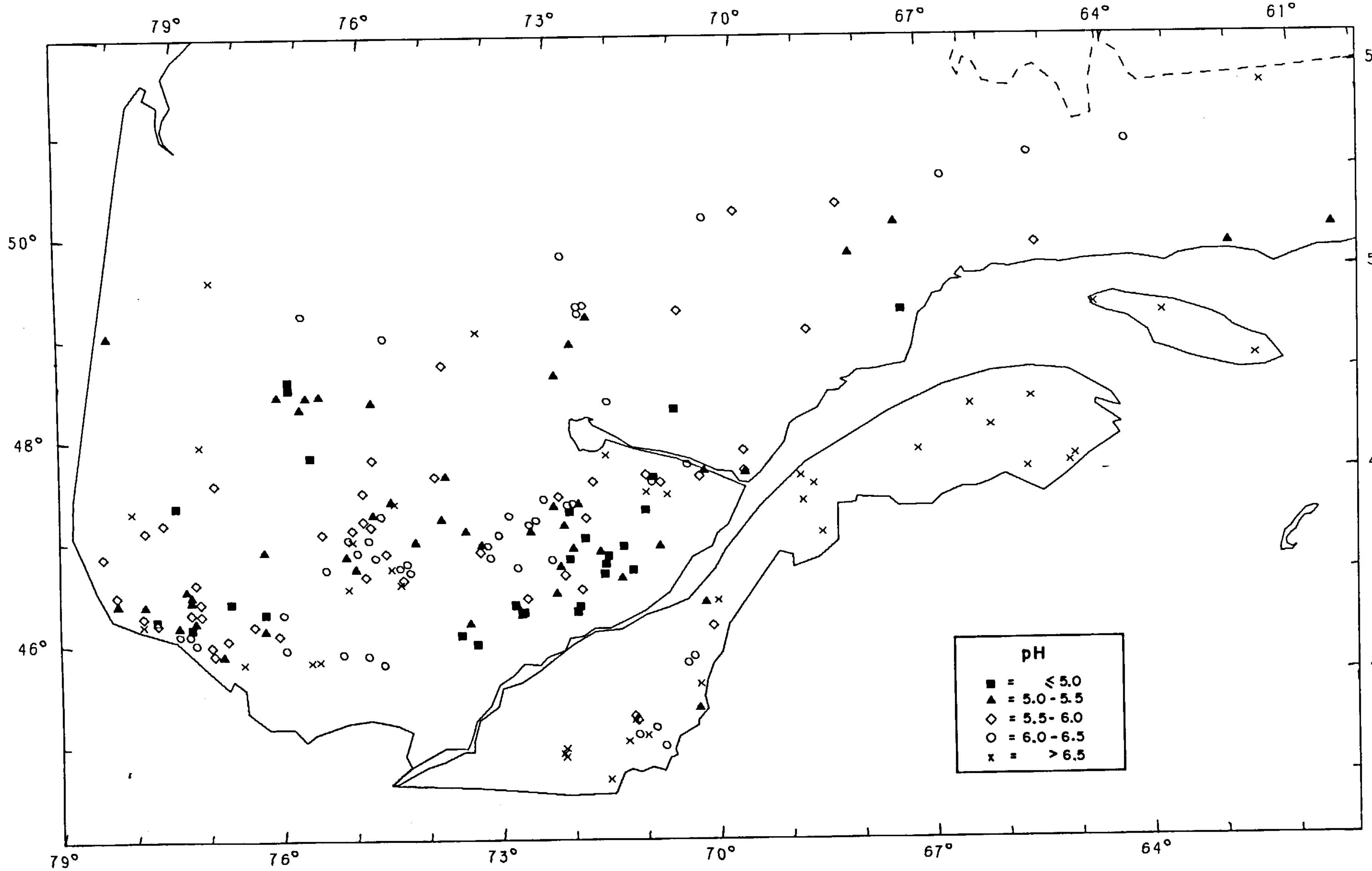


Figure 3-23. pH Values for Quebec lakes, summer 1980 (Bobée et al. 1982).

> According to Dickson (1975), this ratio should greatly exceed one in lakes not influenced by (atmospheric) sulphates. In the southern portion of the Shield region (in Quebec), the sulphate ion dominates in these lakes. For the entire area of the Shield (in Quebec), 84% of the lakes have a HCO_3^-/SO_4^{2-} ratio less than one." [Translated from Bobée et al. 1982] (See Table 3-13 and Figure 3-24.)

3.6.1.4 Atlantic Provinces

Except for isolated regions of calcareous lithology, mostly in northern and eastern New Brunswick, the northern peninsula of Newfoundland and all of Prince Edward Island, the Atlantic provinces have soils and bedrock that provide limited acid neutralizing capacity. Much of the area is of very complex geology which has been indicated in the sensitivity maps (see Section 3.5). However, summaries of the surface water chemistry by Clair et al. (1982), Wiltshire and Machell (1981), and Thompson et al. (1980) have shown that large portions of these waters are very dilute and poorly buffered. Clair et al. (1982) have summarized the Atlantic Provinces water chemistry in terms of the Calcite Saturation Index (Kramer 1976). CSI maps for New Brunswick, P.E.I., Nova Scotia, Island of Newfoundland and Labrador are illustrated in Figures 3-25, 3-26 and 3-27. If CSI of 3 or greater is taken as an index of highly sensitive waters, it is evident that large portions of the surface waters are sensitive to acidification.

The loss of alkalinity and consequent decline in pH of some lakes and rivers of Nova Scotia have been well documented (see Thompson et al. [1980], Watt et al. [1979], Wiltshire and Machell [1981]). Wiltshire and Machell (1981) applied Henriksen's (1979) comparative relationship to data from 16 lakes in Nova Scotia and suggested that acidification (loss of alkalinity) of 40 to 50 µeq/L has occurred over the past two decades to 1979, which is consistent with measured pH declines. Watt et al. (1979) have shown similar pH declines for lakes near Halifax but attribute this decline to sulphate deposition from local sources. Some pH increases have also been identified in rivers of southwestern Newfoundland, (Thompson et al. 1980). Thompson and Hutton (1982) concluded that lower levels of sulphate deposition over Newfoundland and Labrador have apparently resulted in only moderate alkalinity replacement.

Bogs are a common feature of the Atlantic provinces and waters often carry significant organic contents. Although there is a need to more clearly define the role of these natural acids in determining the acidity of waters and subsequent influences in metal availability, ionic balances by Thompson (1982) for a number of these waters suggest that the major acidity is due to inorganic ions.

TABLE 3-13. SOME STATISTICS ON THE RATIOS OF HCO_3^-/SO_4^{2-} FOR WATERS OF QUEBEC DERIVED FROM LEGENDRE ET AL. (1980), BY HYDROGRAPHIC REGION (see Figure 3-13).

LAKES NORTH OF THE ST. LAWRENCE RIVER

WEST EAST

HYDROGRAPHIC REGION

VALUES OF THE RATIO	04		05		06		07	
	N	%	N	%	N	%	N	%
0.6	24	21.5	5	8.6	3	50.0	9	64.3
0.6 - 1.2	41	36.6	15	25.9	1	16.7	3	21.4
1.2 - 1.8	19	17.0	14	24.1	1	16.7	2	14.3
1.8	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

VALUES OF THE RATIO	03		02		01	
	N	%	N	%	N	%
0.6	21	95.4	13	76.5	5	100.0
0.6 - 1.2	1	4.6	3	17.6		
1.2 - 1.8	-	-	0			
1.8	-	-	1	5.9		
TOTAL	22	100.0	17	100.0	5	100.0

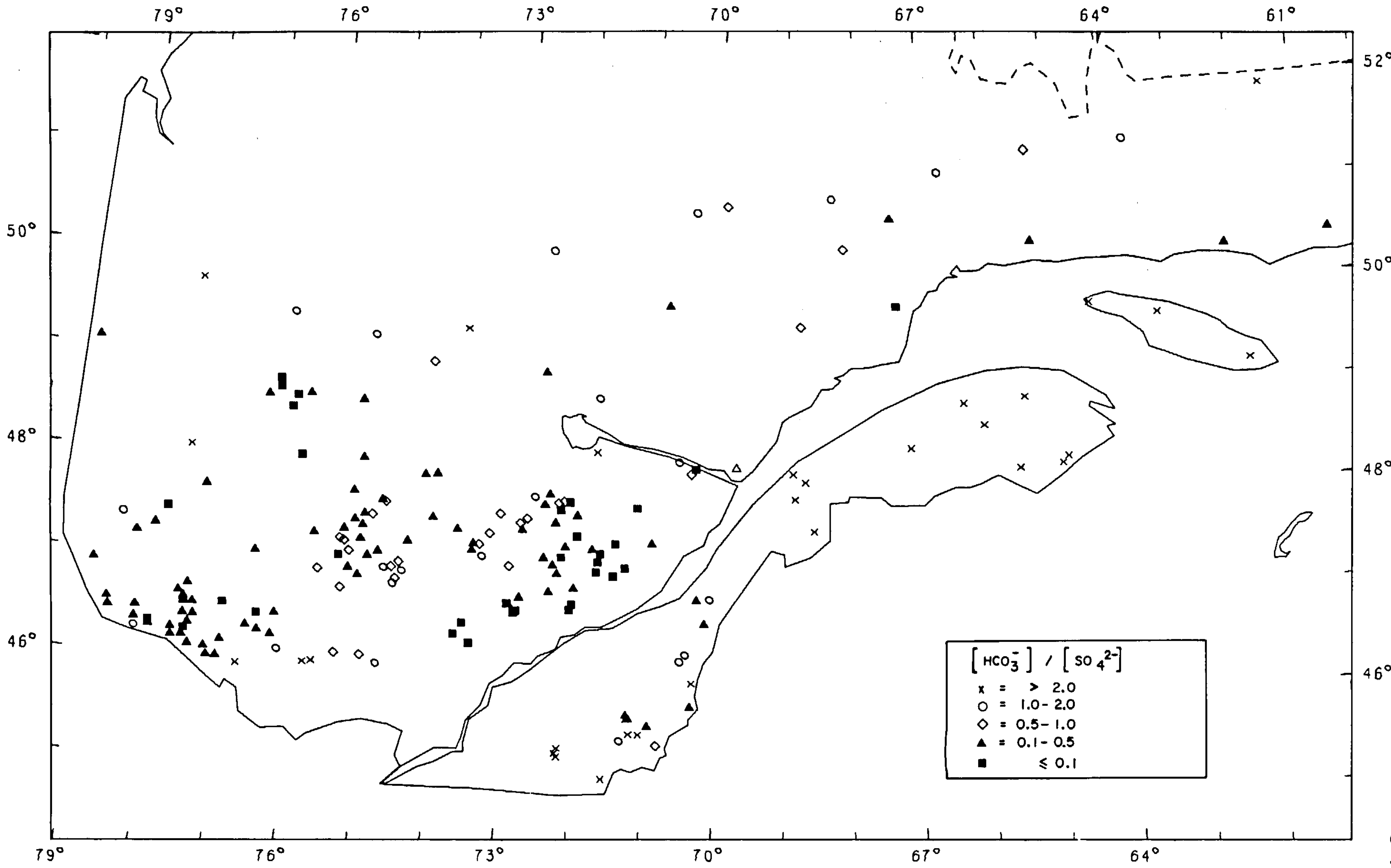


Figure 3-24. HCO_3^-/SO_4^{2-} values for Quebec lakes, summer 1980 (Bobée et al. 1982).

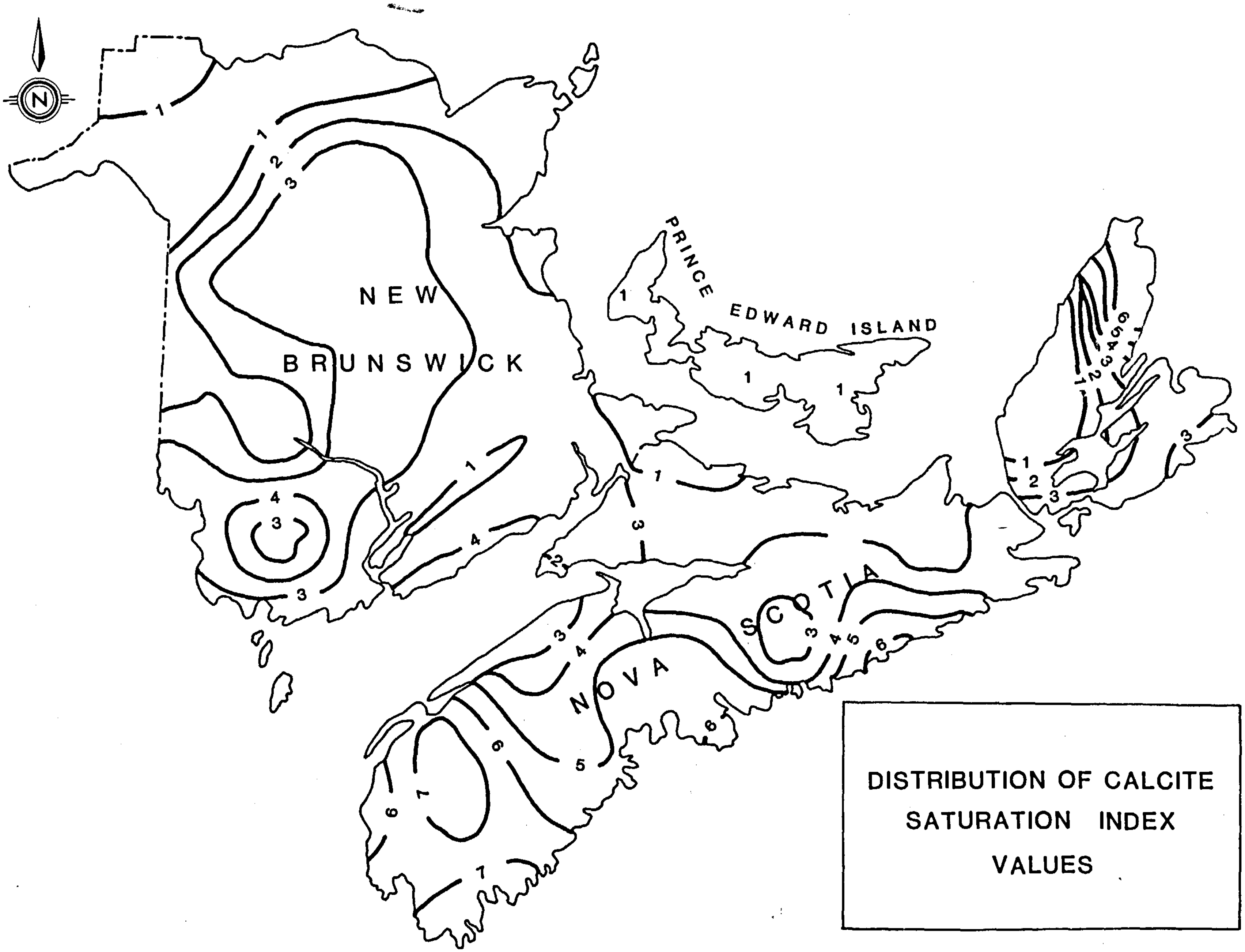


Figure 3-25. Distribution of calcite saturation index values for New Brunswick, Prince Edward Island and Nova Scotia (modified from Clair et al. 1982).

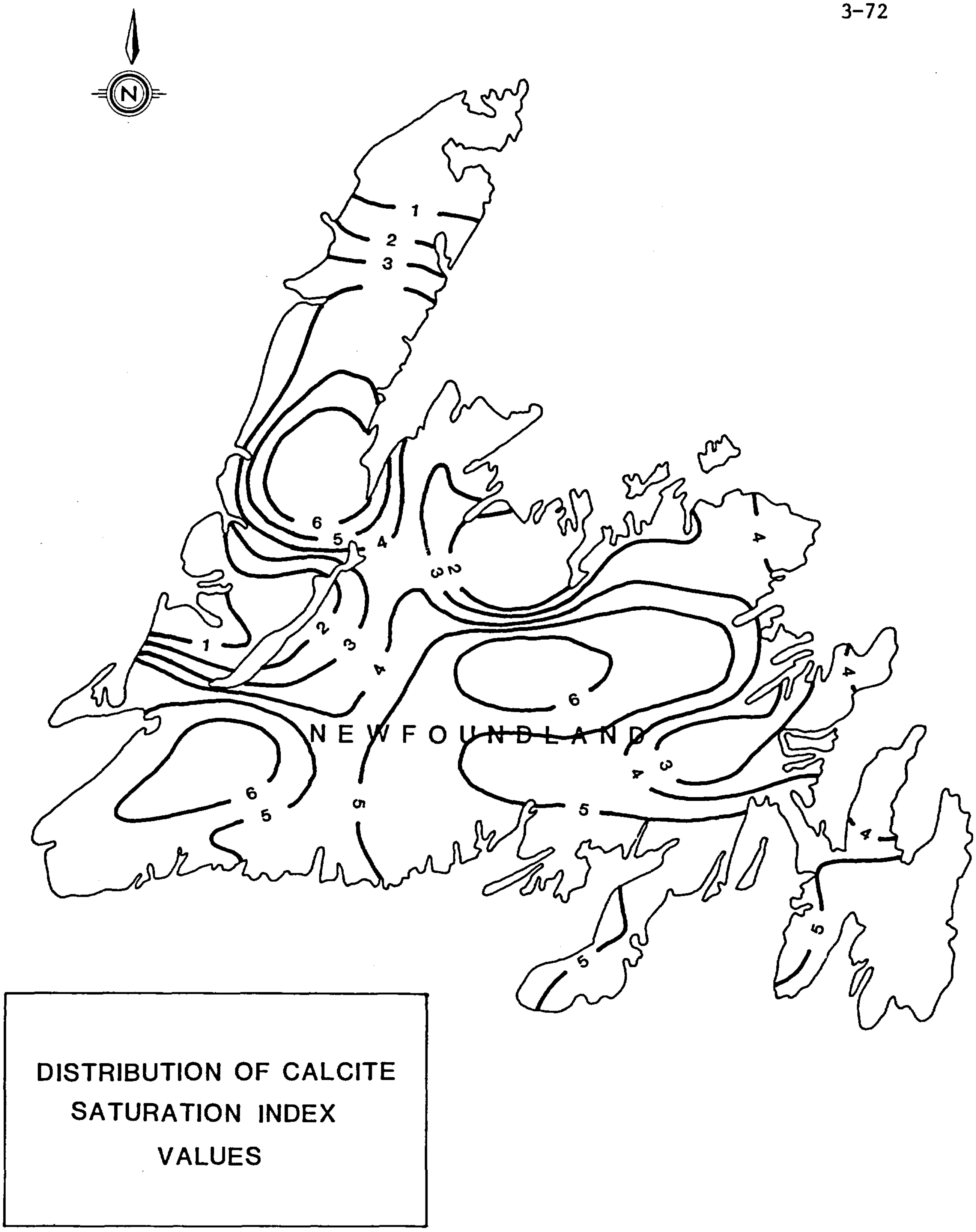


Figure 3-26. Distribution of calcite saturation index values for Newfoundland (modified from Clair et al. 1982).

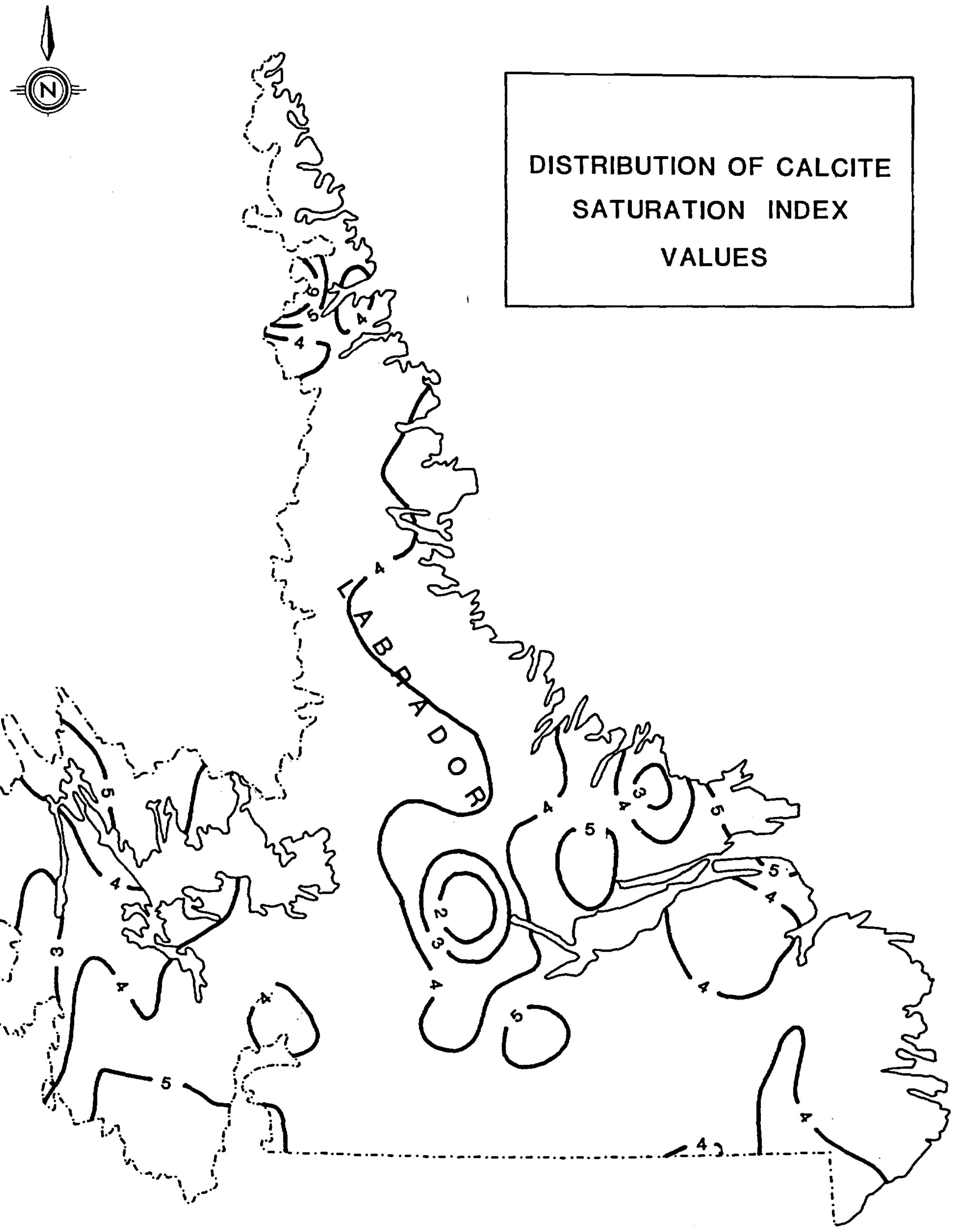


Figure 3-27. Distribution of calcite saturation index values for Labrador (modified from Clair et al. 1982).

3.6.1.5 United States

The national map of total alkalinity of surface waters by Omernik and Powers (1982) illustrates general patterns of surface water sensitivity to acidic deposition on the conterminous United States (Figure 3-28 in map folio). A large number of regions in the U.S. have mean annual alkalinity values below 200 μeq/L in surface waters. In the portion of the country where continental glaciation resulted in high densities of natural lakes, these low alkalinity areas comprise: (1) much of New Hampshire and central and southern Maine; (2) the Adirondacks in northeast New York; and (3) the northeastern tip of Minnesota and a portion of northcentral Wisconsin. An analysis of 300 headwater lakes and streams in six northern New England sites shows that alkalinity values of less than 200 μeq/L cover most of the regions examined, with widespread values <20 μeq/L as shown in Figure 3-29 (Haines 1981b; Haines and Akielaszek 1982). In the West, streams and lakes with average alkalinity values below 200 μeq/L are generally found in the higher mountainous areas, particularly the Cascade Range of Oregon and Washington and the Sierra Nevadas in California.

Elsewhere in the United States, sensitive surface waters are primarily streams, small lakes and general purpose reservoirs. For these waters there are several areas of low alkalinity values: (1) a discontinuous region extending from southeastern New York to western Pennsylvania and central West Virginia; (2) eastern North Carolina; (3) central South Carolina and southeastern Georgia; (4) an area centered on the southwestern end of the Blue Ridge Mountains; (5) a band extending from southeastern Louisiana to northeastern Florida; (6) southeastern Texas and westcentral Louisiana; and (7) smaller areas in southern New Jersey, northwest Alabama, southern Arkansas and northern Louisiana, and the Quachita Mountains across the Oklahoma/Arkansas border.

As indicated by the cautionary note on the face of the alkalinity map, the "map is intended to provide a synoptic illustration of the regional patterns of surface water alkalinity in the United States. As such, it affords a <u>qualitative</u> graphic overview of the sensitivity of surface waters to acidification. <u>The map should not be used for making quantitative assessments</u> of the extent of alkalinity or sensitivity" (Omernik and Powers 1982).

3.6.2 <u>Time Trends in Surface Water Chemistry</u>

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 natural trends or an anthropogenic effect. 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

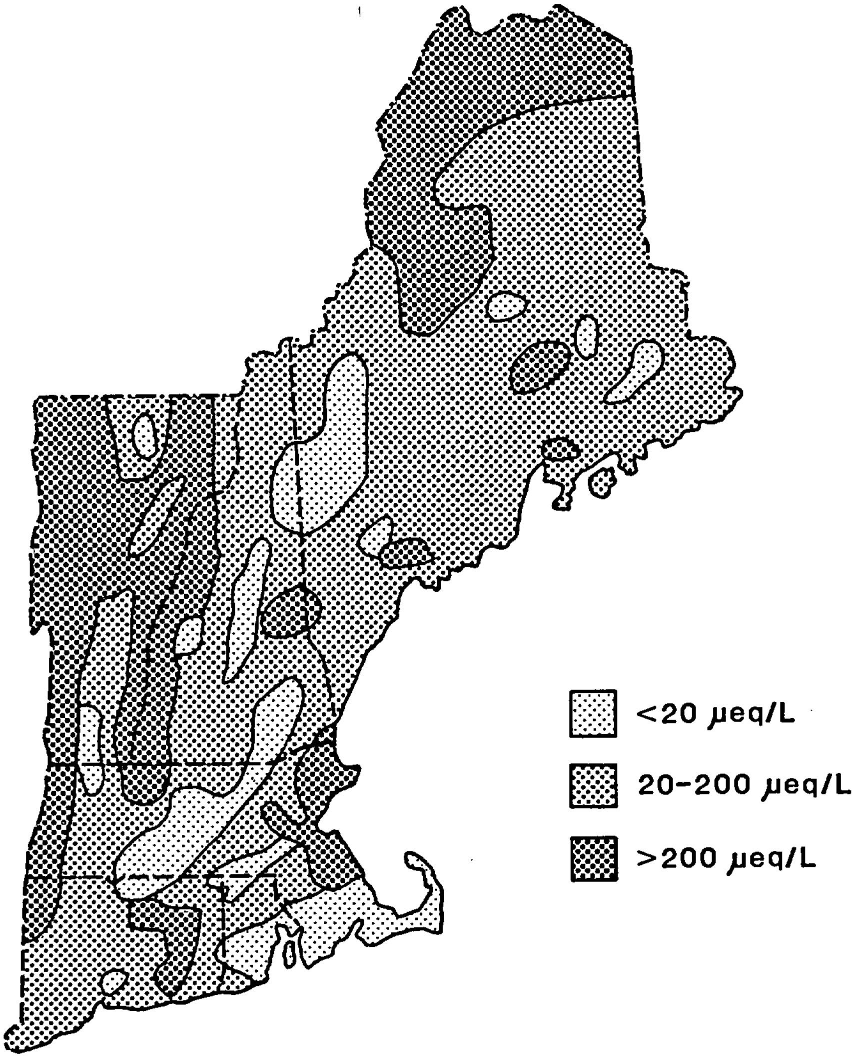


Figure 3-29. Surface water alkalinity of New England states (Haines 1981b).

differences, but these corrections add uncertainty to some of the comparisons.

3.6.3 Time Trends in Representative Areas

Historic water quality data exist for several areas in eastern North America. The data must be verified based on sampling and analytical methodologies before comparisons with modern measurements can be made. Acidification represents a loss of alkalinity, but measurements of alkalinity are sparse, and therefore, most time trend comparisons have been restricted to pH changes. The following section will review time trends in pH measurements and alkalinities where available.

3.6.3.1 Time Trends in Nova Scotia and Newfoundland

Several rivers in Nova Scotia and Newfoundland were sampled and analyzed by Thomas (1960) during the period 1954-55 in Newfoundland using carefully described analytical methods. Several of the same sample locations were continued under the Environment Canada, National Water Quality monitoring program in 1965. This monitoring on a monthly basis was continued through 1974 after which most stations were reverted to seasonal sampling. Monthly sampling was reinstated for some stations in 1979. The methodologies are described and data are archived in the Environment Canada National Water Quality Data Archive, NAQUADAT. pH has been determined potentiometrically throughout the period of record. Laboratory samples from the early data of Thomas were stored in soft glass sample bottles which may have caused a small increase in the laboratory measured value of pH. This factor would be unimportant for the field measured pH values. Sulphate was measured by a $BaCl_2$ precipitation gravemetric method prior to 1954. Later determinations were by the colourimetric procedure which was automated in 1973.

This data set has been employed in several studies to analyze trends and changes that may have occurred in the chemistry of the waters during the period of record. Thompson et al. (1980) examined the pH records for three rivers of Nova Scotia and three rivers of Newfoundland. The pH values were accepted as comparable and, while statistical analysis was not undertaken, there appears to have been a decrease in the discharge-weighted mean pH of the Tusket, Medway and St. Mary's Rivers of Nova Scotia during the period 1966 through 1974. The one year of record 1954-55 indicates a discharge-weighted mean pH greater than the following years of record. The Isle aux Morts, Garnish, and Rocky Rivers of Newfoundland indicate minimum discharge-weighted pH in 1972 or 1973 in the period of record 1966-1980 or 1981. Values have increased since that period.

Clair and Whitfield (1983) have subjected portions of the record of several of these rivers to statistical analysis, where the record was continuous and uniform. They classified the rivers by the CSI sensitivity index (greater than -3, insensitive and less than -3 sensitive). Periods of record were limited to 1965-66 through 1978-79 and some records terminated in 1973-74. They have reported decreasing trends for pH of the Medway, Isle aux Morts, and Rocky Rivers and stationary records for the Piper's Hole, Lepreau and Mersey. Among the insensitive rivers, all were either stationary or increasing in pH records. Clair and Whitfield (1983) also analyzed the trend of sulphate but did not apply a correction for seasalt contribution. While some trends were reported, they are likely to be strongly influenced by seasalt in this marine coastal environment and cannot be interpreted as trends in excess sulphate.

Watt et al. (1983) has compared the major ion concentrations (corrected for seasalt) for several Nova Scotia rivers for the 1954-55 through 1980-81 period using the same data set. He has found smaller values of bicarbonate, greater values of sulphate and greater hydrogen ion concentrations, all at greater than 1% significance level for the Roseway, Medway, Mersey, and La Have Rivers as shown in Table 3-14 (from Watt et al. 1983). While caution is required in interpreting SO_4^{2-} trends due to interference of organic anions in measurement procedures, the bicarbonate and hydrogen ion concentration trends are not subject to such caution. Other major ions did not show significant changes. Farmer et al. (1980), using the same data base, has compared major ion concentrations (unweighted) for 1954-55 with 1978-79 for the Mersey River. The pH has decreased from 5.8 (range 5.4 to 6.6) in 1954-55 to 5.2 (range 4.9-5.4) in 1978-79 while sulphate has increased from 1.6 mg/L (range 0.1 to 3.0 mg/L) in 1954-55 to 3.3 mg/L (range 1.0 to 5.0 mg/L) in 1978-79. Other rivers of Southwest Nova Scotia examined by Farmer et al. (1980) include the Tusket, Clyde, Roseway, Jordan, and Medway. Decreased pH values were observed in all these rivers. pH of the La Have River has changed little over the same time period "... reflecting deposits of sandstone in this area."

Farmer et al. (1980) have stressed that the Nova Scotia rivers having the greatest pH change and the lowest pHs in 1978-79 were also the most highly coloured. Thus the contribution of humic and/or fulvic acids to the total acidity may be significant. Extensive direct measurements of the organic anion concentration have not been reported. Preliminary measurements by Oliver and Slawych (1982) of samples from the West, Medway and Mersey Rivers indicated an organic acidity of 95, 94 and 53 μeq/L respectively as compared to an estimated precipitation acidity of 29 μeq/L. Thompson (1982) has observed that for the Roseway, Mersey and Medway rivers while "their pH's have been thought to be dominated by naturally occurring organic acids, their low pH's can be explained quite well on the basis of simple inorganic chemistry." More direct measurements of the organic anion concentrations are needed to define the relative contributions to these waters of very low total ionic strength.

TABLE 3-14. MEAN CONCENTRATIONS (meq/L) OF IONS IN THE WATER OF FOUR NOVA SCOTIA RIVERS IN 1954-55 AND 1980-81. AVERAGE DIFFERENCES WERE CALCULATED AS 1980-81 CONCENTRATION MINUS 1954-55. THE SIGNIFICANCE LEVELS (EXCEPT H^+) ARE FROM THREE-WAY VARIANCE ANALYSES. THE $SO_4{}^{2-}$, Na^+, K^+, Ca^+, AND Mg^{2+} IONS HAVE BEEN CORRECTED FOR SEASALT INFLUENCE (Watt et al. 1983)

		Ion Concentrations							
River	Years	HCO_3^-	SO_4^{2-}*	Na^+	K^+	H^+	Ca^{2+}	Mg^{2+}	Al^{3+}
Roseway	1954-55	0.049	0.033	0.002	0.016	0.014	0.060	0.004	0.014
	1980-81	0.007	0.089	0.031	0.007	0.040	0.028	0.010	0.027
Medway	1954-55	0.055	0.031	0.016	0.006	0.001	0.047	0.016	0.007
	1980-81	0.013	0.059	0.018	0.005	0.005	0.045	0.017	0.014
Mersey	1954-55	0.044	0.023	0.014	0.008	0.002	0.045	0.010	0.009
	1980-81	0.022	0.053	0.017	0.005	0.006	0.031	0.012	0.016
LeHave	1954-55	0.072	0.040	0.019	0.008	0.001	0.070	0.017	0.007
	1980-81	0.036	0.081	0.024	0.006	0.001	0.069	0.030	0.017
Average difference		−0.036	+0.039	+0.010	−0.004	+0.009	−0.012	+0.006	+0.009
Significance level		<0.001	<0.001	N.S.	N.S.	<0.001	N.S.	N.S.	<0.001

* Caution is required in interpreting SO_4^{2-} trends due to the interference of organic anions in measurement procedures.

The time records of the median pH and excess sulphate discharge for two rivers of Nova Scotia (Medway and St. Mary's) and for two rivers of Newfoundland (Rocky and Isle aux Morts) are shown in Figure 3-30. The pH values are the median value for the n observations of the calendar year. Maximum and minimum pH observed are also shown. Excess sulphate (seasalt corrected) discharge calculated from the n observations of sulphate concentration and the measured run off (calculated as indicated on the figure) are also shown. Figure 3-30 illustrates the difficulty in making statistical analysis of the observations. Record breaks are present and unevenly spaced observations render statistical analysis to establish trends over time impossible. Thus Clair and Whitfield (1982) could treat only portions of the record. Figure 3-30 may be examined to illustrate the temporal variability of pH and excess sulphate discharge which is not revealed by the statistical trend analysis or the changes between two time periods as reported by Watt et al. (1983) or Farmer et al. (1980). The dominant feature is the minimum pH that occurs in the 1971-73 period. Excess sulphate discharge reaches a maximum for the Newfoundland rivers during the same period.

Wiltshire and Machell (1981) have reported on a re-survey of 16 lakes in Nova Scotia and New Brunswick, which had historical data going back to the 1930s in some cases. Eleven of the lakes are remote from local sources in Halifax and Saint John. The data for 10 remote lakes with the most reliable historical information are summarized in Table 3-15. Between 1950 and 1979 data indicate that there has been a decline in pH in all cases, most notably since the 1950s. All but one of the 10 lakes, however, still had a pH $>$ 5.5 in 1979.

Calculated alkalinity changes (Table 3-15) show declines ranging from 5.5 to 55 μeq/L.

3.6.3.2 Historical Trends in Northern Wisconsin

Juday et al. (1935) described the pH-CO_2 relationships of lakes in northeastern Wisconsin. Between the period 1925-41, measurements were made of pH, alkalinity and conductivity in 518 lakes. Historic pH was measured colorimetrically between 1925 and 1932; from 1932 to 1941 a quinhydrone electrode was used. Two groups have remeasured pH, alkalinity and conductivity in separate subsets of the 518 lakes (Bowser et al. 1982; Eilers et al. 1982). The 53 lakes sampled by Bowser et al. (1982) ranged from alkaline, mesotrophic lakes to brown-water bogs to clear-water, oligotrophic lakes. Multiple historical measurements were available and modern-day sampling was adjusted to a similar seasonal sampling period. All three lake types showed increases in pH, alkalinity, and conductivity over the 50-year period. Bowser et al. (1982) attributed their results to: (1) short duration of acidification of precipitation in Wisconsin; (2) changes in vegetation and shoreline land use; and (3) the importance of groundwater to many of the lakes. Eilers et al. (1982) sampled 275 of the lakes surveyed by Birge and Juday. They selected 180 for analysis and comparison with earlier measurements. They also found

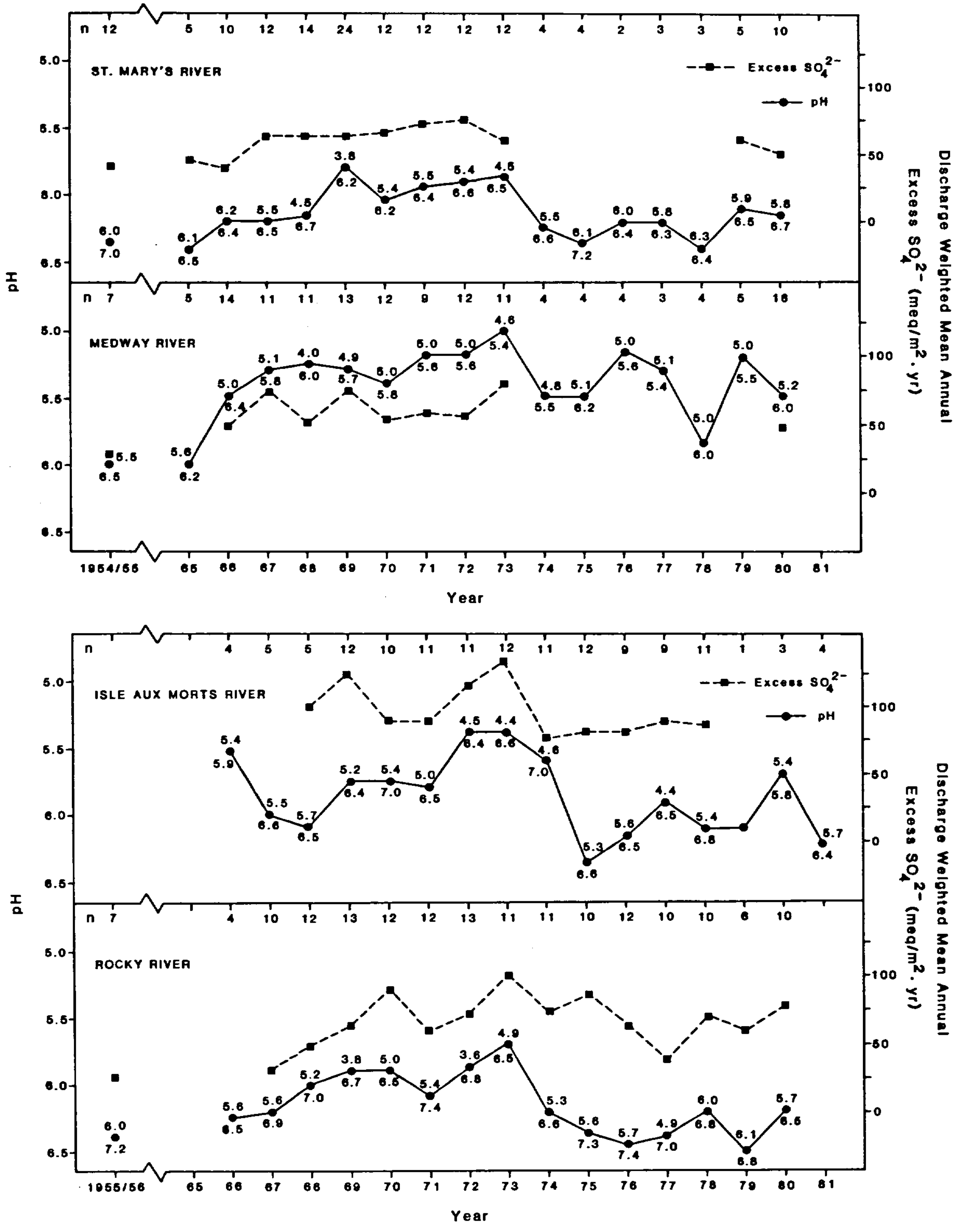


Figure 3-30. Annual changes in median pH and mean discharge-weighted excess SO_4^{2-} for the St. Mary's and Medway Rivers, Nova Scotia, and the Isle aux Morts and Rocky Rivers, Newfoundland. Data are from the sources indicated. Upper and lower numbers shown represent range of values, (●) is median and n is the number of samples for each year.

Figure 3-30. CONTINUED

Data for Figure 3-30 were calculated according to following format:

1. Excess SO_4^{2-} = Total SO_4^{2-} - $0.14Cl^-$ (both in mg/L)

2. Mean discharge-weighted excess SO_4^{2-} = $\frac{\Sigma(\text{Excess } SO_4^{2-} \text{ times Sample Date Discharge})}{\Sigma \text{ Sample Date Discharge}}$

3. Runoff = Mean Annual Discharge (m^3/yr) divided by drainage area (m^2)
   = m/yr = m^3/m^2.yr.

4. Runoff for Water Years 1954/07 - 1955/06 and 1955/07 - 1956/06 were calculated from mean monthly discharges. For the Mersey the long-term runoff times simple mean SO_4^{2-} concentration was used.

5. Excess SO_4^{2-} (meq/m^2.yr) = Mean discharge-weighted excess SO_4^{2-} times Runoff.

6. Chemical data are from NAQUADAT. Discharge data are from various reports of the Water Survey of Canada, Ottawa.

TABLE 3-15. APPARENT CHANGES IN SUMMER pH VALUES IN LAKES IN NOVA SCOTIA AND SOUTHERN NEW BRUNSWICK DURING THE PERIOD 1940-79 (Wiltshire and Machell 1981)

	pH			pH change		Calculated alkalinity change[d] in μeq/L	
	ca 1940[a]	1950s[b]	1979[c]	pre-1950s	post-1950s	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, 1937b, 1948, 1952, 1961.

[b] Data from Hayes and Anthony 1958.

[c] Wiltshire and Machell 1981.

[d] Calculated by Liljestrand pers. comm. PCO_2 assumed as $10^{-3.5}$ atm. (a global mean) with bicarbonate as major buffer.

that most lakes had increased in pH, alkalinity and conductivity. The lowest pH values were found in lakes having no inlet or outlet and no contact with groundwater (Eilers et al. 1982; Schnoor et al. 1982).

3.6.3.3 Historical Trends in New York State

Peters et al. (1981) analyzed precipitation data and stream water chemistry data from a nine-station monitoring network in New York State. The data covered the years 1965-78. Sulphate concentration in precipitation decreased 1-4%/yr, while NO_3^- increased by 4-13% each year. An increase in the total amount of precipitation over the period resulted in an increase in total acid loading. Variable neutralization of hydrogen ion, perhaps by particles in dry deposition, was suggested because the observed trends in hydrogen ion concentration do not correlate well with those for sulphate or nitrate.

In most areas of New York, urbanization, farming and carbonate soils have masked any effects of increased acid loading. For the East Branch of the Sacandaga River in the Adirondacks, nitrate increased 0.004 meq/L.yr, while sulphate decreased 0.0041 meq/L.yr. Sulphate concentrations exceed bicarbonate for the stream indicating little interaction with soils or ground water. Consequently, with the increases in acid loadings in precipitation over the period, alkalinity has decreased 0.083 meq/L.yr (Peters et al. 1981).

In a survey designed to identify acidic lakes in the Adirondacks, Schofield (1976c) sampled 214 high altitude lakes (Figure 3-31). A complete set of chemical analyses was obtained, but no internal checks can be made on the data, because sulphate was determined by difference. The pH range of sampled waters was 4.3-7.4. Fifty-two percent were listed as pH <5.0; 7%, pH 5.5-6.0. pH measurements were made in the laboratory following aeration of the sample.

Increased elevation and low pH of ponds and lakes were positively correlated. The combined influences of heavier precipitation at higher elevations, the smaller surface area and watershed size which characterizes most headwater ponds, the prevalance of granitic bedrock and shallow soil deposits in the higher elevations, and the direct impingement of acidic cloud water are all possible factors. In addition, N.M. Johnson (1979) showed that neutralization occurs as contact time with the substrate increases, such as occurs as water flows downhill into progressively larger streams.

For a subset of 40 of these 214 high elevation lakes, historical data on pH are available from the 1930s (Schofield 1976c; Figure 3-32). These early pH values represent colorimetric measurements. Several authors (Norton et al. 1981a; Pfeiffer and Festa 1980; Schofield 1982) have examined the agreement between the two pH methods. Although certainly not exact, qualitative comparisons appear appropriate. For this subset of 40 lakes, in 1975, 19 lakes had pH

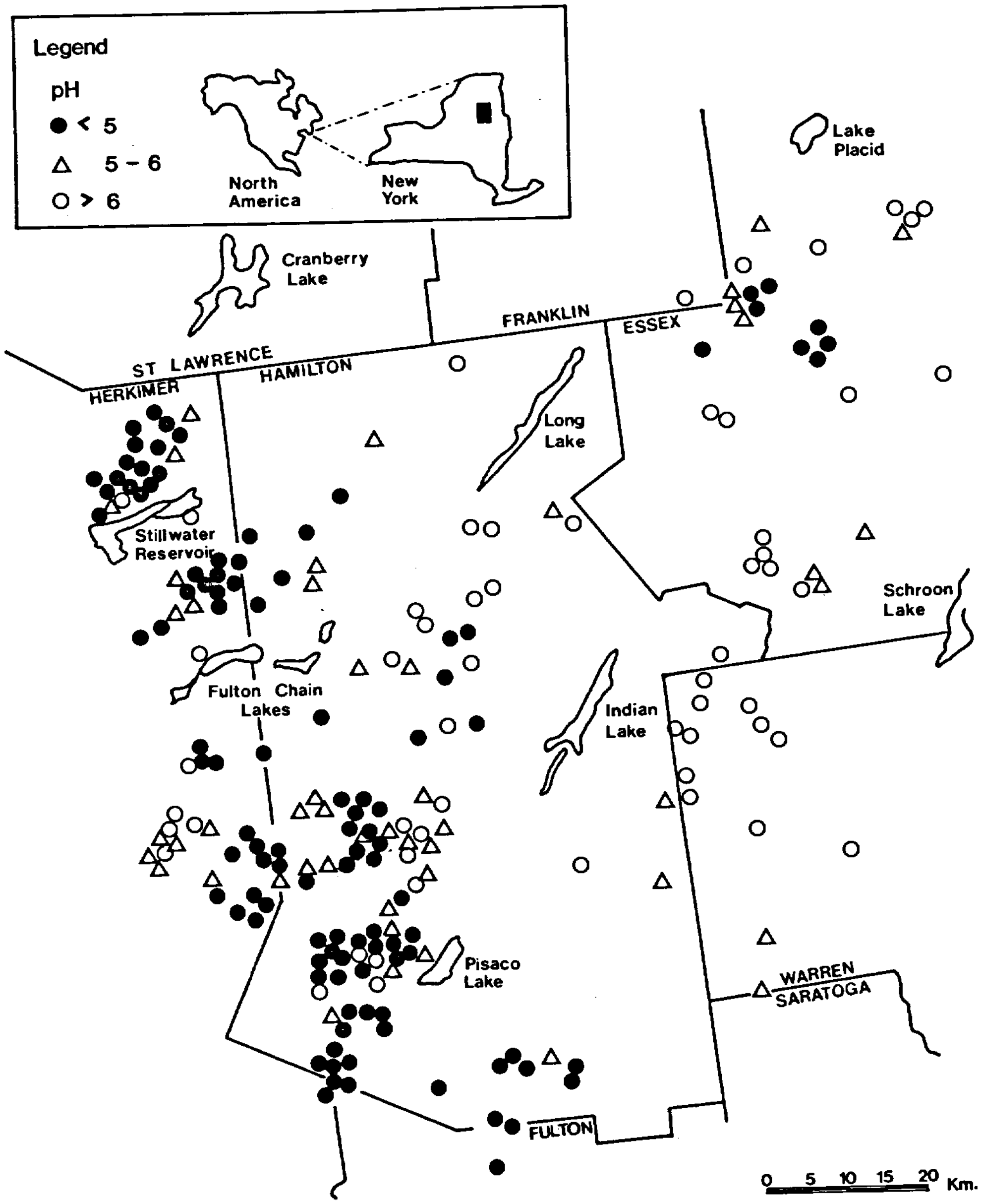


Figure 3-31. Geographic distribution of pH levels measured in Adirondack lakes higher than 610 metres elevation, June 24-27, 1975 (Schofield 1976c).

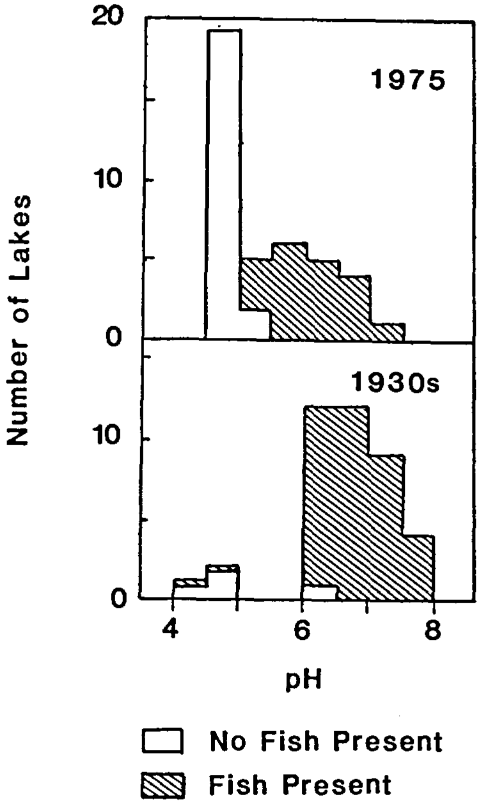


Figure 3-32. Frequency distribution of pH and fish population status for 40 high elevation lakes surveyed in the 1930s and again in 1975 (Schofield 1976c).

below 5.0 and all of these lakes had no fish. In the 1930s, only 3 lakes had values below 5.0 and a total of only 4 lakes had no fish (Schofield 1976c).

In a larger survey that included Schofield's 1975 sites (Schofield 1976c), a 1980 report by the New York Department of Environmental Conservation (NYDEC) (Pfieffer and Festa 1980) reported that 264 of 849 (25%) lakes sampled in the Adirondacks had a pH <5.0. The report linked this acidity to fish losses in these lakes. Since publication of this report, however, both the NYDEC (1982) and others (Schofield 1982) have recognized that many of the pH values reported were too low (due to problems with the pH meter). Pfeiffer and Festa (1980) also presented a comparison of colorimetric pH measurements for the 1970s and 1930s for a set of 138 Adirondack lakes. In general, historic pH readings were higher than the comparable current measurements.

3.6.3.4 pH Changes in Maine and New England

Several synoptic studies have been done for New England surface waters. Davis et al. (1978) studied 1936 pH readings taken from 1,368 Maine lakes during the period 1937-74 in an effort to see if they could find pH decreases associated with the acidic precipitation of that area ($4.4 < \text{pH} < 5.0$ since at least 1956; Cogbill 1976; Likens 1976). Samples and data were from a variety of sources (Davis et al. 1978) but apparently most samples were taken over the deepest portion of each lake, near mid-day, during the summer. Wallace-Tiernan colorimetry was used to measure pH "until the 1960's"; then pH was measured with portable meters. "The two methods were found to agree within 0.1 pH units" (Davis et al. 1978).

The authors noted initially that the mean pH of 196 samples from 1937 to 1942 was 6.81 and that the mean for 289 samples from 1969 to 1974 was 6.09; a 5.2-fold acidity increase. They also noted that most of the change seemed to occur in the early 1950s and that overall the change might have been greater if it had not been for some cultural euthrophication beginning in the 1950s. The authors realized that these preliminary results might have been affected by regional edaphic differences in lake types and also by differences in precipitation acidity across the state. Amounts and seasonal patterns of precipitation also may have played a part (Davis et al. 1978). In an attempt to minimize such potential regional distortions, they analyzed the data by using three procedures based on H^+ concentration changes in individual lakes.

They found 258 lakes had pH readings separated by at least a year. There was a mean of 2.9 readings per lake and a mean of 12.7 years between successive readings (pairs) for a total of 376 pairs during the period 1937-74.

Procedure I of Davis et al. (1978) was as follows. They used data pairs to calculate slopes (H^+ concentration vs. time) for individual lakes and then mean slopes from 1937 to 1974. The mean slopes were added to obtain a total H^+ concentration change for the entire period. Given a starting pH of 6.89 (mean of 123 values 1937-42), the final (1974) pH would be 5.79, an increase in acidity of 12.6 times. Using a t-test, the authors also found that the mean annual increase in H^+ concentration based on the mean slopes for each year was significantly different from zero change with $p < 0.0001$. The authors noted, however, that this procedure more strongly weights data pairs with long time separations, thus possibly invalidating the use of a t-test.

The second procedure Davis et al. (1978) used was to average the 376 single slope values. This gave a mean of 0.115 µeq/yr H^+ concentration change. By t-test, this mean is significantly different from zero $p < 0.1$, but not at $p < 0.05$. If a disproportionately greater decrease in pH occurred in the 1950s (as the authors hypothesized), this procedure would give greater weighting to the more frequent data pairs beginning about that time and would thus overestimate total change (Davis et al. 1978).

Procedure III the authors used was to weight each data pair (H^+ concentration) slope linearly in inverse proportion to the time interval between each reading. These weighted slopes were then averaged for each year that they applied. Using an initial pH of 6.89 in 1937, the authors noted that pH decreases by 1950 to only 6.83. By 1961, however, the pH has decreased to 5.91, so that 73% of the increase in acidity has occurred in this latter time period. The authors believed that this 73% increase in acidity was actually an underestimate for this time period.

Davis et al. (1978) also discussed some alkalinity data they had for 44 of the 258 lakes cited above. These data were from the period 1939-71, a total of 96 values and 52 pairs. No information was given on the analytical method(s) used to determine alkalinity. Applying their Procedure I to those data, they obtained a decrease of about 6.34 ppm (as $CaCO_3$; from 11.82 to 5.48 ppm, typically; corresponding to a decrease of 127 µeq/L from 236 to 109 µeq/L) over the period. This was much less than expected from pH changes from the same period and observed relationships between pH and alkalinity. The authors noted that "the discrepancy may be due in large part to the inadequate sampling and great variance of the alkalinity data, including the fact that 67% of the pairs had their initial member in 1960 or later" (Davis et al. 1978).

The authors concluded from their study that between the years 1937 and 1974 H^+ concentration in Maine lakes increased about 1.0 µeq and pH decreased from about 6.85 to 5.95. Further, nearly three-quarters of this change occurred in the 1950s. "This is the first demonstration of a pH decrease due to acidic precipitation on a large region of lowland lakes in the United States" (Davis et al. 1978).

Norton et al. (1981a) measured pH in 94 New England lakes (82 in Maine, 8 in New Hampshire, 4 in Vermont) for which historical pH existed from the period 1939-46. Eleven (12%) of these lakes had pH <5.0 in 1978-80. The lakes sampled were small, oligotrophic-mesotrophic, and located in forested areas on noncalcareous bedrock. The recent sampling (1978-80) was done during July-October but not on the same monthly dates as the historic sampling. These samples were collected at 1 m depths, and the lakes were stratified at the time of sampling.

The pH values of the recent samples were measured in the field with (1) a portable pH meter with combination electrode, and (2) a Hellige color comparitor. Except for three spurious cases of low pH lakes, the authors found that "reasonable agreement exists for these two methods, especially at higher pHs" (Norton et al. 1981a).

The authors presented their results in plots of: (1) old colorimetric pH vs. recent colorimetric pH, and (2) recent colorimetric pH vs recent electrometric pH. They concluded that their study "confirms the results of Davis et al. (1978) regarding an overall decrease in the pH of Maine lakes" (Norton et al. 1981a).

Norvell and Frink (1975) found that the pH and alkalinity in sensitive (alkalinity < 200 μeq/L) lakes in Connecticut had not changed significantly from 1937 to 1973. Haines (1981a) reports a number of Connecticut rivers as being "sensitive", due to alkalinities <200 μeq/L, but pH in these waters is 6.4-7.1 except in smaller lower order streams. In Maine, the pH of major rivers is greater than 6.5, with the lowest values in eastern Maine (the area with the highest precipitation pH in New England) (Haines 1981a).

Haines and Akielaszek (1982) sampled 95 lakes for which there were historical pH data from the 1930s to the 1960s. Of these, 36% either had the same or higher pH while 64% were lower. For 56 lakes there were also fixed end point titrations of alkalinity. A comparison of historical alkalinities to modern values indicated that 30% of the lakes had increased and 70% had decreased in alkalinity. The historical alkalinity values averaged 166 μeq/L and recent samples 68 μeq/L.

3.6.3.5 Time Trend in New Jersey

A.H. Johnson (1979) described a 17-year decline in pH of headwater streams in the New Jersey Pine Barrens which drain relatively undisturbed watersheds (Figure 3-33). The trend is statistically significant and has amounted to approximately 0.4 pH units over the period. In the sandy soils of this region, relatively little neutralization of acid inputs 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. The great

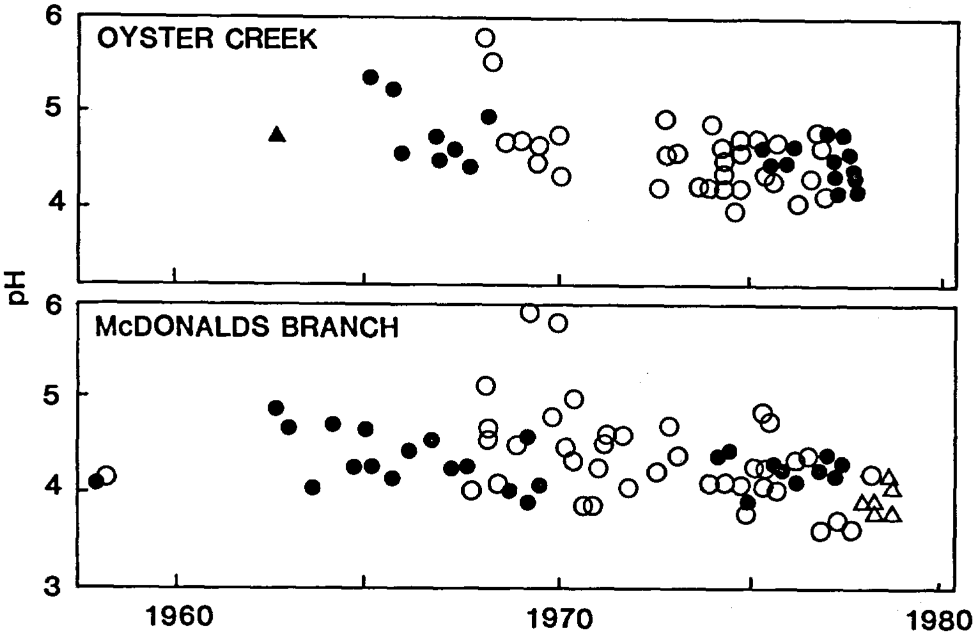


Figure 3-33. New Jersey stream pH, 1958-1979, Oyster Creek and McDonalds Branch. Closed circles represent samples in which anion and cation equivalents balanced, and calculated and measured specific conductances were equal. Open circles are samples for which the chemical analyses were incomplete, or 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 (A.H. Johnson 1979).

variability in pH values of streams in 1978-79 is thought to be due to storm events.

Some precipitation pH data suggest a trend toward lower pH values in southern New Jersey (A.H. 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. Samples collected near Oyster Creek for seven 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.

3.6.4 Paleolimnological Evidence for Recent Acidification and Metal Deposition

To supplement the sparse information from long term records on water quality in eastern North America alternative techniques have been developed to define time trends related to surface water acidification.

Paleolimnological analyses of lake sediments have traditionally been used to reconstruct many aspects of the evolution of lake/drainage basin ecosystems including terrestrial and aquatic vegetational succession (Bradstreet et al. 1975), fire history (Patterson 1977), trophic status (Davis and Norton 1978; Stockner and Benson 1967) and even the occurrence of blight or disease (Bradstreet and Davis 1975). Long-term changes in meteorology, morphology of the lake basins, soil development, land use, or surface water chemistry can be partially determined from the sediment record.

Both chemical and biological records are left in the sediment record. By studying modern biota in relation to modern water quality for many lakes, changes in ecosystems which have taken place over time can be reconstructed for water quality parameters, for example, pH (Davis and Berge 1980; Davis et al. 1980, 1982; Renberg and Hellberg 1982). Normally, measurable changes in natural acidity are on the order of centuries and are accompanied by changes in other sediment characteristics. Land use changes such as logging followed by reforestation can bring about perturbations in pH of surface waters (both increases and decreases) with a general return to equilibrium in 10 to perhaps as much as 50 years (Likens et al. 1978; Pierce et al. 1972).

Davis and Berge (1980) and Davis et al. (1980, 1982) have demonstrated, using fossil diatom data, pH declines in the last 30-70 years from pH values of greater than 5.5 to values less than 5 in lakes in Norway with relatively undisturbed drainage basins. The present pH of these lakes is too low to be explained by the concentrations of naturally occurring organic acids. Sulphate is the dominant anion and is apparently atmospheric in origin (Wright and Henriksen 1978).

Norton et al. (1981b), Davis et al. (1982), Evans and Dillon (1982), Dickson (1980), and others have demonstrated that heavy metal (especially Pb, Zn, and Cu) deposition rates started increasing over 100 years ago in eastern North America and Scandinavia indicating polluted air masses existed in the late 1800s. Cores from Swedish Lapland (Davis et al. 1982) do not show these increases. There, the pH of precipitation is approximately 5.0. By inference, precipitation in eastern North America was probably somewhat acidified by the late 1800s. No change in the biology, defined from the sediment cores is observable until at least the early 1900s. Thus biological effects appear to lag behind definable chemical changes (Brakke et al. 1982; Davis et al. 1982).

As the acidity of precipitation increases, leaching of Zn, Cu, Ca, Mg and Mn from organic matter and soils of the terrestrial ecosystem also increase. At near neutral surface water pH (greater than pH 5.5), Zn and Cu from the terrestrial leaching processes are accumulated in the sediments. However, as surface waters become more acidic, Zn and Cu from the watershed remain in the water column to be exported from the lake. As a result, acidification of surface waters will decrease sedimentation of Zn and Cu. Lead, on the other hand, accumulates in sediments independently of pH (Davis et al. 1982).

Calcium, Mg and Mn also decline in lake sediments as acidity increases for two reasons. Firstly, as a result of acidic deposition falling on the watershed, terrestrial detritus becomes depleted of Ca, Mg, and Mn prior to entry into the aquatic ecosystem and incorporation into the sediments. Secondly, acidified waters prevent these metals from being resorbed to sediment organic matter and, like Zn and Cu, are exported from the lake system (Norton et al. 1981b).

Experiments on lake sediment microcosms (Kahl et al. 1982) indicate that if lake water pH is increased, the sediments absorb Ca, Mg, Mn, and Zn from the water column at a rate which would enrich the sediments. The observations and information from field studies suggest that acidification strips cations from terrestrial detritus and prevents them from resorbing onto the detritus (Dickson 1980; Kahl et al. 1982; Norton et al. 1980). Norton et al. (1980) showed that the chemistry of soil organic matter in New England, New Brunswick, and Quebec is partly controlled by atmospheric deposition of acids and metals. They found decreased Zn, Mn, Ca, and Mg in regions receiving high H^+ loading.

Cores from acidic clear water lakes in New England (pH less than 5.5) with undisturbed drainage basins (5 of the 30 lake samples taken over at least the last 50 years) show declines in sediment concentrations of Zn, Ca, Mg, and Mn starting as early as about 1880 suggesting increased leaching of sediment detritus prior to entry into the lakes (Davis et al. 1982; Kahl et al. 1982) or reduced sedimentation rate. All acidified lakes in Norway and New England with pH less than 5.0 have shown declines in Zn and Cu in recent sediment. Lead, on the other hand, is not released from surficial sediments unless the pH is less than 3.0 (Davis et al. 1982).

Measurement of atmospheric loadings via both wet and dry deposition techniques is plagued by a variety of uncertainties (Section 2.2.3). The lake sediments integrate materials deposited directly on the lake surface from the atmosphere with elements leached from the terrestrial watershed. Increased mobilization of metals from watersheds during hydrologic events when pH is depressed has been discussed (Section 3.2.4). The calibrated watershed approach to measuring deposition is ineffective for trace metals because metal levels found in lake and stream water are often below analytical detection limits usually employed. Trace metals are rapidly removed from the water column in most lakes (residence times are typically of the order of days), and stored in the sediment. Calculation of metal loadings to lakes may sometimes be derived from information collected from the lake's sediments. Profiles of lead concentration in four sediment cores from Jerry Lake, Ontario are shown in Figure 3-34.

Dillon and Evans (1982) demonstrated that input of lead from anthropogenic sources to eight lakes in southern Ontario resulted only from atmospheric deposition directly on the lakes' surfaces; that is, deposition on the lakes' watersheds was effectively retained in the watersheds. The whole-lake lead burdens estimate the total atmospheric deposition of lead during the period when anthropogenic emissions have existed. Regional anthropogenic lead burdens measured for Muskoka-Haliburton, Ontario (Dillon and Evans 1982) and a remote northern site, Schefferville, Quebec (Rigler 1981) are 680 (range 610-770) mg/m^2 and 37 (range 31-59) mg/m^2, respectively.

3.6.5 Seasonal and Episodic pH Depression

Although survey data, both current and historical, can be used to document long-term trends in a synoptic sense, the samples usually represent one or a few measurements at any one location and are often collected during 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. Individual pH values during the summer do not reflect these cyclic and episodic aspects of the loading/episodic response relationship. If short-term changes in water chemistry coincide with sensitive periods in the life cycles of fish (e.g., spawning and hatching), significant mortality and reduced reproduction can occur. The following data describe recent results on episodic pH declines; the extent to which these phenomena occurred in the past is not known.

3.6.6 Seasonal pH Depression in Northern Minnesota

Siegel (1981) reported on the effect of snowmelt on Filson Creek and Omaday Lake in northeastern Minnesota. He found concentrations of sulphate increased in Filson Creek and Omaday Lake during snowmelt from less than 2 to 12 mg/L in 1977 and from less than 2 to 4 mg/L in 1979. During snowmelt, pH decreased from 6.6 to 5.5 in 1979.

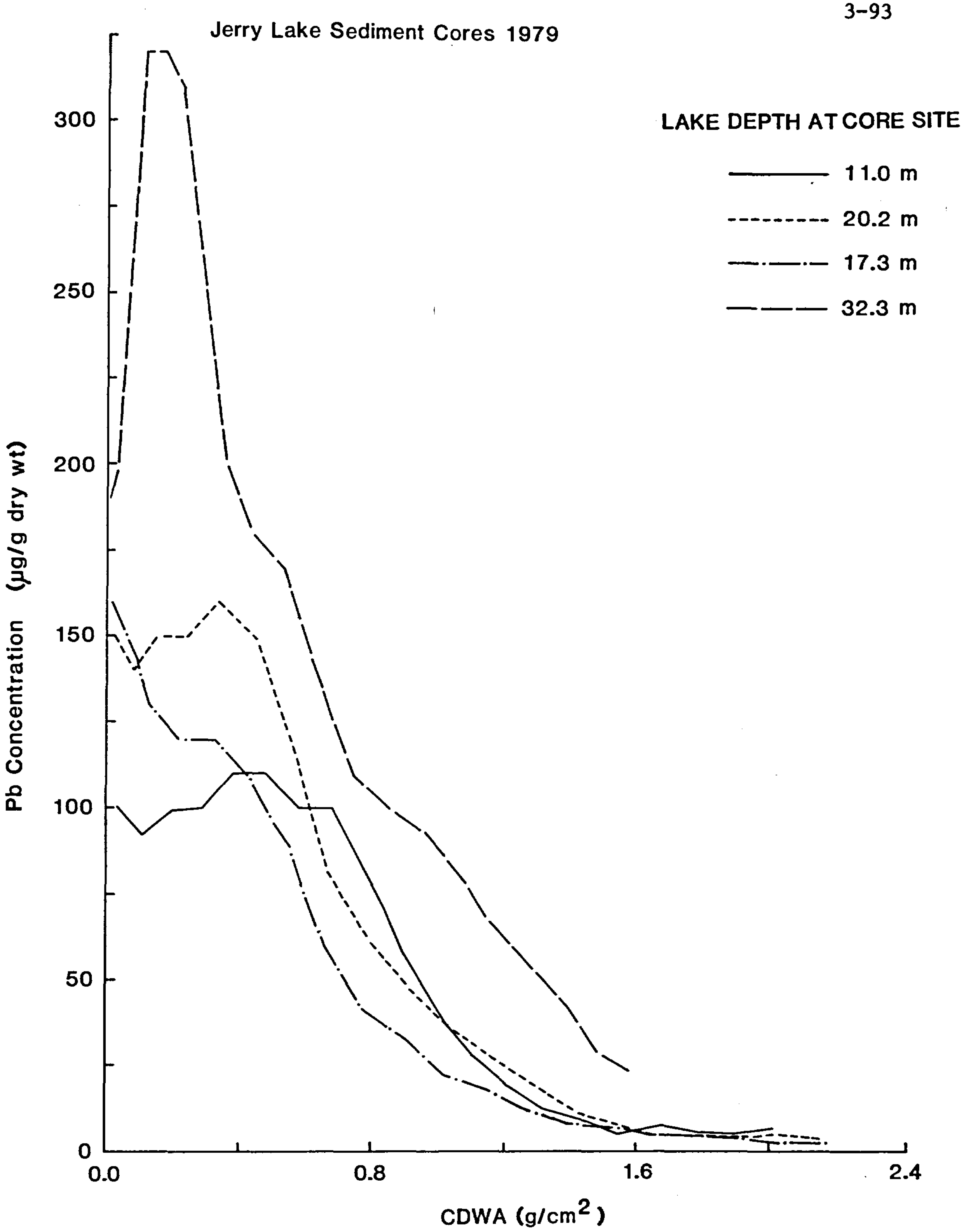


Figure 3-34. Profiles of the lead concentration in four sediment cores from Jerry Lake, Muskoka-Haliburton. Depth within core is expressed as cumulative dry weight per unit area (CDWA) (modified from Dillon and Evans 1981).

Alkalinity and concentrations of total calcium, magnesium, and sodium in the creek during snowmelt reflect the simple dilution of streamflow with more dilute precipitation. Depression of pH values to less than about 5.7 indicate that base flow (pH ~ 6.5) has been diluted with meltwater that contains some mineral acids.

3.6.7 pH Declines During Spring Runoff in Ontario and Quebec

Detailed surface water chemistry studies have been conducted in lakes near Muskoka-Haliburton, Ontario, on 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. The pH declines of the lake outflows demonstrated that the top portions of the entire lakes were acidified. The lowest stream pH values observed, 4.1 to 5.1 (Table 3-16), were within a range capable of causing damage to some aquatic organisms, particularly fish (see Section 3.7.7 for discussion). As much as 77% of the measured annual acid export of the streams occurred in April (Table 3-17). A typical hydrograph and pH response for one of the streams during the snowmelt period is illustrated in Figure 3-35 and Table 3-17.

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 3-36; Scheider et al. 1979b). Heavy fall rains also cause depressed pH in runoff for days at a time. Jeffries et al. (1979) observed as much as 26% of the total annual hydrogen ion runoff, from small watersheds, in October.

As a control for eastern work, ELA is probably one of the best that can be obtained at temperate latitudes. Mean annual pH of bulk precipitation ranged from 4.9 to 5.2 over the past 10 years, calculated on a volume-weighted hydrogen ion basis. No directional trend was observed in pH values. There is a pH depression in the area related to spring snowmelt, of about 0.2 to 0.5 pH units in inflow streams and about 0.2 to 0.3 in lake outlets. Minimum values observed in spring runoff have been as low as 4.5 but are generally above 5.0 (data from ongoing studies at the Freshwater Institute, Fisheries and Oceans, Winnipeg, Canada).

A comparison of the water chemistry of 70 lakes in Quebec, sampled at the spring isotherm and at a summer stratification of 1980, has been performed by Bobée et al. (1982). [This information is summarized in their table 5.2, Table 3-18 in this report.] The authors observed that the mean values of conductivity, alkalinity and pH were generally lower during the spring than during the summer while the ratio $[SO_4^{2-}]/[HCO_3^-]$ was much higher in the spring.

3.6.8 pH Depression During Flushing Events in West Virginia

Seasonally low pH and regular patterns of pH declines have been documented for the Little Black Fork and Shavers Fork Rivers by the

TABLE 3-16. 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) (Jeffries et al. 1979)

Watershed	Stream	pH	
		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

TABLE 3-17. MONTHLY DISCHARGE, HYDROGEN ION LOADS AND PERCENT OF ANNUAL TOTAL FOR PAINT LAKE NO. 1, HARP LAKE NO. 4, AND DICKIE LAKE NO. 10 FROM JUNE 1977 THROUGH MAY 1978 (Jeffries et al. 1979)

	Paint Lake no. 1				Harp Lake no. 4				Dickie Lake no. 10			
	Discharge		H^+ Load		Discharge		H^+ Load		Discharge		H^+ Load	
	$10^3 m^3$	%	Equiv.	%	$10^3 m^3$	%	Equiv.	%	$10^3 m^3$	%	Equiv.	%
June 1977	0.27	0.2	0.53	0.1	6.20	1.0	2.98	0.4	0.00	0.0	0	0.0
July	0.15	0.1	0.24	0.1	2.70	0.4	0.59	0.1	0.00	0.0	0	0.0
Aug.	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0	0.0
Sept.	0.81	0.7	0.72	0.2	25.6	4.2	5.86	0.8	26.9	7.4	599	7.5
Oct.	10.9	9.3	16.7	3.4	61.1	10.0	26.6	3.6	76.4	21.1	2050	25.8
Nov.	15.5	13.2	49.1	10.0	77.1	12.6	40.9	5.5	38.2	10.6	789	9.9
Dec.	6.70	5.7	21.2	4.3	33.2	5.4	21.7	2.9	30.8	8.5	694	8.7
Jan. 1978	3.35	2.9	7.95	1.6	21.0	3.4	9.17	1.2	11.4	3.2	139	1.8
Feb.	1.81	1.5	5.74	1.2	12.5	2.0	5.31	0.7	5.40	1.5	86	1.1
Mar.	3.85	3.3	11.4	2.3	14.8	2.4	4.53	0.6	9.80	2.7	134	1.7
Apr.	53.2	45.3	298	60.8	282	46.1	566	76.6	129	35.6	2870	36.2
May	20.9	17.8	78.9	16.1	75.7	12.4	55.4	7.5	34.1	9.4	575	7.5
Total	117		490		612		740		360		7940	

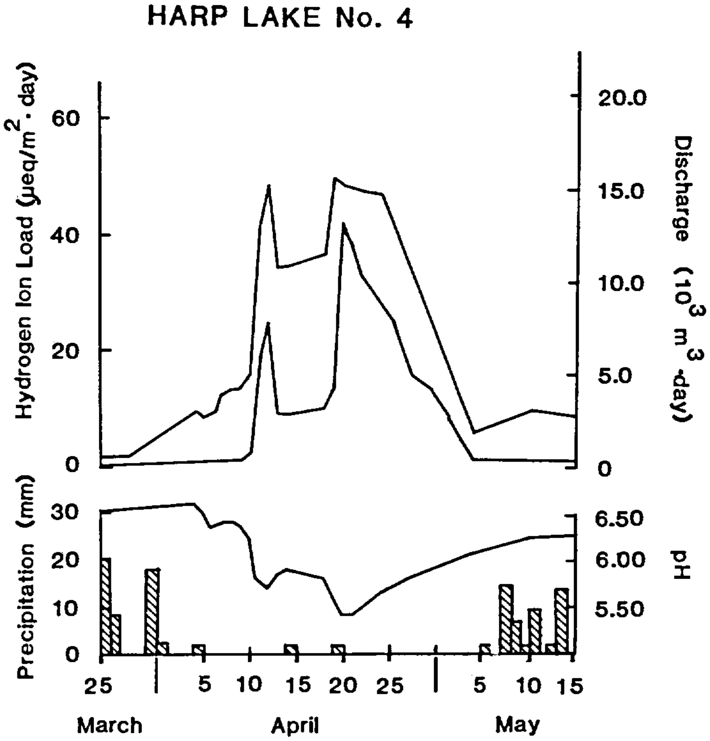


Figure 3-35. Discharge (upper line), hydrogen ion load per unit area (middle line), pH (lower line), and depth of precipitation for each day that a precipitation event occurred for Harp Lake No. 4. Daily H^+ load to the respective lakes can be calculated by multiplying by the watershed area: lake area (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).

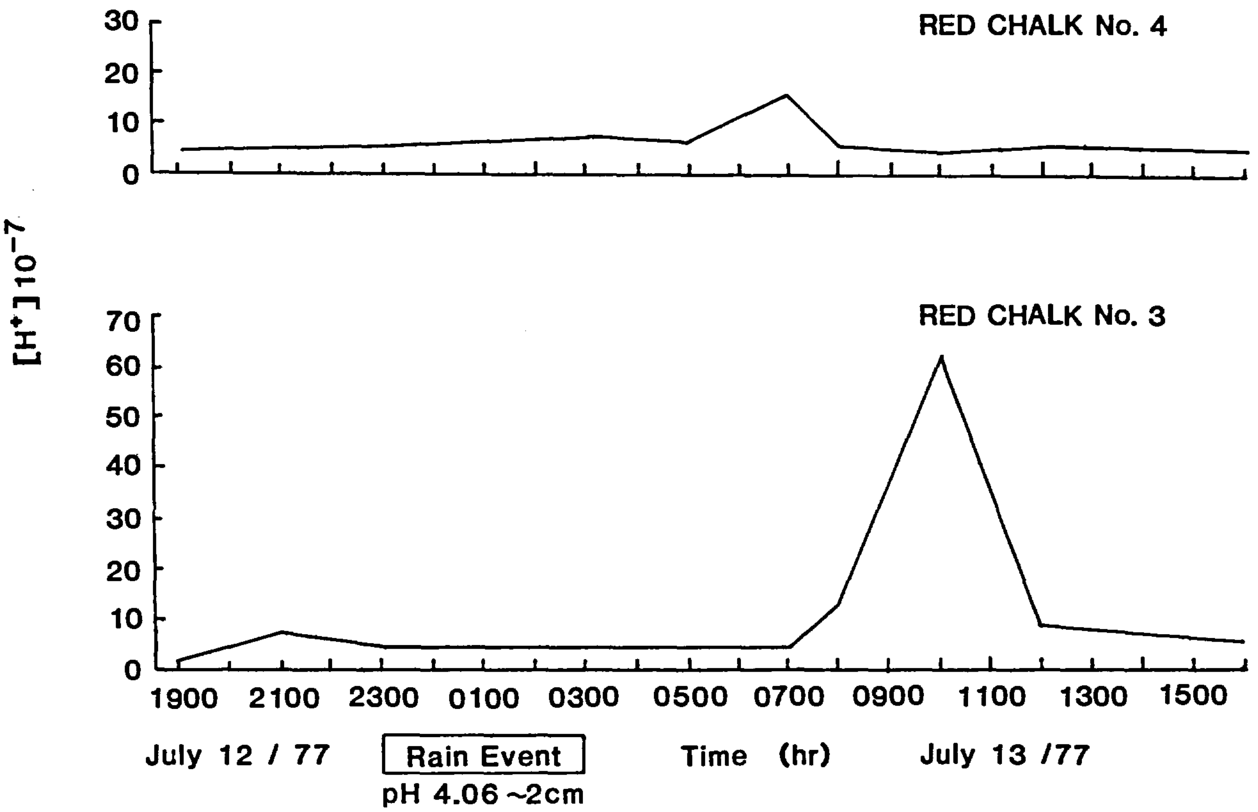


Figure 3-36. Hydrogen ion content of streams draining Red Chalk Lake watersheds No.3 and No.4 (Muskoka-Haliburton, Ontario) showing effects of a 2 cm rainfall (pH 4.06) between 11:00 p.m. July 12, 1977 and 3:00 a.m. July 13, 1977 (Scheider et al. 1979b).

TABLE 3-18. SPRING-SUMMER COMPARISON OF AVERAGE PARAMETER VALUES CALCULATED FOR EACH HYDROGRAPHIC REGION IN QUEBEC, MEASURED IN THE PROJECT LAKE NETWORK (Student t-Test) (from Bobée et al. 1982)

	HYDROGRAPHIC REGION							
PARAMETER	01	02	03	04	05	06	07	08
Total Inorganic Carbon (mg of C/L)	9.6/11.2	8.0/9.2	3.8/5.1	2.4/2.2*	0.7/1.3*	2.3/3.4	0.9/1.6	1.4/2.8
Alkalinity (μeq/L)	765/870	628/645*	233/327*	19/75	14/24*	139/162	20/35*	14/105
pH	7.6/7.4*	6.9/6.8*	6.8/6.9*	5.0/5.8	4.9/5.7	6.1/5.9*	5.7/5.7*	5.1/5.9
Conductivity (μS/cm)	92/95*	87/76*	50/63*	29/35	15/21	27/33	7.2/10	19/34
SO_4^{2-} (μeq/L)	84/85*	140/135*	127/107	142/137*	98/101*	83/69*	46/57*	94/98*
Cl^- (μeq/L)	38/38*	45/45*	88/116*	15/14*	10/9*	18/18*	22/24*	15/15*
Ca^{2+} (μeq/L)	715/825*	599/661*	268/338	175/176*	81/90	121/122	58/53*	128/158*
Mg^{2+} (μeq/L)	144/156	163/173*	143/166	58/55*	35/41*	45/48*	22/20*	65/80*
Calcite Saturation Index	0.9/1.0*	1.6/2.3*	2.6/2.4*	6.1/4.6	5.6/5.4*	4.4/4.5*	5.7/5.4*	6.3/4.4
Total Organic Carbon (mg of C/L)	18/11	15/11*	11/9.4*	11/12*	11/11*	13/10	14/8	14/13*
Colour (mg of Pt)	18/21*	29/30*	19/21*	27/15	41/32*	36/31*	30/21	68/60*
Number of Lakes	9	5	8	11	5	8	15	9

* Nonsignificant differences at the 5% level, paired student t-test.

U.S. Forest Service in Monongahela National Forest (Dunshie 1979). Due to the sandstone geology of the watershed, the tributaries and the river are poorly buffered and subject to rapid changes in water quality. The lowest pH values in both streams (Little Black Fork is a control area, with no logging or coal mining) normally occurred during the winter and early spring, apparently because of snowpack melting. The highest pH occurred during low stream flow periods in the summer and fall. Even though summer and autumn are the periods of highest precipitation inputs (see below), more extensive contact between soils and precipitation may have lead to greater neutralization at these times than during either winter or spring flushing events.

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 periods is shown in Figure 3-37. During the growing season, a storm event with a subsequent increase in discharge can significantly lower river pH below the natural nonstorm 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 0.6 to 0.9 pH units, occurred on July 11 and 26, and on August 15 and 25, 1977. 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.

Nearly 13 years of pH data have been collected at the Bowden Fish Hatchery river intake on the Shavers Fork River, showing lower pH values during winter and spring compared to summer conditions. This is important for aquatic organisms and has been measured in other poorly buffered streams. This pH trend occurred in streams and tributaries independent of watershed disturbance by mining (Dunshie 1979).

3.7 ALTERATION OF BIOTIC COMPONENTS IN AQUATIC SYSTEMS RECEIVING ACIDIC DEPOSITION

Many changes in biota have been linked to acidification of surface waters. In some controlled whole lake and laboratory experiments a causal relationship with decreased pH has been established. In the majority of cases, the observed changes in biota have simply been correlated with observed changes in pH and other parameters, but causality has not been established. For many biological communities, acidification has been accompanied by decreases in species diversity and changes in species dominance. Acidification may also be accompanied by species extinctions, or decreases in overall community standing stocks. This topic has been reviewed recently by Haines (1981c). Generalized summaries of responses of aquatic organisms to low pH are given in Figures 3-38 and 3-39 (Eilers and Berg 1982), and are presented here as a simplified overview of the complex

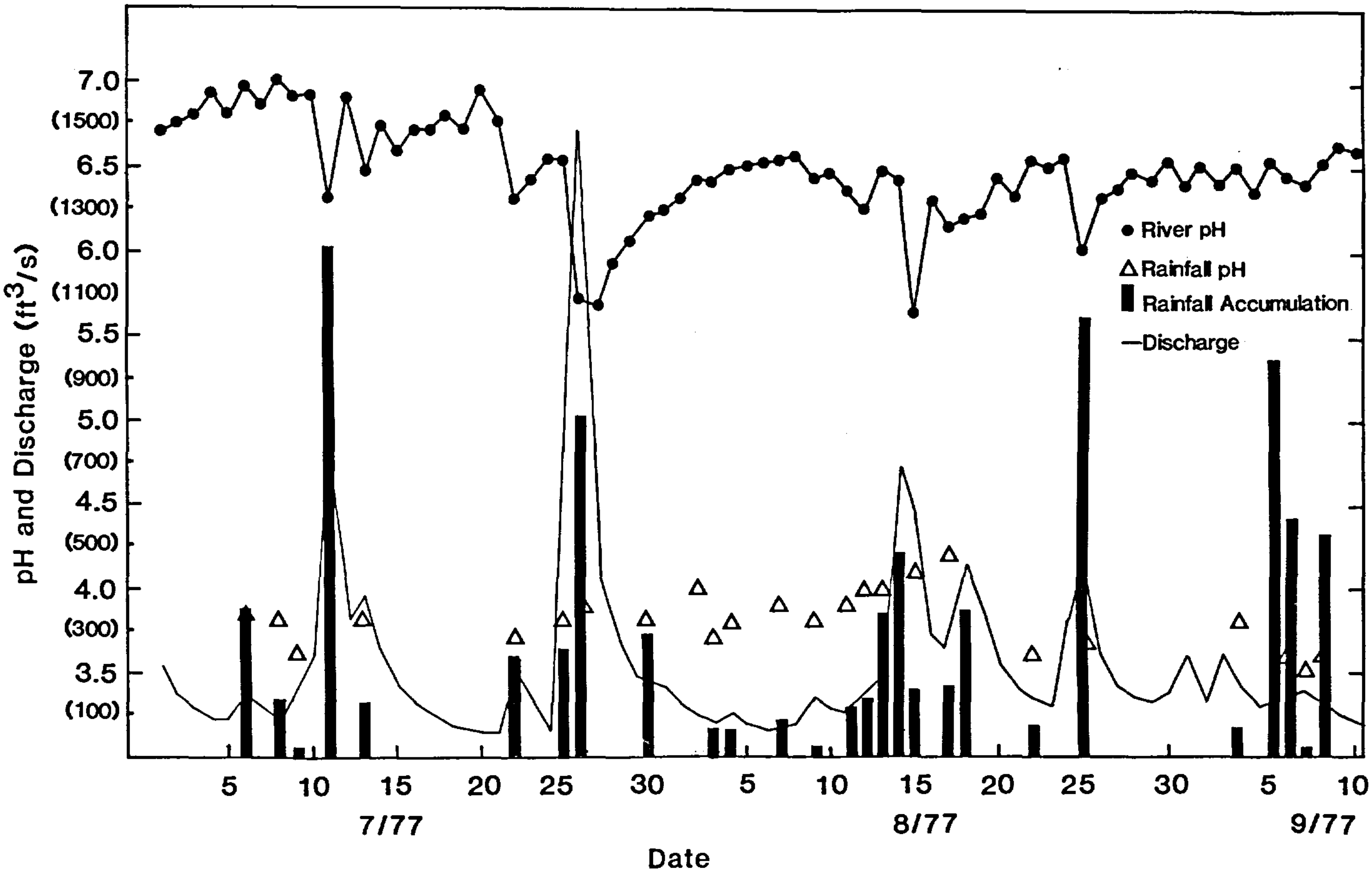


Figure 3-37. Mean daily pH for the Shavers Fork River at Bemis, West Virginia and precipitation event pH and accumulation at Arborvale, West Virginia (Dunshie 1979).

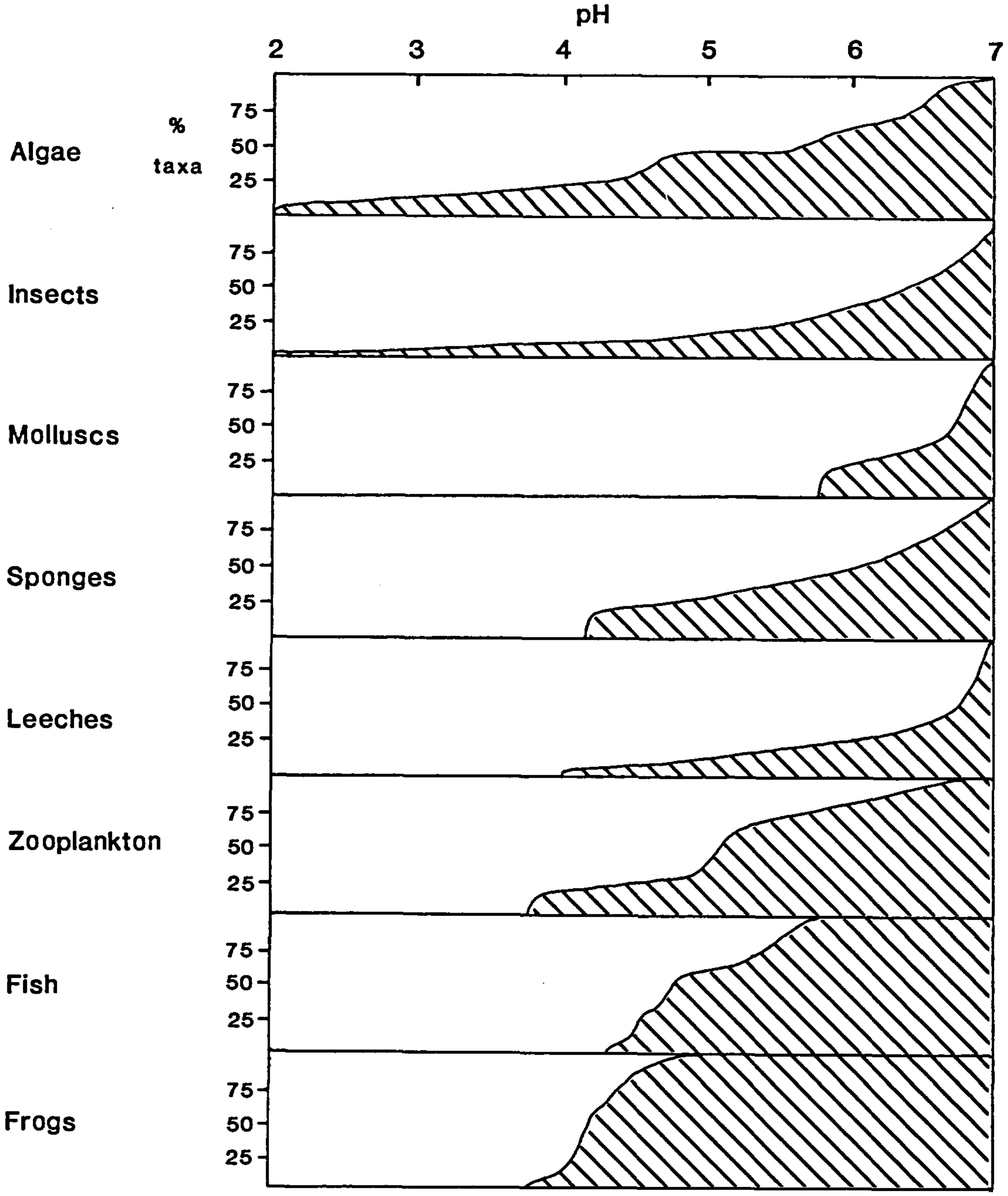
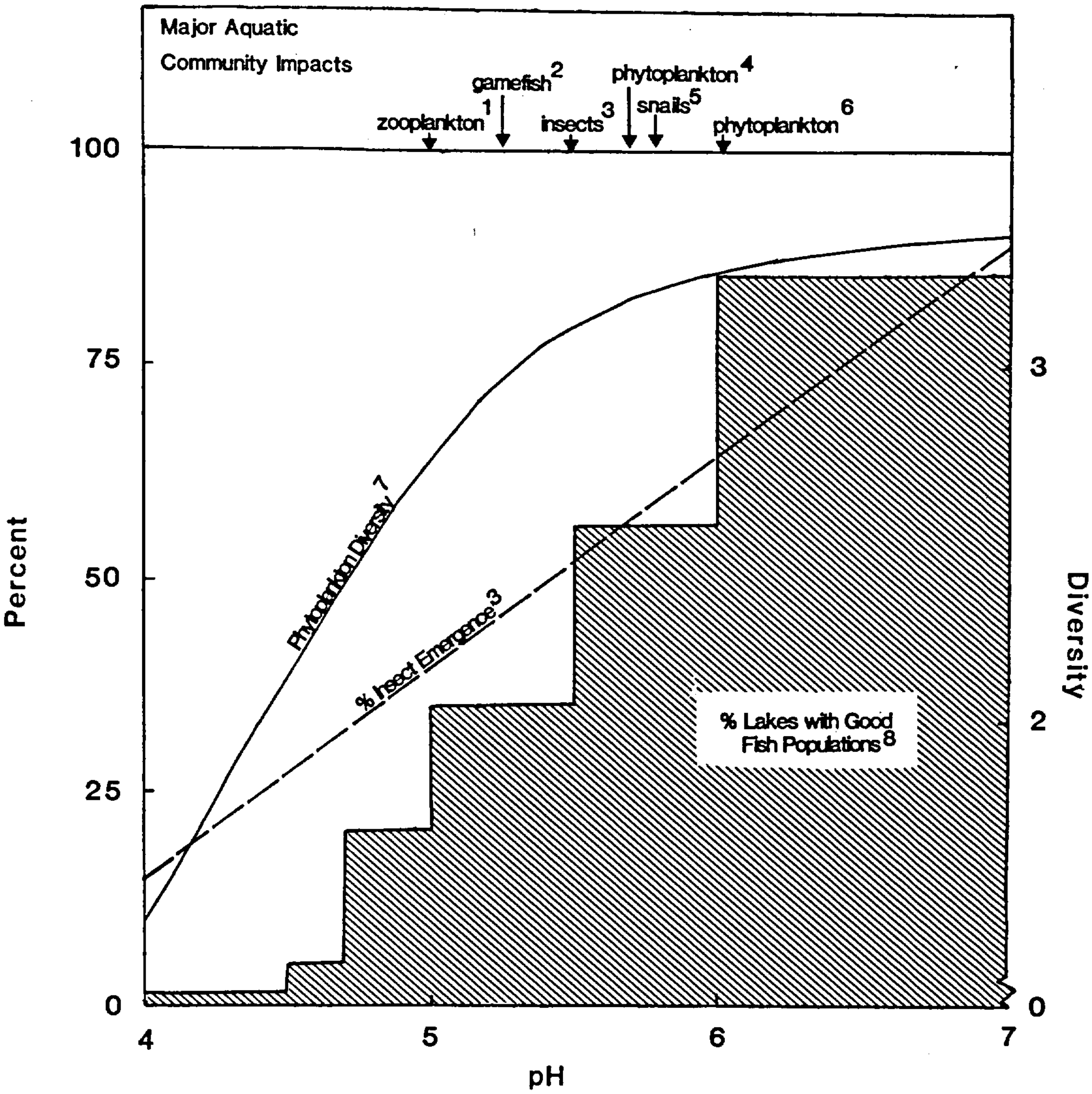


Figure 3-38. Relative number of taxa of the major taxonomic groups as a function of pH (Eilers and Berg 1982).



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

Figure 3-39. Generalized response of aquatic organisms to low pH (Eilers and Berg 1982).

interactions described below. It is important to note that the data were derived from literature surveys of the relationship between the distribution of groups of organisms versus lake and stream pH values. The quantitative description of these relationships may not reflect the response of individual taxa.

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 pH declines, it appears that acidification of surface waters brings about major quantitative and qualitative changes in structure and function of aquatic ecosystems. Disruption of the normal food chains may occur long before the lakes have been acidified in a chemical sense.

3.7.1 Effects on Algae

The free-floating (planktonic) and attached (benthic and epiphytic) 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 indicated that the species diversity of benthic and planktonic algal communities is less in acidified lakes. Yan and Stokes (1976) observed only nine species of phytoplankton in a single sample from Lumsden Lake (pH 4.4; Beamish and Harvey 1972), in the La Cloche Mountains in Ontario, but observed over 50 species in each of two nearby nonacidic lakes, having pH over 6.0. Diversity indices for phytoplankton populations in the La Cloche Mountain lakes are much less in lakes with pH values below 5.6 (Kwiatkowski and Roff 1976). In Scandinavian lakes numbers of phytoplankton species are also much less in lakes with pH values below 5.5 (Almer et al. 1978; Leivestad et al. 1976).

Some long-term functional adaptations to certain 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 brownwater acidic lakes because metals may be complexed 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 often not reduced by acidification. However, if phosphorus (the nutrient that normally limits phytoplankton productivity in soft-water lakes) is immobilized to some degree in acidic lakes because of complexation with aluminum and humic material (Almer et al. 1978), this would result in reduced primary productivity. To date, data from lakes in Scandinavia and eastern Canada indicate no significant correlations between pH and phytoplankton biomass or productivity (Harvey et al. 1981).

Phytoplankton communities of nonacidic 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 dinoflagellates, formed 85% 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% of the phytoplankton biomass in 4 lakes having pH 4.2-4.8, but only 2-30% of the biomass in 10 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. For example, in five lakes in Ontario and New Hampshire with pH 5.5-6.2, obnoxious odours developed during the summers of 1978, 1979, and 1980 (Nicholls et al. 1981). 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 indicate that dominance of this species to an extent causing the serious odour production, is restricted to acidic lakes.

Acidified lakes and streams are often characterized by increased growth of benthic filamentous algae. In Sweden, Ontario and Quebec, unusually dense and extensive masses of filamentous algae (mainly Mougeotia, Zygogonium and Zygnema sp.) proliferate in the littoral zones of many lakes with pH values of 4.5-5.5 (Blomme 1982; Grahn et al. 1974; Hendrey et al. 1976; Hultberg and Grahn 1975; Schindler 1980; Stokes 1981). These filamentous algal growths are associated either with macrophytes or other substrates or exist as floating "clouds" near the lake bottom. The accumulations of algae may reduce light availability to macrophytes, change microclimates for benthic macroinvertebrates and restrict fish feeding and spawning. Some depreciation of shoreline recreational values and activities, especially swimming, may result from this growth of algae.

3.7.2 Effects on Aquatic Macrophytes

Information on the effects of acidification on macrophyte communities of soft-water lakes is still incomplete. Scandinavian investigators have suggested that when lake water pH declines, typical macrophyte dominants are replaced by very dense beds of Sphagnum (Grahn et al. 1974; Hendrey et al. 1976; Hultberg and Grahn 1975). 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 (Raven 1970; Steemann-Nielsen 1944, 1946). 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.

Sphagnum moss coverage of littoral zones creates a unique habitat that 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. Through the release of hydrogen ions and polyuronic acids, *Sphagnum* 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. Zooplankton are an important food for many species of fish, particularly for younger individuals. Thus, they 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 1980). As a result, food availability to higher trophic levels may be decreased.

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. 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 of lakes, increases the concentration of potential toxicants such as Cd^{2+} (Almer et al. 1978) which is toxic to zooplankton at less than 1 μg/L (Marshall and Mellinger 1980), 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 increased acidity, may be quite complex.

The most important components of zooplankton communities are usually the rotifers and crustaceans. Of these, the crustaceans usually form 90% of the biomass (Pederson et al. 1976), while rotifers, because they have shorter generation times, may be responsible for 50% of the zooplankton productivity (Makarawicz and Likens 1979). Available studies on the effects of acidification on rotifer populations are contradictory; both smaller (Roff and Kwiatkowski 1977) and larger (Malley et al. 1982; Yan and Miller 1981) standing stocks have been observed in acidic lakes. Studies from very acidic lakes (Smith and Frey 1971) and the Smoking Hills Lakes of the Northwest Territories (Havas 1980) indicate, however, that some species of rotifers can survive when all crustacean zooplankton have been eliminated or could not survive at the low pH conditions.

The diversity of zooplankton communities has been reported in several studies to be greatly reduced by acidification (Raddum et al. 1980; Sprules 1975). Whereas nonacidic lakes typically contain approximately ten species of planktonic crustacea in mid-summer collections, Sprules (1975) observed that the number of species and species diversity of acidic lakes in the La Cloche Mountains in Ontario was drastically reduced. In several cases only a single species, *Diaptomus minutus*, remained.

The diversity of littoral cladocerans has also declined with acidification (Brakke et al. 1982). The decrease in number of species and diversity is apparently related to low pH and not to changes in aquatic macrophytes (Kenlan et al. 1982). Sediment core studies in New England and in Norway suggest that changes in littoral cladoceran assemblages occurred simultaneously with calculated dates of pH declines based on diatom analyses (Brakke et al. 1982; Davis et al. 1982).

Some predacious zooplankton, for example cyclopoid copepods (Raddum et al. 1980) and *Epischura lacustris* (Malley et al. 1982), 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. 1980a) 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. 1980a).

3.7.4 Effects on Aquatic Macroinvertebrates

Numerous aquatic macroinvertebrates are known to be affected by low pH conditions. In some cases an entire phylum appears to be affected, while in other situations susceptibility is species-specific. Evidence indicates that molluscs, in general, are highly susceptible to reduced pH (J. Økland 1980; Raddum 1980; Wiederholm and Eriksson 1977), often being restricted to habitats with pH greater than 5.8-6.0. Similarly, all species of oligochaetes studied thus far 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 Arachnids, Crustaceans and Insects. Arachnids were only briefly mentioned by Grahn and his co-workers (1974); acarinids were absent in waters with pH values below 4.6. No macro-crustaceans were found below pH 4.6 (Grahn et al. 1974). Gammarus lacustris was absent from waters with pH below 6.0 (J. Økland 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 numbers of species of Ephemeroptera and Plecoptera appear to be positively correlated with pH, larvae of Chironimidae (Diptera), Hemiptera and Megaloptera are often abundant in acid lakes (Almer et al. 1978). Hutchinson et al. (1978) reported an example of extreme tolerance by larvae of red chironomids, Chironomus riparius, to 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, the pH of a natural system has rarely been altered experimentally, and the impacts on invertebrates noted. The documented effects of decreased pH include the disappearance of Mysis relicta in Lake 223, an experimentally acidified lake in the Experimental Lakes Area (Malley et al. 1982), 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 low pH snowmelt, or other events, such as low pH flushing, may be especially sensitive to acid deposition.

In considering the distribution of the above species in relation to waters of varying pH 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 Bacteria and Fungi

The decomposition rate of fixed carbon, both allochthonous and autochthonous organic matter, is largely 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 at low pH values. 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% of control levels, and a shift from bacterial to fungal dominance was observed. Traaen (1980) further observed that rates of weight loss of decomposing 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 (Guthrie et al. 1978; Thompson and Wilson 1975; Tuttle et al. 1968, 1969). Caution must be exercised, however, in extrapolating results from such studies to situations where the source of protons is atmospheric because the pH is often much lower in acid mine drainage lakes, and the concentration of dissolved substances, including metals, much higher.

Rao et al. (1982) studied the effects of acidic precipitation on bacterial populations of the Turkey Lakes, Ontario and Kejimkujik, Nova Scotia. They observed reduced numbers of nitrifying bacteria and sulphur cycle bacteria in low pH lakes and streams. Bacterial activity as measured by oxygen consumption rate and biodegradation or organic material was 50% less and 30-40% less respectively in acid-stressed environments compared to nonacid-stressed areas.

Microbial transformations of sulphur and nitrogen species may influence lake acidity and alkalinity (Brewer and Goldman 1976). Schindler (1980) showed that increases in SO_4^{2-} concentrations stimulated sulphate-reducing bacteria in lakes that develop anoxic hypolimnia. The reduction of SO_4^{2-} yields OH^- thereby increasing akalinity. Stimulation of SO_4^{2-} reduction has been used with success to reclaim acid mine drainage waters. Sulphate-reducing bacteria require anoxic conditions, and are stimulated by large quantities of organic matter (i.e., they prefer conditions typical of eutrophic lakes). However, acidified lakes are not eutrophic and many have oxygenated hypolimnia.

3.7.6 Effects on Amphibians

Many species of frogs, toads, and salamanders breed in temporary pools. These pools are formed by a mixture of snowmelt water and spring rains and may have low pH values during the spring. Because of the vulnerability of this habitat to pH depressions, amphibian populations are expected to be one of the earliest forms of wildlife to be affected by the acidification of fresh waters. Temporary pools used as breeding sites by Jefferson's (*Ambystoma jeffersonianum*) and yellow-spotted salamanders (*A. maculatum*) in New York were found to have pH values 1.5 units lower than nearby permanent ponds (Pough and Wilson 1977). The amphibian species of eastern Canada considered most susceptible to the effects of acid deposition because of their breeding habitat are listed in Table 3-19.

TABLE 3-19. SUSCEPTIBILITY OF BREEDING HABITAT TO pH DEPRESSION FOR THOSE AMPHIBIANS IN NORTHEASTERN NORTH AMERICA WHOSE RANGE OVERLAPS AREAS RECEIVING ACIDIC DEPOSITION (modified from Clark and Fischer 1981)

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

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. The natterjack toad (*Bufo calamita*) was not found in ponds 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 in ponds 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).

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 (1981) 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 1981). Bullfrog (*Rana catesbeiana*) and wood frog (*Rana sylvatica*) densities were also reduced in acidic streams and ponds (Clark and Euler 1981). Strijbosch (1979) reported a negative correlation between pH and percentages of dead and moulded egg masses of frogs and toads in the Netherlands.

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 and found that the embryos were more sensitive than adults. Frogs may undergo iono-regulatory failure due to acidic conditions (Fromm 1981) similar to that reported for fish (Leivestad and Muniz 1976; McWilliams and Potts 1978; Muniz and Leivestad 1980; Packer and Dunson 1970). 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% mortality. Beebee and Griffin (1977) noted abnormalities in natterjack toad spawn exposed to low pH, and Noble (1979) observed delayed development and embryonic mortality in the leopard frog (*Rana pipiens*) at pH less than 4.75. The leopard frog may be more sensitive to low pH than the latter study indicates. Schlichter (1981) found decreased sperm motililty at pH values less than 6.5 and the percentage of eggs which formed healthy embryos decreased below pH values of 6.3. A similar study using the common frog reported that sperm motility was reduced to 50% of maximum at pH values of 6.4-6.7 and to 0% at pH values less than 6.0 (Gellhorn 1927, cited in Schlichter 1981).

Cook (1978) found no significant correlation between pond pH and percent embryonic mortality in either the yellow-spotted salamander or Jefferson's salamander studied in six ponds with mean pH values of 5.3-5.6. In contrast Pough (1976) found heavy embryonic mortalities and deformities for both species in waters with pH values 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). While Hagstrom (1977) reported the elimination of the common toad at pH values of 4.0-4.5, 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 cause detrimental effects upon amphibian development. For example, 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.

Frogs, toads, and salamanders are important components of both aquatic and terrestrial ecosystems. 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). Many birds and mammals depend heavily on these species for food (Burton and Likens 1975a; Cecil and Just 1979; DeBenedictis 1974).

3.7.7 Effects of Low pH on Fish

The purpose of this section is to review briefly how fish respond to low pH conditions. This will be done on the basis of documented changes in fish population related to acidification, other field evidence and laboratory substantiation. For more comprehensive treatments of this subject, the reader is referred to reviews by Fromm (1980), Haines (1981c) and Spry et al. (1981). In addition, there is extensive literature available on laboratory studies (see Doudoroff and Katz 1950; EIFAC 1969), that were 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 with pH values of 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 values ($\sim$5). This is consistent with field observations that fish communities disappear from more dilute waters at higher pH levels than they do from lakes with higher concentrations of salts (Leivestad and Muniz 1976). 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 (Baker and Schofield 1980; Swartz et al. 1978).

Salts are lost from plasma and body tissue of fishes exposed to low pH conditions. Leivestad et al. (1976) found that Na^+ and Cl^- in blood plasma and K^+ in muscle tissue declined in brown trout at low pH levels. Increases in the concentration of Ca^{2+} enabled the trout to regulate better ionic balances (Leivestad et al. 1980). Recent studies by Saunders et al. (1982, in press) have shed light on possible mechanisms affecting survival, growth, and the smolting process in Atlantic salmon. Under low pH laboratory conditions it was found that parr-smolt transformation was impaired, and ATPase activity was lowered, resulting in a decreased salinity tolerance of smolts. Salmon raised under low pH regimes (i.e., pH 4.2-4.7) were found to have significantly lower plasma Na^+ and Cl^- levels, which was indicative of an impaired osmoregulatory ability in fresh water.

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 of fishes (Table 3-20). As well as interspecific differences in sensitivity, variability in sensitivity has also been observed among different strains of the same species (Robinson et al. 1976; Swartz et al. 1978). However, it is likely that the acidification of lakes and rivers in North America is proceeding too rapidly to enable genetic selection for acidic tolerant strains to occur naturally (Schofield 1976b).

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

Hulsman and Powles (1981) conducted experiments on walleye eggs. The eggs were incubated <u>in situ</u> in a series of small streams in the La Cloche area of Ontario. The various sites ranged in pH from 4.60 to 6.72. Hatching success was significantly reduced in the clear dilute streams with pH values less than 5.40.

TABLE 3-20. APPROXIMATE pH AT WHICH FISH IN THE LACLOCHE MOUNTAIN LAKES STOPPED REPRODUCTION (Beamish 1976)

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

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 lakes, Ryan and Harvey (1980) reported evidence of recruitment failure in yellow perch (Perca flavescens) populations in the two lakes of lowest pH values: 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 3-40. Ryan and Harvey (1981) 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 individuals in populations of fish in some acid-stressed lakes has also been reported (Harvey 1980; Ryan and Harvey 1980). This effect is illustrated by the changes in age composition of white suckers in George Lake, Ontario from 1967 to 1979 (Figure 3-41). 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.

In the field, there have been several reports of fish kills apparently related to the low pH 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, although Al was not measured in either case.

In North America, Harvey (1979) reported mortalities of several species, primarily pumpkinseeds (Lepomis gibbosus) in Plastic Lake, Ontario, during spring snowmelt runoff and pH depression. 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. Three nonmetal cages of 35 fish were situated at each location. No mortality occurred at any of the cage sites in the control lake (pH 6.09-7.34, alkalinity 132-390 μeq/L). In Plastic Lake, however, mortality ranged from 12% at the lake outlet site (pH 5.0-5.85) to 100% at the inlet site (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.

3.7.8 Effects of Aluminum and Other Metals on Fish

Concentrations of metals can be elevated in acid-stressed lakes (Beamish 1974a; Haines 1981c; Scheider et al. 1979b) because of increased atmospheric deposition, increased mobilization from the sediments and/or mobilization from the watershed (see Section 3.2.4).

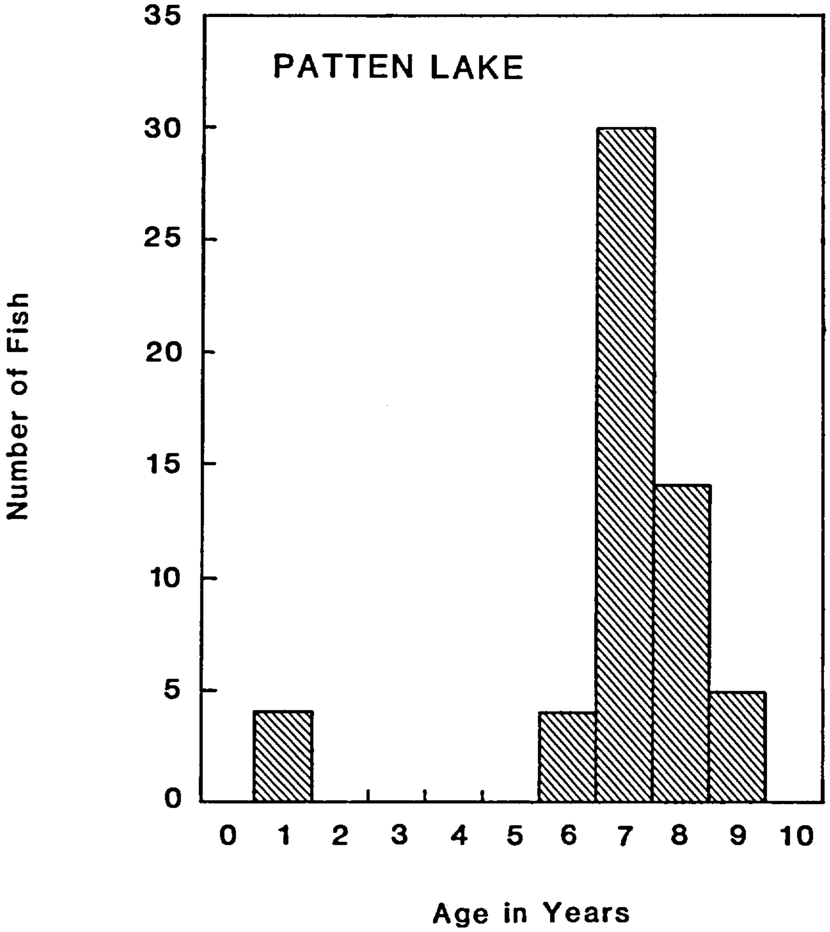


Figure 3-40. Age composition of yellow perch (Perca flavescens) captured in Patten Lake, Ontario, pH 4.1 (Ryan and Harvey 1980).

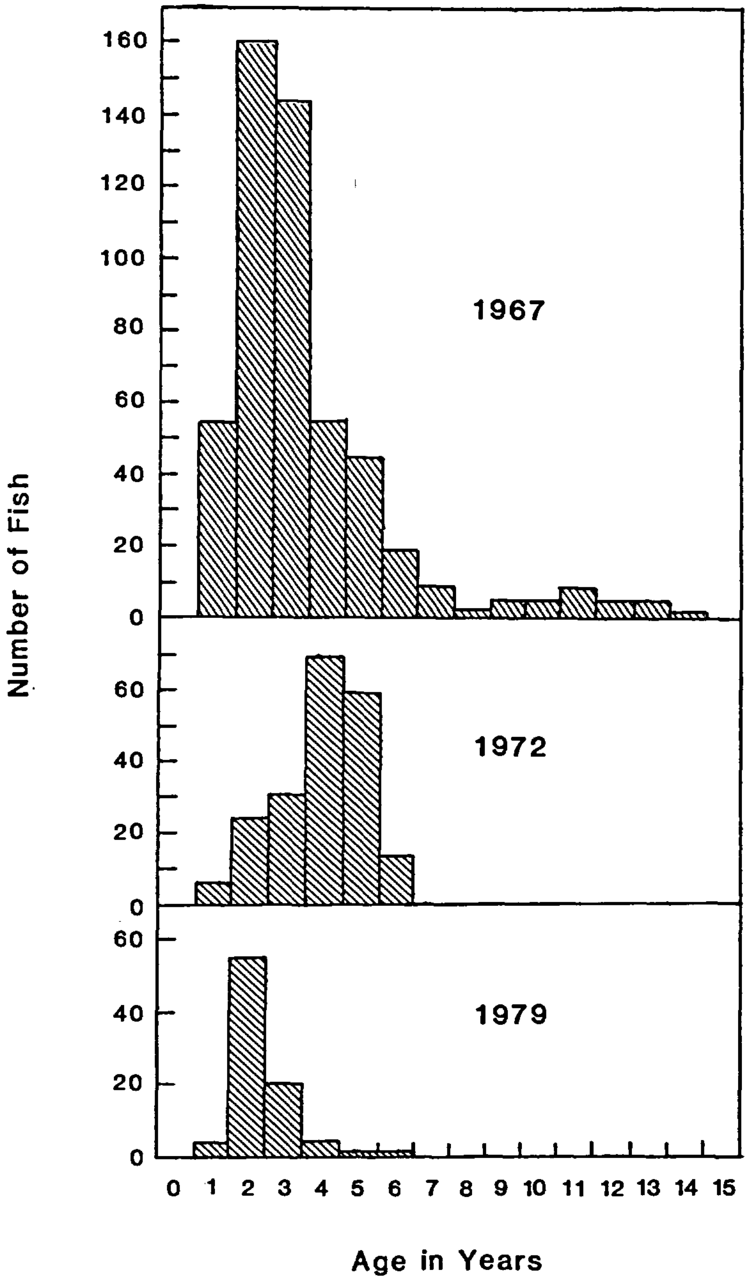


Figure 3-41. Changes in the age composition of the white sucker (Catostomus commersoni) in George Lake, Ontario (Harvey et al. 1981).

One of the most important consequences for fishes of watershed acidification is the mobilization of aluminum from the watershed to the aquatic environment (Cronan and Schofield 1979). Elevated levels of aluminum in waters have been shown to have serious effects on fish within the pH range normally considered not harmful to aquatic biota (Baker and Schofield 1980).

Spry et al. (1981) give a simplified description of the complex chemistry of aqueous aluminum. The solubility of aluminum is minimal at pH 5.6-6.0, increasing as pH increases or decreases outside this range (Figure 3-42). 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, $Al(OH)_3(s)$, which is minimally soluble at pH values of 5.6-6.0 (Driscoll 1980b). Fewer hydroxyl ligands at lower pH allow the aluminum to become cationic, eventually becoming Al^{3+} at pH values less than 4.5 to 5.0. Cationic aluminum is able to form complexes with a number of ligands, including soluble organics and fluoride, decreasing its toxicity (Figure 3-42) (Baker and Schofield 1980; Driscoll et al. 1980).

Laboratory studies have shown significant reductions in fish survival at inorganic aluminum concentrations of 100 and 200 μg/L and greater for white suckers (Catostomus commersoni) and brook trout (Salvelinus fontinalis), respectively (Baker and Schofield 1982; Schofield and Trojnar 1980). Inorganic aluminum levels as high as 600 μg/L have been measured in acidic Adirondack waters (Driscoll 1980b). Baker and Schofield (1980) note that fry exposed soon after initiation of feeding and yolk sac absorption were more sensitive to elevated aluminum concentrations than were eggs and sac fry prior to yolk absorption. 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 3-43). The greater susceptibility of fry at these extreme pH values may reflect 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 (Baker 1981; Leivestad and Muniz 1981). At higher pH values (5.5), precipitation of $Al(OH)_3(s)$ damages the gills and leads to clogging by mucous (Baker 1981; Schofield and Trojnar 1980). 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.

Schofield and Trojnar (1980) suggested that levels of aluminum, rather than pH alone, may be the primary factor limiting survival of brook trout stocked in Adirondack lakes. Muniz and Leivestad (1980) and Schofield and Trojnar (1980) suggested that mass mortalities of fish, observed during episodes of acidification in the spring, were

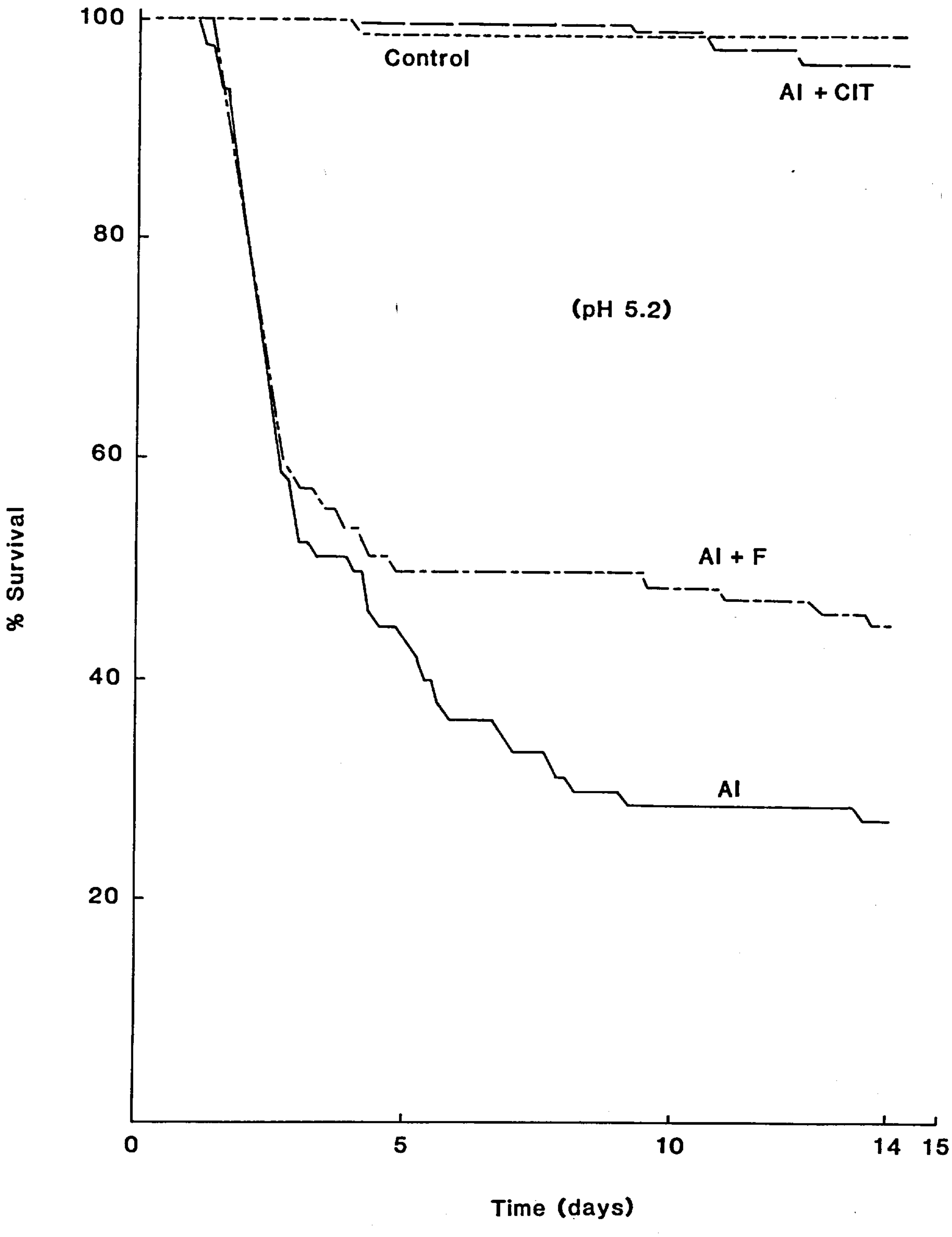


Figure 3-42. Percent survival of brook trout fry plotted as a function of time in treatment waters at pH level 5.2 with no aluminum (control) or with 0.5 mg Al added per liter with no additional complexing agents (Al) or with 0.5 mg fluoride/litre (Al + F) or with 30 mg (Baker and Schofield 1980).

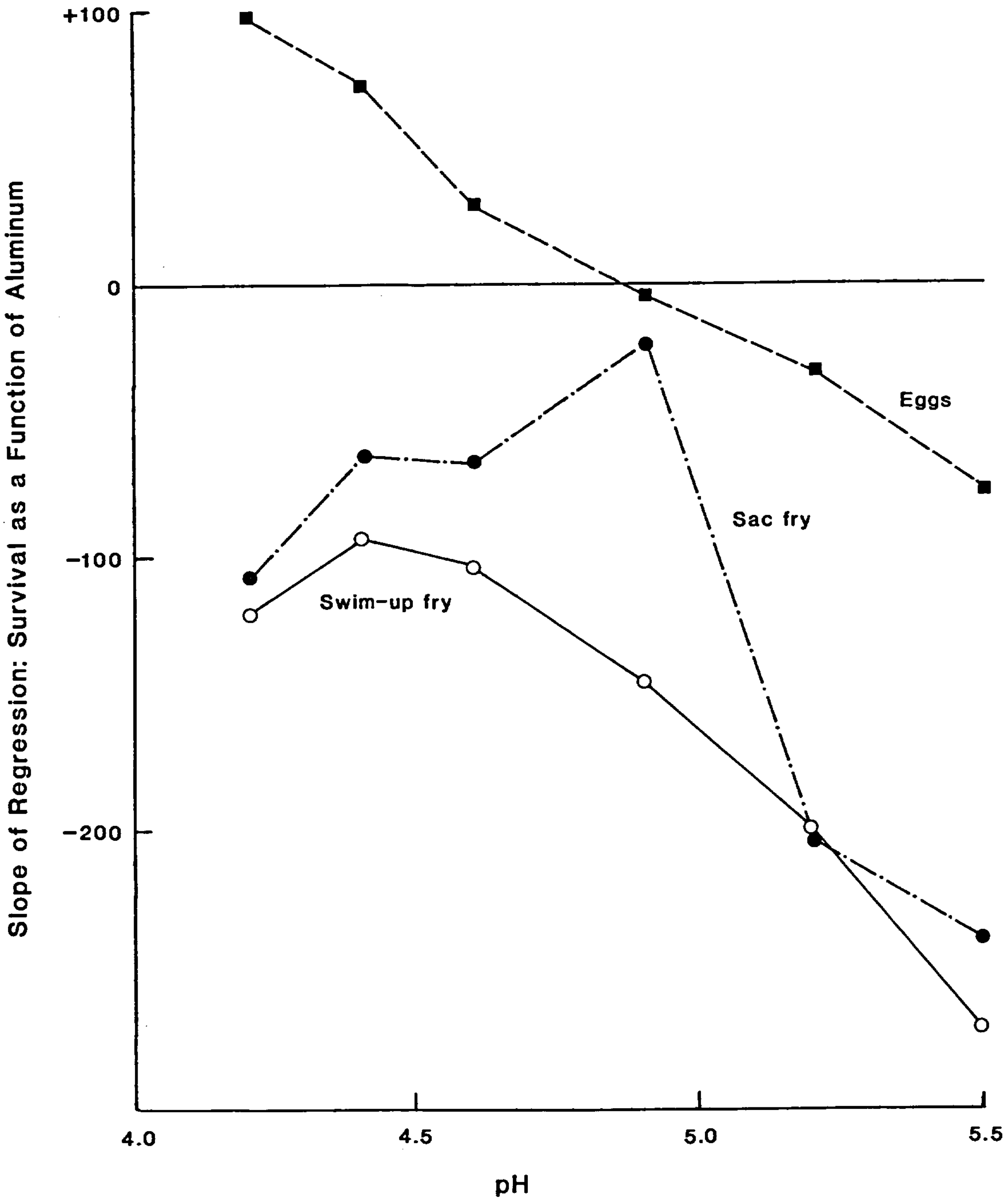


Figure 3-43. Slope of the regression line of brook trout survival (arcsin transformation) as a function of total aluminum concentration at each pH level, plotted as a function of pH level. A positive slope indicates presence of aluminum improved survival: a negative slope indicates detrimental effects of aluminum (Baker and Schofield 1980).

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 declines 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 (Muniz and Leivestad 1980).

Aluminum levels in streams in the Adirondack Region of New York State (Driscoll 1980b), 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) (Ontario Ministry of Environment data from ongoing studies), fall within levels demonstrated to be lethal to fish in laboratory conditions. However, as the laboratory studies have demonstrated, 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.

Other metals besides aluminum also occur at elevated levels in acidic waters (Section 3.2.4). Harvey et al. (1982) reported increased lakewater concentrations of manganese were associated with decreasing pH for 50 lakes in the Wawa area of Ontario. They found Mn was elevated when pH values were less than 5.0 and reached very high concentrations in strongly acidified lakes. In the La Cloche Mountain lakes, Mn was correlated inversely with pH and Mn declined in acidified lakes in the Sudbury area following neutralization (Harvey et al. 1982).

Manganese has been considered a relatively non-toxic element, and thus toxicological data are very limited. Lewis (1976) determined that manganese concentrations up to 770 μg/L had no effect on survival of rainbow trout in soft waters with pH levels 6.9 to 7.6. Concentrations of manganese in acidic waters have been measured up to 130 to 350 μg/L (Dickson 1975; Schofield 1976c). Available data suggest that manganese levels, by themselves, have no apparent adverse effects on fish, although Harvey et al. (1982) found elevated Mn concentrations in the vertebrae of white sucker (Catostomus commersoni) from acid lakes.

Although laboratory bioassays examining effects of zinc on fish are numerous, none of these studies considered soft waters with pH levels below 6. Chemical models predict that as the pH level declines, an increasing proportion of the total zinc concentration should exist as the free aquo ion (Stumm and Morgan 1970). For many metals, the free aquo ion (i.e., Me^{2+}) is considered the most toxic form (Spry et al. 1981). This has not been confirmed to be true for zinc but care should be taken in extrapolating bioassay data and maximum acceptable toxicant concentrations (MATC) determined for pH levels above 6 to conditions in acidic waters. For the most part, however, lethal concentrations of zinc in bioassays are 10 times the zinc concentrations found in acidic lakes (Spry et al. 1981). Sinley et al. (1974) estimated that the MATC for rainbow trout (Salmo gairdneri) exposed to zinc in soft, circumneutral water was between 140 and 260 μg/L. Benoit and Holcombe (1978), in life cycle experiments with fathead minnows (Pimephales promelas) in soft water, determined that the threshold level for significant adverse effects on the most sensitive life history state was between 78 and 145 μg/L. Zinc concentrations in acidic waters range up to 23 to 56 μg/L (Henriksen and Wright 1978; Norton et al. 1981a; Schofield 1978; Spry et al. 1981).

In some regions, concentrations of cadmium, copper, lead and nickel (see Section 3.2.4) are also elevated in acidic lakes. Relationships between pH levels and cadmium, copper, lead, and nickel concentrations, however, vary markedly between regions. High concentrations of these metals probably result primarily from increased atmospheric loading and deposition, and occur principally in surface waters in close proximity to pollutant sources (e.g., Sudbury, Ontario, Nriagu et al. 1982). Concentrations of some of these metals in lakes in the vicinity of Sudbury have been demonstrated to have definite adverse impacts on fish and other aquatic biota (Conroy et al. 1976; Yan and Strus 1980). Excluding lakes within 50 km of Sudbury, acidic Ontario surface waters have concentrations of metals ranging up to about 0.6 μg/L Cd, 9 μg/L Cu, 6 μg/L Pb and 48 μg/L Ni (Spry et al. 1981). Spry et al. (1981) reviewed bioassay data available and noted no significant adverse effects on fish survival and reproduction at concentrations up to 0.7-11.0, 9.5-77, 13-253, and 380 μg/L for cadmium, copper, lead, and nickel, respectively. In general, concentrations of metals in acidic waters are below these "safe" concentrations (unless there is a local source of metal emissions). However: (1) most of these bioassays were conducted in waters with pH levels above 6, and (2) the possibility for synergistic effects has not been evaluated.

In some regions, bioaccumulation of mercury in fish has been correlated with low pH levels in lakes. These elevated levels of mercury in fish may have adverse effects on consumers (e.g., man or fish-eating birds and mammals; Sections 3.7.12 and 5.2). However, no data have been reported to indicate that this bioaccumulation has any adverse effects on the fish themselves (Haines 1981c).

Survival of fish populations in acidic waters is determined primarily by levels of pH and inorganic aluminum (Baker 1982; Schofield and Trojnar 1980). Although concentrations of a number of metals are increased in acidic lakes and streams, definite effects on fish have been demonstrated only for aluminum (except for lakes immediately around Sudbury, Ontario). Other metals may play a lesser, but as yet undefined, role.

3.7.9 Accumulation of Metals in Fish

3.7.9.1 Mercury

There is substantial evidence of the effect of pH on mercury content in fish (Brouzes et al. 1977; Hakanson 1980; Landner and Larsson 1972). 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 more acidic waters retain the monomethyl-form of mercury in solution. It is, however, important to recognize that pH is not the only variable which determines the mercury burden 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).

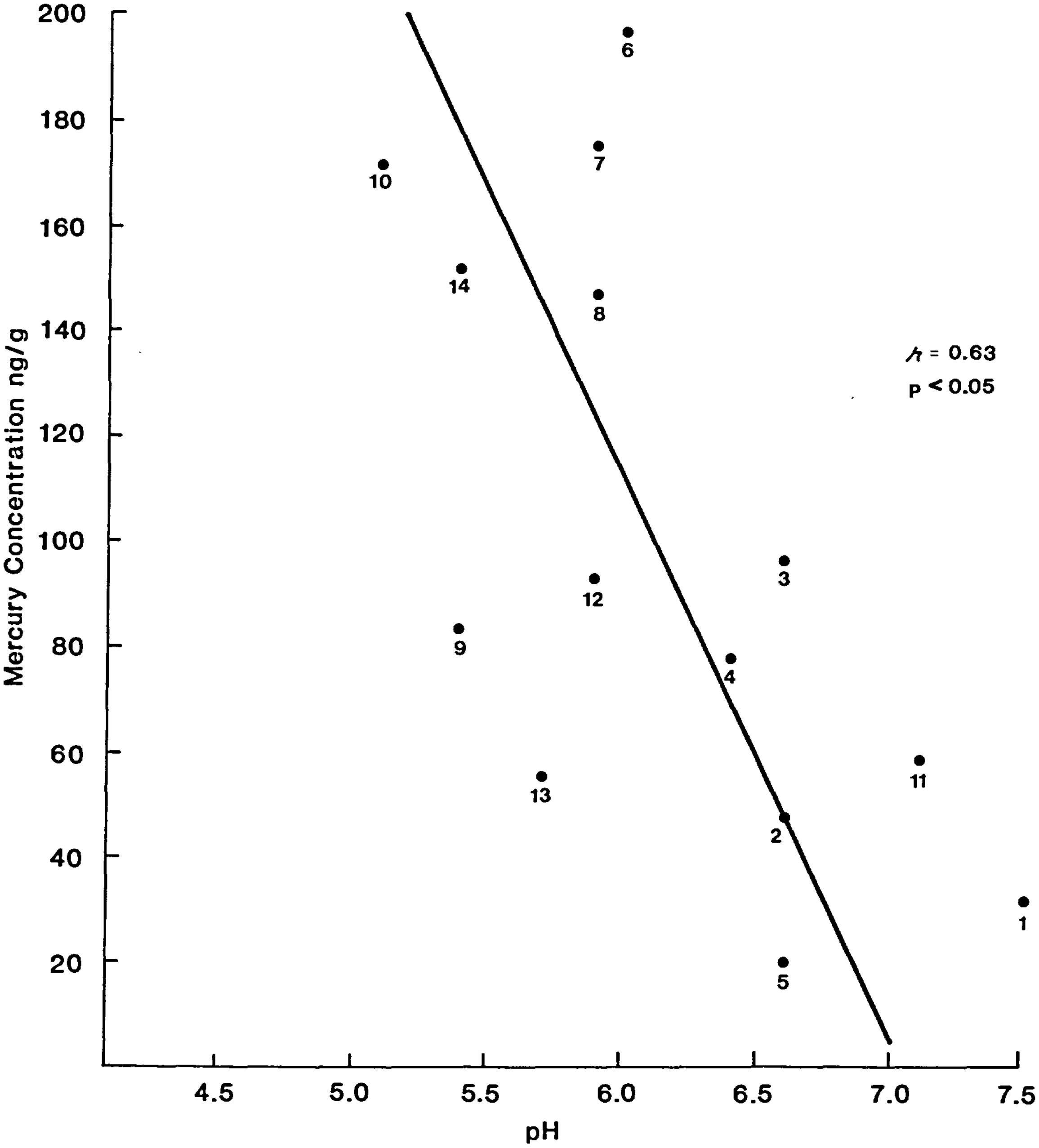
Few data exist to link mercury concentrations in fish to lake acidification. However, an increase in concentrations of mercury in fish from 1970 to 1978 is evident in some lakes in the Adirondack Mountains (Schofield pers. comm.). In Ontario, Suns et al. (1980) sampled young-of-the-year and yearling fish for contaminant studies. Their data (Figure 3-44) demonstrate increased mercury concentrations with decreasing pH in lakes in the Muskoka-Haliburton area. At any given pH level, however, the variation of mercury concentrations in fish is substantial. For lakes with similar pH, the mercury concentrations were higher 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 concentrations in fish. Data for 1981 are shown in Table 3-21 (Suns 1982). In 1980, the survey was extended to include adult smallmouth bass. Fish from six of the nine lakes studied had average mercury concentrations above the Canadian guideline (500 ng/g) for unlimited human consumption. In one lake mercury concentrations in fish exceeded the U.S. guidelines of 1000 ng/g (Suns 1982).

Because of increased mobility and leaching under acidic conditions and/or deposition, it is possible that metals other than mercury may be accumulating in fishes. At present, however, the data base is extremely limited (Haines 1981c).

In a survey of Ontario lakes by Suns (1982), yearling yellow perch were analyzed for body burdens of lead, cadmium, aluminum, and manganese. The data are shown in Table 3-21 and are summarized below.

3.7.9.2 Lead

A significant (p less than 0.01; $r = -0.74$) correlation was found to exist between lead residues in perch and lake pH. Mean lead residues as high as 428 ng/g were found from Moot Lake (pH 5.5) and 403 ng/g from Fawn Lake (pH 5.4).



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 3-44. Mercury concentrations in yearling yellow perch vs. epilimnetic pH for selected lakes in Ontario (Suns et al. 1980).

TABLE 3-21. METALS RESIDUES IN YEARLING YELLOW PERCH - 1981. LAKES ARE IN THE MUSKOKA-HALIBURTON AREA OF ONTARIO (Ontario Ministry of Environment Data)

Lake	pH	Hg (ng/g)	Pb (ng/g)	Cd (ng/g)	Al (ng/g)	Mn (ng/g)
1. Duck	7.5	37 ± 5	65 ± 37	33 ± 5	4.4 ± 2.1	4.8 ± 1.2
2. Cranberry	7.1	61 ± 9	74 ± 33	41 ± 7	9.4 ± 1.2	19.6 ± 4.2
3. Little Clear	6.6	99 ± 12	N.A.	N.A.	N.A.	N.A.
4. Harp	6.6	190 ± 15	N.A.	N.A.	N.A.	N.A.
5. Brandy	6.5	140 ± 9	148 ± 31	47 ± 32	7.5 ± 2.1	14.5 ± 2.0
6. Bigwind	6.5	125 ± 43	152 ± 50	35 ± 14	4.9 ± 1.7	5.4 ± 1.9
7. McKay	6.1	153 ± 8	130 ± 63	108 ± 5	6.2 ± 2.7	7.5 ± 0.8
8. Healy	5.9	147 ± 34	280 ± 122	65 ± 8	8.5 ± 1.1	7.2 ± 1.0
9. Leech	5.9	117 ± 10	119 ± 94	71 ± 15	3.6 ± 0.7	6.5 ± 1.1
10. Dickie	5.8	130 ± 43				
11. Chub	5.7	179 ± 24	363 ± 37	120 ± 23	6.7 ± 1.9	3.4 ± 0.7
12. Clear	5.7	30 ± 6	278 ± 79	73 ± 8	15.1 ± 7.1	22.5 ± 6.4
13. Heeney	5.6	176 ± 15	233 ± 27	219 ± 42	4.6 ± 2.5	6.6 ± 1.4
14. Crosson	5.5	200 ± 22	294 ± 113	144 ± 32	13.9 ± 13.4	4.0 ± 1.2
15. Moot	5.5	156 ± 10	520 ± 233	50 ± 14	9.9 ± 1.8	9.9 ± 4.2
16. Leonard	5.4	129 ± 26	230 ± 58	113 ± 20	5.5 ± 1.2	18.4 ± 3.7
17. Fawn	5.4	259 ± 24	403 ± 387	102 ± 27	9.5 ± 2.2	7.3 ± 1.3

Although there is evidence that lead concentrations in water as low as 8 ng/L can cause neurological disorders in fish (Davies et al. 1976; Hodson et al. 1978; Holcombe et al. 1976), no data are available to relate body-burden accumulations to any significant biological response.

3.7.9.3 Cadmium

A statistically significant ($p < 0.05$; $r = 0.60$) correlation exists between cadmium residue levels and lake pH (Table 3-21). Little reference material is available at this time to evaluate the environmental significance of these cadmium accumulations. However, a laboratory study using relatively hard water (pH 7.5; alkalinity 980 µeq/L) showed that 80 µg/L killed 50% of the test population of young-of-the-year largemouth bass in 82 days. The same study discovered that 8 µg/L induced "abnormal behaviour" in the young fish in 12-week exposure (Clearley and Coleman 1974). The young bass average body-burden accumulations of cadmium were 38 ng/g after a four month exposure to a concentration of 80 µg/L. Although it is difficult to apply these laboratory data to field conditions, it is apparent that cadmium residue accumulations in fish tissue from Ontario lakes, particularly in the more acidic lakes, were considerably higher than accumulations observed under laboratory conditions to cause biological effects.

3.7.9.4 Aluminum and Manganese

No correlations between lake acidity and mean residue accumulations were apparent in the 1981 collections. It is likely that differences in lake complexing capacities influence aluminum availability for uptake. Therefore factors other than pH and alkalinity will have to be considered to evaluate fully residue accumulations.

Moreau et al. (1982) compared the chemical content of opercula and scales of brook trout from lakes in Laurentian Park classified by Richard (1982) as more acidic (Group 1, described in Section 3.7.10) with the same calcified tissue from brook trout from three nonacidic lakes (Group 3, also described in Section 3.7.10). They reported that the content of manganese, zinc and strontium was significantly higher in the calcified tissue of brook trout from the acidic lakes.

3.7.10 Effects on Fisheries in Canada and the United States

3.7.10.1 Adirondack Region of New York

The Adirondack region is one of the largest sensitive lake districts in the eastern United States, and it is also receives the highest annual loading of wet sulphate. A recent inventory of Adirondack waters classified lakes by type of fishery supported (Pfeiffer and

Festa 1980). These authors suggest that acidic deposition has exerted the greatest negative impact on the brook trout fishery. Brook trout are frequently the only game fish species present in the many small headwater ponds located at high elevations in the Adirondacks and particularly susceptible to acidic deposition.

It is difficult to evaluate exactly how many fish populations have been lost from Adirondack waters as a result of acidification. The Adirondack region encompasses approximately 2877 individual lakes and ponds. Pfeiffer and Festa (1980) note that 180 Adirondack ponds that formerly sustained brook trout populations (either naturally or by stocking) no longer support such populations. It has not however been formally demonstrated that all (or most of) these populations extinctions occurred as a result of acidic deposition. For at least a few lakes (reviewed in Pfeiffer and Festa [1980]) historic records of fish population status, fish management procedures, and water chemistry do suggest that population declines were associated with a decrease in pH level and that alternative explanations for the loss of fish other than surface water acidification seem unlikely. Schofield (1976a) surveyed high elevation Adirondack lakes (total 214 lakes). For 40 of these lakes, historical data on fish and pH were available (Figure 3-32). In the 1930s, only 8% of these lakes had pH <5.0, 10% had no fish whereas in the 1970s, 48% had pH <5.0 and 52% had no fish. In some cases, entire fish communities consisting of brook trout, lake trout, white sucker, brown trout, and several syprinid species apparently have been eliminated over the 40-year period (Schofield 1976a, 1981, 1982).

The present-day distribution of fish in Adirondack lakes and streams in relation to pH provides additional circumstantial evidence of the impact of acidification on fish. For high elevation lakes, Schofield (1976b, 1981, 1982) noted that the occurrence of fish was reduced at pH levels below 5.0 (Table 3-22 and Figure 3-32). Brook trout occur less frequently in lakes with pH <5.0, white suckers at pH <5.1, creek chub at pH <5.0, lake chub at pH <4.5 to 5.0, and brown bullhead at pH <4.7 to 5.0 (Schofield 1976b). About 50% of high elevation lakes had pH levels below 5.0 in 1975 and 82% of these acidic lakes were devoid of fish (Schofield 1976b). High elevation lakes, however, constitute a particularly sensitive subset of Adirondack lakes. It cannot be inferred that 50% of all Adirondack lakes have pH <5.0, nor that all lakes currently without fish once had fish and have lost their fish populations as a result of acidification.

Indices of fish population status in Adirondack streams (sample of 42 streams) were also found to be positively correlated ($p < 0.05$) with pH measurements (Colquhoun et al. 1980).

In addition to these observations of fish population status in Adirondack waters as related to acidity, Schofield and Trojnar (1980) examined the effect of water quality on fish stocking success. Poor survival of brook trout fall fingerlings stocked into Adirondack

TABLE 3-22. DISTRIBUTION AND FREQUENCY OF OCCURRENCE OF FISH SPECIES COLLECTED DURING SURVEYS OF ADIRONDACKS LAKES > 610 METRES ELEVATION. NUMBERS IN BRACKETS REFER TO EXTINCT POPULATIONS (Schofield 1976b)

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	

lakes was significant, ($p < 0.05$) associated with low pH levels and elevated aluminum concentrations.

Schofield (1982) summarized available data relating water acidity and fish population status for the eastern United States. With the exception of studies in the Adirondack region, very few of these studies included comprehensive inventories of fish populations and no adverse effects of acidic deposition on fish have been definitely demonstrated. Discussions generally refer only to "potential impact".

3.7.10.2 Ontario

More data on inland fisheries resource effects resulting 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 smelters. Some of the lakes had no 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 fish capture records dating to the early 1960s, and from observations by local anglers and residents for some species prior to 1960:

1950s - 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 loss of fish from nearby Lumsden III, Lumsden II and O.S.A. lakes. 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 overfishing was not responsible. The loss of populations of lake trout, lake herring, white suckers and other species was attributed to decreasing pH. Historical data available for Lumsden Lake indicated that in one decade (1961-1971) the lake pH had decreased from approximately 6.8 to 4.4. Measurements of pH from 1961 or earlier were available for eleven other La Cloche Mountain Lakes, and corresponding 1971 measurements for these lakes indicated that pH had decreased one to two units in the decade.

Beamish (1974a) also examined fish populations in O.S.A. and Muriel Lakes. He found that few fish remained in O.S.A. Lake. While several 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 this period. 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 concomitant loss of fish populations. He also examined other possible explanations for the response of fishes in these lakes. He concluded that decreased pH appeared to be the principal agent stressing the fish populations, as well as controlling the concentrations of metals.

Examination of the age distribution of white suckers in George Lake in 1972 indicated no missing year classes and it was concluded that no major reproductive failures had occurred prior to 1972 (Beamish et al. 1975). The pH of George Lake was measured colorimetrically in 1960 as 6.5, ranged between 4.8 - 5.3 in 1972-73 and was 5.4 in 1979 (Harvey et al. 1981). In 1967, the white sucker population contained fish up to 14 years of age. By 1972, almost no fish were older than 6 years. Sampling in 1979 revealed that 90% of the population was composed of two- and three-year old fish (Figure 3-41).

Harvey (1980) also showed that the white sucker population of Crosson Lake (pH 5.1; Muskoka-Haliburton) had a truncated age distribution with few fish older than five years (Figure 3-45) compared with the age composition of white suckers in less acidic Red Chalk (pH 6.3) and Harp (pH 6.3) lakes. Such a comparison must be viewed with caution due to the natural variability of age structure between lakes. However a change to a similar age structure patten was observed, coincident with declining pH, in George Lake (Harvey et al. 1981).

Kelso et al. (1982) have recently reported on a survey of 75 headwater lakes varying in size from 1.6 to 120 ha in the Algoma area

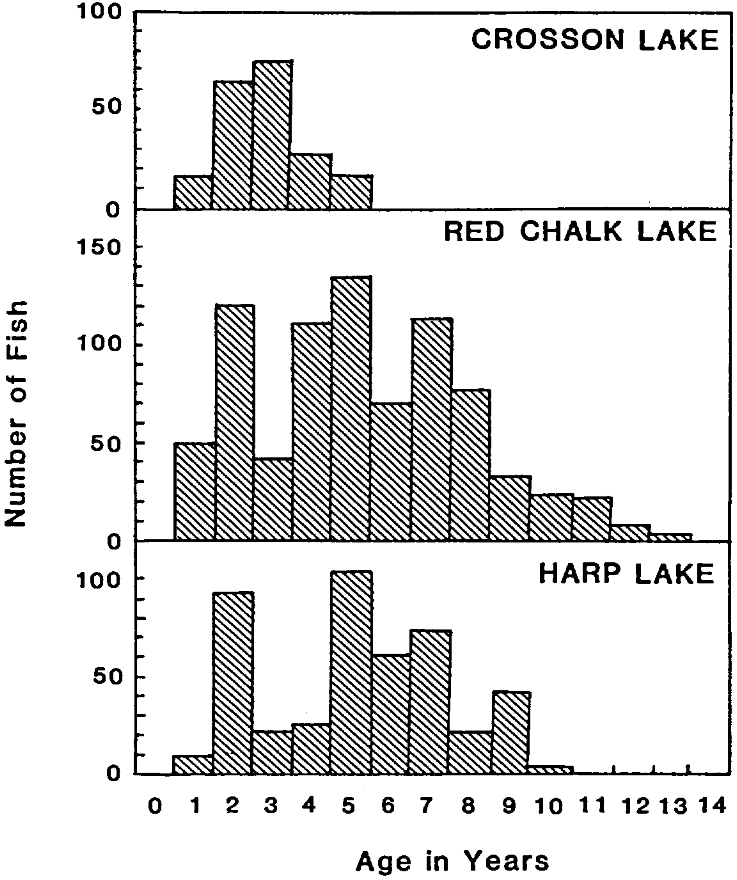


Figure 3-45. Age composition of the white sucker population of three lakes in the Muskoka-Haliburton Region of Ontario (Harvey 1980).

of central Ontario. Most were found to be poorly buffered with 65% of the lakes having alkalinities less than 200 μeq/L, 26% less than 40 μeq/L and 8% less than or equal to 0 μeq/L. In 55 of the lakes sulphate concentrations were found to exceed bicarbonate. None of the eight lakes with alkalinity values less than zero were found to contain any sport fish, including brook trout, the primary sport fish in this area of the Province.

Minns (1981) analyzed the Aquatic Habitat Inventory data base of the Ontario Ministry of Natural Resources (OMNR). This data base contains conductivity, pH, lake morphometry and fish species presence information for 6,393 Ontario lakes (as of September 1980, the time of analysis). The lakes contained in the data base were assumed to be representative of lakes in the area surveyed. Analysis of the data base for the presence of dystropic lakes indicated that very few were included and therefore their affect on the analysis would be minimal. Using relationships beween alkalinity, conductivity and pH, lakes were classified into categories in terms of their acidification status and the results were extrapolated to areas represented by the sample. Minns estimated that 1,200 lakes in the province are too acidic to sustain fish communities (lake pH less than 4.7) and approximately 3,500 other lakes are approaching that condition (lake pH 4.7-5.3). Most of these lakes are situated in watersheds in the region of Sudbury and are small (i.e., less than 10 hectares). Minns suggested that esocid and most percid communities are not currently at risk whereas the brook trout, lake trout and bass communities represent the most vulnerable resources.

3.7.10.3 Quebec

Fisheries investigations in the province of Quebec have concentrated in the Laurentian Park. To determine the relationship between the level of acidity and fish productivity in these lakes, the Quebec Ministry of the Environment sampled 158 lakes in the area. Water samples were collected through the ice, three weeks after the beginning of snowmelt in March 1981. Most of the lakes sampled were headwater lakes ranging in size from 10 to 25 hectares, with brook trout populations.

Richard (1982) classified the lakes into three groups using a multivariate analysis. The variables accounting for the greatest between group variance are described following:

Group	Number of Lakes	pH	Alkalinity (μg/L)	HCO_3^-/SO_4^{2-}	Total Aluminum (μg/L)
1	23	5.2	8.5	0.1	230.0
2	65	5.9	45.6	0.6	143.8
3	57	6.4	130.6	1.8	71.2

In each group of lakes the average annual yield, the angling effort and the mean weight of the fish caught (from detailed daily records prepared by all fishermen) were compared (Richard 1982). Only those lakes with nine years of continuous exploitation were included in the analysis (12 lakes in Group 1, 30 lakes in Group 2, 36 lakes in Group 3). During the last four years of study (1978-81) the mean yield from Group 1 lakes (the most acidic) was not statistically different from that of Groups 2 and 3. This conclusion was corroborated by examination of data from 34 additional lakes that had been fished continuously for from four to six years (Richard 1982).

Fisheries management practices within the Laurentian Park provide for closure to fishing when angling success was reduced as defined by a lower mean weight or lower number of fish caught, or when spawning habitat was disrupted. Forty-four lakes were not included in the analysis as they had been closed to fishing for one or more years preceding 1981. The 44 lakes which were closed to fishing included 43.5% of the most acidic lakes (Group 1) as compared with 36.9% of Group 2 lakes and 17.5% of the Group 3 lakes. This comparison suggests lower productivity in lakes in Groups 1 and 2, the more acidic and acid-stressed lakes, than in Group 3 lakes.

Although the frequency of fisheries management problems was higher in the more acidic and acid-stressed lakes, one cannot assume a direct cause-and-effect relationship with low pH, but only a general association between fish productivity, pH and the oligotrophic conditions of these waters.

3.7.10.4 Nova Scotia

There are 37 rivers flowing through Nova Scotia for which there are records to verify that they are (or once were) Atlantic salmon rivers (Farmer et al. 1980). For 27 of these rivers, almost complete angling catch records are available (annual reports from federal fishery officers) from 1936. Of these 27 rivers, 5 have undergone major salmon stock alterations since 1936 by dam construction/removal, and/or extensive hatchery stocking. Watt et al. (1983) examined the effect of low pH on angling by dividing the remaining 22 rivers into two groups, based on 1980 pH levels. For the 12 rivers presently at pH values greater than 5.0, only one shows a statistically significant decline in angling success since 1936, another shows a significant increase, and 10 show no significant trend. Of the 10 rivers with pH values less than 5.0, 9 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 in that river 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 3-46) reveal virtually identical angling catches in the two

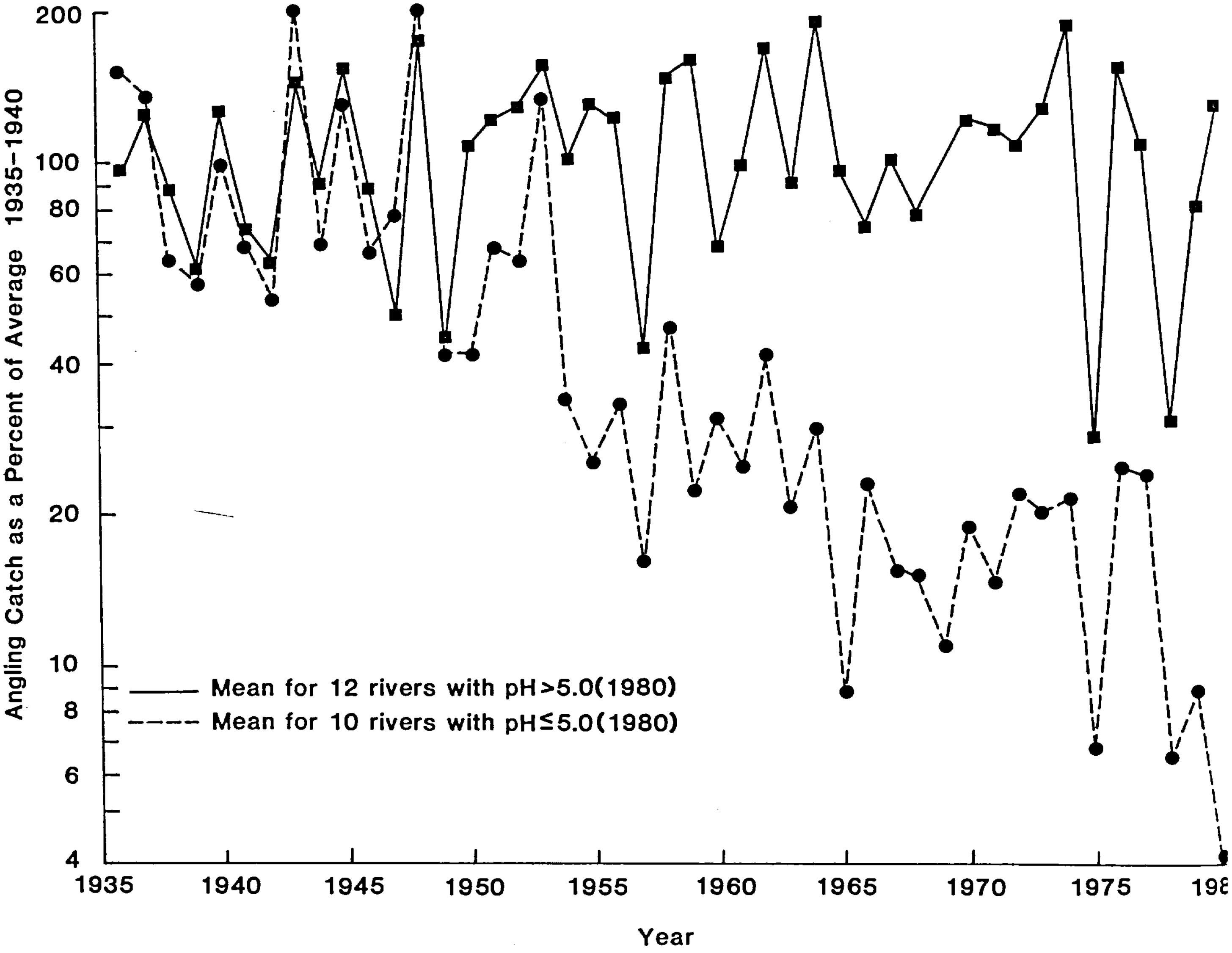


Figure 3-46. Atlantic salmon angling data normalized to facilitate the comparison between high and low pH rivers. Each river's catch was expressed as a percentage of the mean catch in 1936-40 so as to give all rivers equal weighting, and the two groups were then averaged by year (Watt et al. 1982).

groups until the early 1950s; after which the angling catches in rivers of pH less than 5.0 declined, while the catch in rivers of pH more than 5 continued to show no significant trend with time. Factors other than pH (e.g., stream flows and sea survivals) also affect the angling success. Variation from these other factors should, however, affect both groups similarly. The apparent reason for the difference in angling success between the two groups of rivers is a difference in pH since the 1950s.

Historical water chemistry data are available for some of these affected rivers from surveys performed in 1954 and 1955 (Thomas 1960). 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 values were below zero in the Tusket, Clyde, Roseway and Jordan rivers in 1979-80 (Watt et al. 1983), but was greater than zero during Thomas' study 25 years earlier. Although Thomas (1960) sampled some of these rivers only once, his data on river pH suggest that salmon reproduction in a few rivers may have been adversely affected due to acidity by the early 1950s, consistent with the catch data presented in Figure 3-47.

Within Nova Scotia, the pH of surface waters is well correlated with geology (Watt 1981). Seasonal variation in the pH of those rivers is about 0.5 units, with the annual minimum occurring in mid-winter, and a maximum in late summer. At present there are seven rivers with pH less than 4.7 that previously had salmon but now have no salmon or trout reproduction; 11 rivers are in the pH range 4.7-5.0, where some salmon mortality may be occurring; and seven rivers are in the pH range 5.1-5.4, which is considered borderline for Atlantic salmon (Figure 3-48). Those rivers represent 2% of the total Canadian habitat potential for Atlantic salmon, and 30% in Nova Scotia.

The numbers of salmon angled, recorded by Canadian federal fisheries officers since 1936 in six Nova Scotia rivers are illustrated in Figure 3-47. The Clyde River with a mean annual pH of 4.6 in 1980-81 has produced no angled salmon since 1969. Electroseining in the last several years also produced no salmon. The Ingram River with a mean annual pH of 5.0 (range 4.8-5.8) apparently still has a small reproducing population; it was at one time a good producer of Atlantic salmon. Federal fisheries officials consider this river to be in imminent danger of losing its remaining stock. This river has been identified by Canada Department of Fisheries and Oceans personnel as a candidate for liming in order to create a refuge for maintaining the gene pool of this stock.

One of the Nova Scotia rivers "threatened" by pH declines, 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

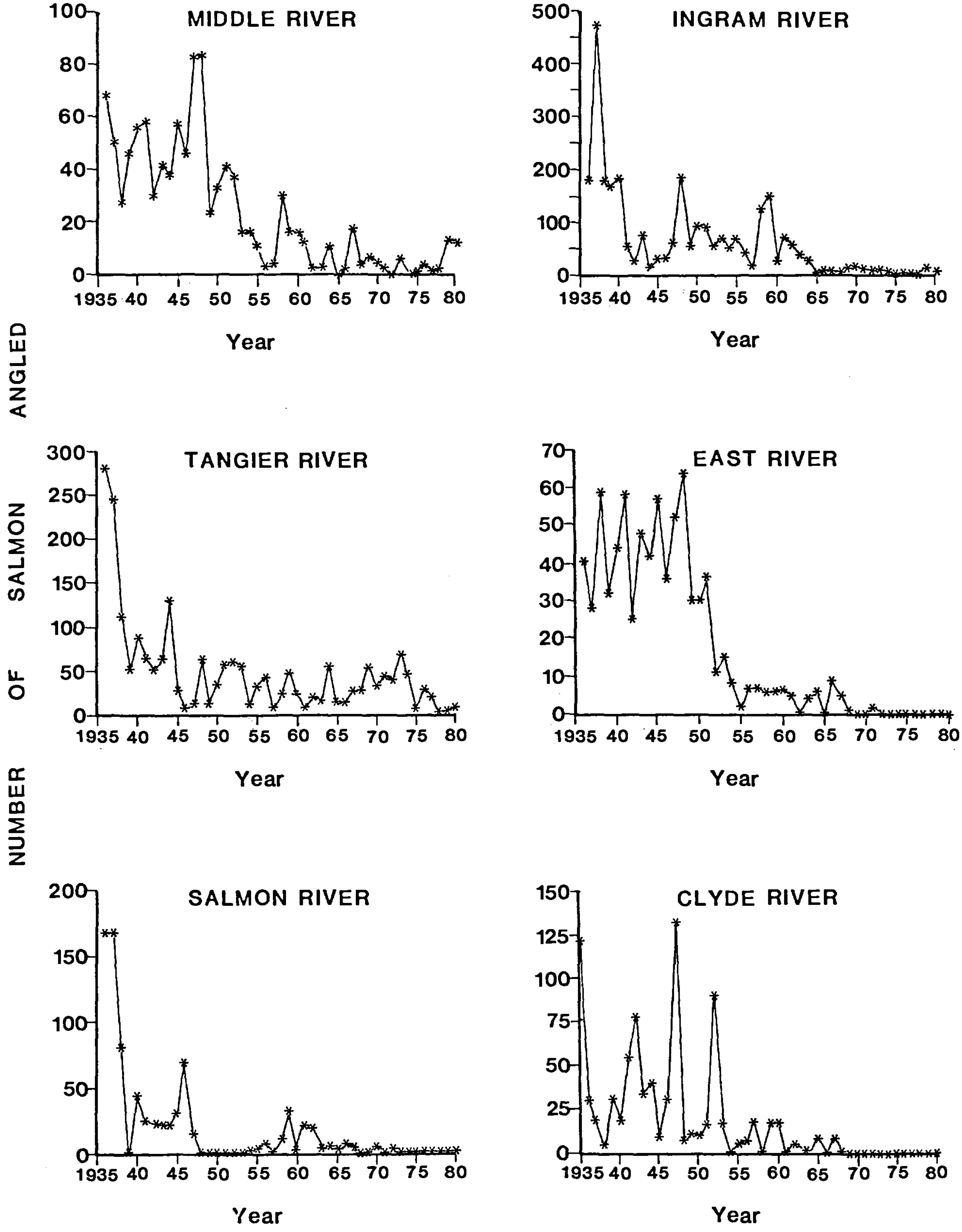


Figure 3-47. Angling records for six Nova Scotia Atlantic coast rivers with mean annual pHs (1980) <5.0 (Watt et al. 1983).

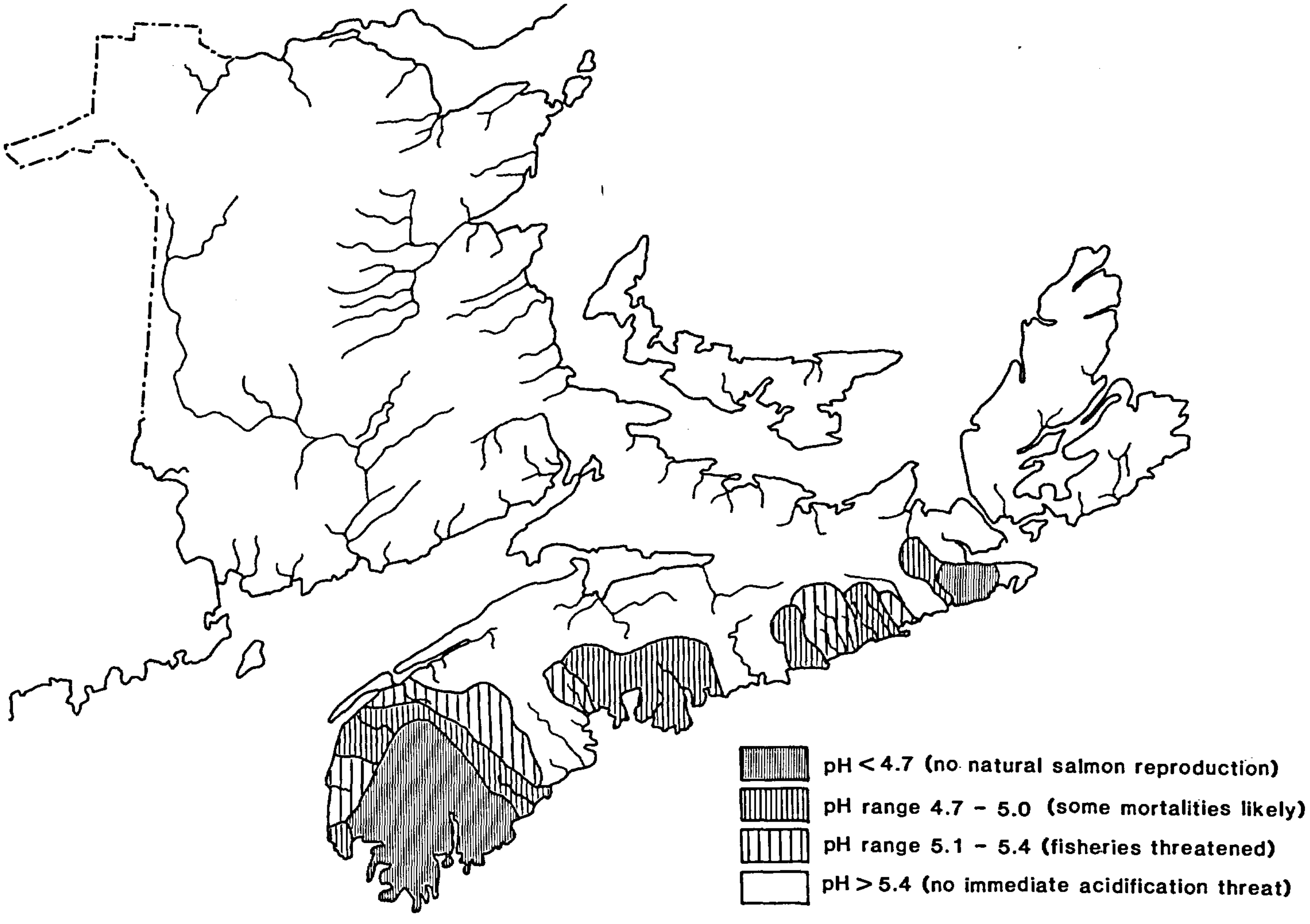


Figure 3-48. The Altantic salmon rivers of the Maritimes have been divided into 4 pH (estimated mean annual) categories based on significance to salmon reproduction. Present evidence indicates that salmon cannot reproduce at pHs below 4.7. Juvenile mortalities of 30% or more are expected in the pH range 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).

river in 1978-79 was less than 10 μeq/L, while mean pH was 5.2 (range of 4.9-5.4) (Farmer et al. 1980). 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 48 μeq/L $CaCO_3$, with a range from 20 to 88 (Thomas 1960). Mean sulphate values have been estimated to have increased from 76 μeq/L in 1954-55 to 158 μeq/L in 1978-79. During the period 1975-78, mortality of Atlantic salmon parr reared at the Mersey hatchery typically occurred during the third and fourth 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% to 3% (Farmer et al. 1980). In 1980, the water was again treated and produced the same increase in survival of parr.

Farmer et al. (1980) noted that, even though all rivers classified as presently unsuitable for salmon historically sustained Atlantic salmon populations, these rivers are all also naturally somewhat acidic and historically had relatively low fish production. Of the 20 readings of apparent water colour (rel. units) (an indicator of the presence of organic acids) presented for the 7 rivers classified "unsuitable" by Farmer et al. (1980), 16 were 100. For "threatened" rivers, only one of 21 readings was 100; the remaining readings averaged 69. For rivers classified neither "unsuitable" nor "threatened," and with pH readings above 5.5, the mean measure of apparent colour was 44. High degrees of colour are largely attributable to humates from peat deposits and bogs common in this area. Inputs from these materials probably contribute to the low pH levels in "unsuitable" and "threatened" rivers. Historical records of pH in these rivers do, however, indicate that acidity has increased in recent years. Watt et al. (1983) concluded "the Atlantic coast rivers of Nova Scotia have become more acidic over the past 27 years in response to increased acid loading in the precipitation." This increase in acidity has been clearly correlated with declines in populations of Atlantic salmon in the same rivers.

3.7.10.5 Scandinavia

Hendrey and Wright (1976) reported that "acid precipitation has devastated the salmonid 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 acidic deposition. Portions of Canada's Atlantic salmon fishery appear to have declined as a result of acidification as has been experienced in Norway and Sweden.

3.7.11 Response to Artificial Acidification

While we know that the end-product of acidification includes the disappearance of important fisheries, many of the early changes which occur in acidified ecosystems are relatively unstudied. Furthermore, it is not known whether declines in fish stocks are due singly or in combination to the toxic effects of hydrogen ion, to hydrogen ion and aluminum or other metals synergisms, to food-chain effects resulting from elimination of critical species of animals and plants or disruption of nutrient cycles.

A whole-lake acidification experiment was done in Lake 223 in the Experimental Lakes Area, Ontario, in order to examine some of these possibilities. The pH of the lake was progressively lowered from a natural value of 6.5 to 6.9 ($\bar{x} = 6.7$) to an average value of 5.1 by additions of sulphuric acid between 1976 and 1981. Detailed monitoring of chemical, physical and biological changes, as well as physiological and ecotoxicological studies, were done throughout this period. Earlier biological results were summarized by Schindler et al. (1980), Schindler (1980), Malley and Chang (1981), and Schindler and Turner (1982).

Biological changes in the lake as it was artificially acidified and the pH thresholds at which these changes occurred are summarized in Table 3-23. The first changes which could have adversely affected lake trout and white sucker populations occurred in 1978-79, when populations of two species which are the usual prey of trout, fathead minnow (*Pimephales promelas*) and oppossum shrimp (*Mysis relicta*), collapsed. Despite these changes, no effects were detected in trout populations. A succession of strong white sucker year-classes in 1978-80 and greatly increased abundance of pearl dace were adequate food alternatives for trout. Apparently, the pearl dace partially occupied the vacated fathead minnow niche, while the primary food source of white suckers, benthic dipterans, increased in abundance (Davies pers. comm.). In addition, the appearance of excessive growths of *Mougeotia* in the littoral beaches probably provided excellent nursery areas for sucker fry, but increased water transparency (Schindler 1980) perhaps made prey capture easier for trout.

Even though many changes have occurred in lower trophic levels, juvenile and adult white sucker and lake trout populations have shown little indication of stress, except for recruitment failures in the very recent years of acidification, at pH values of 5.35 and below. Up to 1981, populations of both species increased, and their growth rates have remained high. Relative condition (a quantitative measure of fish fatness) has decreased progressively for trout from 1977 to 1980, and for white suckers from 1978 to 1980, but this would be expected due to the increased abundance of both species over the same time period.

The relatively swift collapse of the fathead minnow population is due to two factors. Firstly, a recruitment (year-class) failure occurred

TABLE 3-23. SUMMARY OF BIOLOGICAL EFFECTS OBSERVED IN LAKE #223 DURING ACIDIFICATION BY SULPHURIC ACID ADDITIONS (Schindler pers. comm.)

Year	pH		Reference
1976	6.8	Increased bacterial sulphate reduction	Schindler et al. 1980; Schindler and Turner 1982
1977	6.1	Increased abundance of rotifers	Malley and Chang 1981
		Increased abundance of Chlorophycean phytoplankton	Schindler 1980
		Decreased abundance of Chrysophycean phytoplankton	Schindler 1980
		Increased dipteran emergence	I. Davies, unpublished data
1978	5.8	Disappearance of the copepod *Diaptomus siciles*	Malley et al. 1982
		Recruitment failure of fathead minnow (*Pimephales promelas*)	K. Mills, unpublished data
		Possible increase in embryonic mortality of lake trout (*Salvelinus namaycush*)	Kennedy 1980
1979	5.6	Increased hypolimnetic primary production	Schindler 1980
		Development of algal mats (*Mougeotea* sp.) along shoreline	Schindler 1980
		Disappearance of the opossum shrimp *Mysis relicta*	Nero 1981
		Decreased calcification of crayfish (*Orconectes virilis*) exoskeleton	Malley 1980; France 1980
		Severe decline in fathead minnow abundance	K. Mills, unpublished data
		Decreased abundance of slimy sculpin (*Cottus cognatus*)	I. Davies, unpublished data
		Increased abundance of white sucker (*Catostomus commersoni*)	K. Mills, unpublished data
		Increased abundance of lake trout	K. Mills, unpublished data
1980	5.4	Disappearance of the copepod *Epischura lacustris*	Malley et al. 1982
		First appearance of the cladoceran *Daphnia catawba* X *schoedleri*	Malley et al. 1982
		Increased infestation of crayfish with microsporozoan *Thelonia* sp.	France 1982
		Reproductive impairment of crayfish	France 1982
		Decreased abundance of crayfish	I. Davies, unpublished data
		Increased abundance of pearl dace (*Semotilus margarita*)	K. Mills, unpublished data
		Reproductive failure of lake trout	K. Mills, unpublished data
1981	5.1	Recruitment failure of white sucker	K. Mills, unpublished data

in 1978 (pH ≃5.8). This agrees well with the results of Mount (1973), who found that impaired reproduction of the same species occurred at this pH in laboratory studies done at a variety of pH values. Secondly, even under preacidification conditions, this species had a very short life span of three years in Lake 223. Even under natural conditions, during the second and third years of life an extremely high natural mortality rate occurred, over 50% per year (Mills pers. comm.), presumably caused in large part by trout predation. Very few individuals remained after the second year of life. Therefore, the failure of one year class in 1978 would leave few spawning adults (age 2 and 3) the following year. Population recovery was, therefore, almost impossible. The combination of successive year class failures in 1978 and 1979 assured the rapid disappearance of this species from Lake 223.

The thresholds observed for disappearance of key species and appearance of others in Lake 223 agree well with observations made in other acidified lakes.

For example, Mysis in Lake 223 disappeared in the same pH range as benthic crustaceans with similar food habits disappeared in Scandinavian lakes (Økland and Økland 1980). Mougeotia epidemics in Lake 223 began at almost the same pH values as in Swedish waters (Hultberg pers. comm.). Recruitment failures in lake trout and white sucker began in the same pH range that year classes began to be absent in lakes near Sudbury and in Scandinavia (Harvey 1980; Muniz and Leivestad 1980; Haines 1981b,c).

The Lake 223 results also demonstrate the danger of assessing biological damage from acidification solely on the basis of game fish populations. Major alterations to fish habitats and prey species occurred several tenths of a pH unit above where initial damage to lake trout was detectable, even with an extremely intensive study of the trout population. The predation habits of lake trout appeared to allow them to easily switch to pearl dace after the disappearance of the fathead minnows which had been their normal prey.

In summary, the Lake 223 experiment clearly shows that alterations to aquatic food chains begin at pH values slightly below 6.0. The remarkable agreement between these whole lake experiments and observational studies in Scandinavia and eastern North America provides strong evidence that the observed declines in fisheries are caused by acidification and not by other ecological stresses.

3.7.12 Effects of Acidic Deposition on Birds and Mammals

While birds and mammals are not affected directly by acidic deposition they are vulnerable to changes in their habitat caused by acidification, particularly to changes affecting the availability and quality of their food. Although adults may continue to find sufficient food in areas adjacent to their traditional nesting or breeding sites, they may be unable to obtain sufficient food to raise young. In Scandinavia there have already been reports of such effects on aquatic bird populations. Almer et al. (1978) reported that, "fish-eating birds, such as mergansers and loons, have been forced to migrate from several acidic 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." While the extent of the problem has not yet been documented in Sweden, 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, and several species of waterfowl and gulls. From the results of this study it was 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 (Nilsson and Nilsson 1978). Eriksson et al. (1980) also proposed that reduced reproduction of fish in acidified lakes may decrease the availability of fish of the size classes appropriate to young diving water birds.

Losses of other aquatic organisms such as clams, snails, and amphibians have been documented in acidified lakes and ponds (Section 3.7.6; Hagstrom 1977; Hall and Likens 1980; J. Økland 1980; K.A. Økland 1980). While wildlife are largely opportunistic feeders, reductions of these organisms could affect the food availability for many wildlife groups such as waterfowl and semi- aquatic mammals. The effects of changes in food and habitat will be difficult to witness in the short term but, in time, breeding densities may decline and eventually productivity could fall in response to reduced food availability.

The diet of the common loon (Gavia immer) is approximately 80 percent fish, the remainder being made up of crustaceans, molluscs, aquatic insects, and leeches (Barr 1973). Because the food requirements of loons while rearing young are high and many of their food organisms are quite sensitive to acidification, the nesting densities of this species may be reduced. In eastern Canada, the common loon nests on lakes throughout the susceptible terrain of the Precambrian Shield (Godfrey 1966). In central Ontario and Quebec as well as in the Adirondack Mountains of the northeastern U.S., a number of lakes have already been reported as devoid of fish as a result of acid loading (Beamish 1976; Schofield 1976a). Studies in New York indicate that loon productivity has remained high but nesting densities have declined in the Adirondack region (Trivelpiece et al. 1979). To date, however, changes in loon populations in the Adirondacks have been interpreted only with respect to human disturbance; the probable role of food depletion has not been investigated. In Quebec, fish-eating birds were found more often on the nonacid lakes (DesGranges and Houde 1981). The common merganser (Mergus merganser) and the kingfisher (Megaceryle alcyon) were observed only on those lakes where the summer pH is higher than 5.6. In the vicinity of Schefferville, Quebec, important differences in numbers and composition of lake-dwelling bird communities were found: a third as many species and a quarter of the total number of aquatic birds were observed on lakes with pH less than 4.5 compared to lakes with pH greater than 6.0 (DesGranges and Houde 1981). The situation is less clear, however, for lakes of pH 4.5-5.5. It has been suggested that the biomass of some forms of benthic invertebrates increases with low to moderate inputs of acid because there are fewer fish predators (Henrikson and Oscarson 1978; Eriksson 1979; Henrikson et al. 1980). This may explain the larger number of invertebrate-feeding ducks which are found on moderately acid lakes in southern Quebec (DesGranges and Houde 1981) and in central Ontario (McNicol and Ross 1982).

Insectivorous birds such as swallows, flycatchers, and kingbirds may be affected by lake acidity since this group of birds feed on emerging insects and it is during the emergence that many insects are most sensitive to high acid levels (Bell 1971). Because a number of species of aquatic insects emerge in early spring during the peak of acid input to lakes and ponds they are particularly vulnerable to the effects of acid loading. It is also in early spring that the birds have higher food requirements in nesting and raising young. In southern Quebec, the tree swallow (Iridoprocne bicolor) was more common during the breeding season in the vicinity of lakes of pH >6.0 while in northern Quebec this species was not observed in the area of lakes of pH <4.5 (DesGranges and Houde 1981). This was also the finding from the studies of insectivorous birds in the Killarney area of Ontario (Blancher 1982). The presence or absence of these birds will largely be determined by the biota of the nearby lakes.

Effects of acidification on lower life forms such as microorganisms, essential to decomposition and nutrient cycling have been found (Hendrey et al. 1976; Leivestad et al. 1976). A loss in productivity at the base of the food chain due to decreased nutrient availability could result in progressively larger reductions at each succeeding trophic level. The implications for wildlife at the top of the chain are a critical loss in biological production and severely reduced carrying capacity of their habitat (Clark and Fischer 1981).

Increased solubility and mobility of metals from sediments have been reported as a result of acidification (Schindler et al. 1980). The higher concentrations of metals produced in lake waters have important implications for biological organisms as described in previous sections. Studies by Nyholm and Myhrberg (1977) and Nyholm (1981) have implicated aluminum in the impaired breeding of four species of passerines. Reductions in the reproductive success of these birds was highly correlated with the distance of their nests from acid-stressed lakes in Swedish Lapland. Breeding impairment was manifested as abnormal egg formation producing thin and porous shells. In addition, clutch size and hatching success of the "affected" birds were reduced and egg weights were lower in the birds closer to the acid-stressed lakes. The link between the acidified lakes and the breeding impairment has been related to the high aluminum content of the limnic insects upon which the birds feed (Nyholm 1981). Birds feeding closest to the stressed lakes have the highest proportion of contaminated insects in their diets (Nyholm pers. comm.; Eriksson et al. 1980). Similar findings of decreased egg size and weight were found for the eastern kingbird (Tyrannus tyrannus) in the Killarney area of central Ontario (Blancher 1982). Although severe abnormalities in shell formation were not evident in the eggs examined in this preliminary study, egg porosity as measured by the rate of water loss over the incubation period was negatively correlated with pH.

Elevated mercury levels have been found in fish in lakes with low pH in central Ontario (Suns et al. 1980). In the Bohuslan area of Sweden, elevated levels of mercury were found in eggs of goldeneye (Bucephala clangula) (Eriksson et al. 1980b). Raccoons (Procyon lotor) from the Muskoka area of Ontario support liver mercury levels of 4.5 ppm, a concentration five times greater than specimens from an area with nonacidified waters (Wren et al. 1980). Because neither of these areas receives point source inputs of mercury, the sources are believed to be leached from the watershed by acids or mobilized from sediments. Methylation of mercury has been related to the process of acidification and the formation of methyl mercury, a stable and soluble form which readily bioaccumulates, is believed to be favoured at low pH (Fagerström and Jernelöv 1972).

Results of a preliminary study of metal accumulation in the tissues of moose (Alces alces) have established an age dependent increase in cadmium for tissues collected from 38 moose and 56 roe deer in Sweden (Frank et al. 1981; Mattson et al. 1981). Almer et al. (1978) reported a 10-fold increase in levels of cadmium in acidified lakes on the Swedish west coast compared with those in nonacidified lakes in the same region. Cadmium may be accumulated in large concentrations by some terrestrial and aquatic plants (Anderson and Nilsson 1974; Hutchinson and Czyrska 1975), and therefore, metal contamination of wildlife feeding on these plants may be an indirect effect of acidic deposition.

A summary of potential effects on selected species of birds and mammals dependent upon the aquatic ecosystem for their food and habitat is presented in Table 3-24. 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.

3.8 CONCERNS FOR IRREVERSIBLE EFFECTS

3.8.1 Loss of Genetically Unique Fish Stocks

Loss of fish populations with specific gene characteristics from lakes and rivers may be an irreversible process. Over several thousand generations, most species appear to have evolved discrete

TABLE 3-24. AVIAN AND MAMMALIAN SPECIES MOST LIKELY TO BE INFLUENCED BY A REDUCTION IN FOOD RESOURCES DUE TO ACIDIC DEPOSITION, 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*)	none
		Osprey (*Pandion haliaetus*)	none
	Littoral zone	Great Blue Heron (*Ardea herodius*)	none
		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*)	
		Northern Waterthrush (*Seiurus boracensis*)	
		Alder Flycatcher (*Empidonax alnorum*)	
		Wilson's Warbler (*Wilsonia pusilla*)	
		Lincoln's Sparrow (*Melospiza lincolnii*)	

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 specific lake conditions. Surface water acidification is a stress that may reduce genetic variability in populations of native fishes in sensitive areas. As an example, 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 (Olver pers. comm.).

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 (Haines 1981c; Loftus 1976; Ryman and Stahl 1981).

Loss of discrete stocks may inhibit effective re-establishment of naturally reproducing populations in waters undergoing rehabilitation and affect future opportunities for fisheries management.

3.8.2 Depletion of Acid Neutralizing Capacity

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 most strictly as a failure to recover over geologic 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.

Although irreversible reduction in acid neutralizing capacity of lakes and watersheds is one of the potential effects of acidic deposition, our present information base is insufficient to determine its probability in impacted areas.

3.8.3 Soil Cation and Nutrient Depletion

The loss of soil cations, particularly Ca^{2+} and Mg^{2+}, which can lead to decreases in soil fertility (Overrein et al. 1980), is another potentially irreversible consequence of watershed titration. However, the extent to which these cation losses represent a significant depletion of total available material is unknown.

3.9 ATMOSPHERIC SULPHATE LOADINGS AND THEIR RELATIONSHIP TO AQUATIC ECOSYSTEMS

The previous sections have discussed chemical and biological changes observed in some 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-} and NO_3^- ions originating from atmospheric deposition. This section will consider the significance of these levels of chemical alterations, with a comparision of the annual deposition that could be associated with acidification of the most sensitive streams and lakes. This analysis requires consideration, not only of 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 total acidic loading rate from runoff events is expressed.

Emphasis has been placed on deriving as much information as possible from comparisons of observed water quality and biological effects in areas of varying deposition. These empirical observations integrate many "unknowns" regarding soil water interactions which are implicitly taken into account by empirical comparisons. Loading rates estimated from conceptual models of aquatic systems are compared to the empirical observations. Such empirical approaches to support environmental management are common. For example, flood structure designs can be based on empirical relationships between discharge, precipitation and physical characteristics of the watershed (Chow 1964). Vollenweider and Dillon (1974) used an empirical modeling approach to set phosphorus loading criteria for eutrophication control in lakes and reservoirs, and these have proven effective.

The following are the principal findings presented in previous sections important in evaluating aquatic effects related to measured acidic deposition:

1. Precipitation over most of eastern North America has hydrogen ion concentrations up to 100 times those expected for distilled water in equilibrium with atmospheric carbon dioxide.

2. Large quantities of sulphate and nitrate ions are deposited with H^+ ions in precipitation in eastern North America.

3. Lakes in eastern North America with low alkalinities are receiving elevated acid loadings. Such lakes, and their associated streams, may suffer low pH and elevated metal concentrations for short periods of time, particularly during snowmelt and other periods of heavy runoff.

4. Stressed fish populations have been observed in lakes that experience short-term low pH and elevated metal concentrations. Mortalities of adult fish have been observed in one study lake experiencing these conditions.

5. There are numerous examples of streams and lakes in Canada and the United States that have experienced and are probably now experiencing depletion of alkalinity. Fish populations that

survive short-term low pH conditions, will eventually be lost if alkalinity is depleted and pH values fall below critical levels causing successive reproductive failure. Long-term acidification has caused losses of fish populations in some lakes and streams.

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-} have some potential for altering lake and stream water acidity. Soil and plant interactions with nitrate ions allow nitric acid to be largely assimilated by the terrestrial portion of the watershed, except during periods of heavy runoff (Section 3.2.2) (McLean 1981). In contrast, in many regions with poorly developed soils, that are limited in ability to neutralize acid, biological uptake of sulphate is 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. In a number of areas studied, where there exist no significant terrestrial sources or sinks of sulphur, SO_4^{2-} is a conservative ion whose export to surface waters is directly related to deposition in precipitation.

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

1) the relative magnitude of SO_4^{2-} and NO_3^- in the rain and snow inputs, their variation during the year, and long-term trends;

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 changes in biomass over long periods;

3) the production of alkalinity in terrestrial and aquatic systems when NO_3 is assimilated by plants; and

4) the contact time of precipitation inputs with the watershed.

Data presented in map form in Section 2 and other data presented by Galloway et al. (1980g), McLean (1981) and by Harvey et al. (1981) indicate that acidic sulphur inputs exceed acidic nitrogen inputs over eastern North America on an annual basis. The net yield of these anions to streams and lakes is predominantly SO_4^{2-} on an annual basis (Harvey et al. 1981). Because nitrate reaches surface waters in small amounts relative to its loadings on an annual basis and does not accumulate in surface waters, its influence on long-term surface water acidification is less than that of sulphate.

Further evidence that nitrate deposition is not principally responsible for long term surface water acidification is given in Table 3-25. Data for 21 headwater streams in the Muskoka-Haliburton area of Ontario with a range of mean annual pH values from 4.08 to 6.18 show that as acidity increases, the relative importance of NO_3 declines. The acid (H^+) concentration exceeds the NO_3^- concentration on a chemical equivalents basis for annual pH values of 5.5 or less, so that lower pH values cannot be explained by the presence of nitric acid. The H^+/SO_4^{2-} ratios are also given for the same streams (Table 3-25). At lower pH values, H^+/SO_4^{2-} ratios increase. The ratio is always less than one which indicates that the acid concentration can be explained by the presence of sulphuric acid. The SO_4^{2-}/NO_3^- ratios range from 14 to 337 with a median value of 170, demonstrating the dominance of SO_4^{2-} over NO_3^- in surface waters in the Muskoka-Haliburton region (Jeffries et al. 1979; Scheider et al. 1979c; and ongoing studies by Ontario Ministry of the Environment).

Nitrate may be important on an episodic basis by adding to the pH depression caused by sulphate. At Sagamore Lake, New York, nitrate concentrations in the lake outflow increased during spring pH depression, while sulphate concentrations did not increase (Galloway et al. 1980g). Sulphate concentrations still exceeded nitrate concentrations on an equivalent basis, even during spring runoff.

Uptake of nitrate ions by algae and aquatic plants results in the production of alkalinity in surface waters (Goldman and Brewer 1980). This has been shown to occur in one of the study lakes at Muskoka-Haliburton. 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).

The evidence available, and the published interpretations of that evidence (Harvey et al. 1981; Overrein et al. 1980), lead to the conclusion that, for surface water systems, increases in acidity are the result of dilute solutions of strong acids reaching these waters. Further, Harvey et al. (1981) following extensive analysis of Canadian data and Overrein et al. (1980) following extensive research in Scandinavia conclude that most of the acidity is due to the changes observed in SO_4^{2-} concentration attributable to sulphate and sulphuric acid deposition (Harvey et al. 1981; Overrein et al. 1980). Both sulphuric and nitric acid contribute acidity to surface waters during periods associated with pH depressions and fish stress. However, there is no strong evidence at present for anticipating any appreciable reduction in long-term lake or stream acidification from a reduction in nitrate inputs. In contrast, it is important to note there is a strong correlation between between sulphate deposition and surface water concentrations to suggest that a reduction in sulphate

TABLE 3-25. MEAN AND RANGE OF pH VALUES, MEAN H^+/NO_3^-, H^+/SO_4^{2-} AND SO_4^{2-}/NO_3^- RATIOS (calculated as µeq/L) FOR 21 HEADWATER STREAMS IN MUSKOKA-HALIBURTON, ONTARIO 1976-1980 [Data is from an ongoing study, methods and study area as described in Jeffries et al. (1979) and Scheider et al. (1979b)]

Stream	Mean pH	Range pH	H^+/NO_3^- (µeq/L)	H^+/SO_4^{2-} (µeq/L)	SO_4^{2-}/NO_3^- (µeq/L)
Dickie 11	4.08	3.53-5.61	93.60	0.457	245
Red Chalk 2	4.30	3.68-4.81	60.00	0.188	265
Dickie 5	4.34	3.71-4.76	58.30	0.318	233
Dickie 6	4.35	3.74-5.05	60.20	0.297	247
Dickie 10	4.59	3.92-5.10	25.90	0.119	170
Chub 2	4.82	4.12-6.08	23.90	0.071	236
Dickie 8	5.03	4.04-5.87	12.60	0.049	284
Harp 6A	5.19	4.34-6.39	9.57	0.028	337
Harp 5	5.34	4.66-6.60	2.49	0.017	145
Chub 1	5.41	4.48-6.61	5.49	0.019	232
Harp 3	5.64	4.89-6.39	1.05	0.009	156
Harp 6	5.77	5.20-6.90	0.83	0.007	130
Red Chalk 1	5.81	5.19-6.69	1.74	0.009	174
Red Chalk 3	5.95	5.17-6.65	0.21	0.006	34
Harp 3A	5.95	5.30-7.30	0.29	0.004	100
Red Chalk 4	5.96	5.28-6.71	0.24	0.006	37
Jerry 3	5.98	5.27-6.67	0.51	0.004	134
Jerry 4	6.07	5.49-6.55	0.46	0.003	118
Harp 4	6.08	5.29-6.90	0.15	0.003	57
Blue Chalk 1	6.16	5.71-6.62	0.67	0.003	198
Jerry 1	6.18	5.58-6.74	0.04	0.003	14

loading to watersheds would reduce the sulphate concentrations and associated acidification of surface waters.

3.9.2 Data and Methods for Associating Deposition Rates with Aquatic Effects*

The evidence available on the effects of acidic deposition on aquatic resources indicates that present loadings rates are in excess of the ability of watersheds to reduce the acidity for some lakes in some areas. This section will explore the association between loading levels of acids or sulphates and negative effects on the aquatic environment. In the following analysis, it is implied that sulphate deposition can be used as a surrogate for the acidifying potential of precipitation.

The use of sulphate in precipitation as a surrogate for the acidifying potential of deposition should not be interpreted to mean that wet sulphate is the only substance potentially damaging to aquatic systems. It is recognized that dry deposition of sulphate and SO_2, and wet and dry nitrates contribute to the concentrations of acids. Sulphate in precipitation is reliably measured and therefore, is used here as a surrogate for the total sulphur deposition because dry deposition cannot be measured accurately. Similarly, this surrogate does not reflect the contribution of nitrate to acidity of precipitation.

Surface water quality alterations fall into two categories:

1) short-term pH depressions during snowmelt or heavy rains, and

2) long-term reductions in alkalinity, with corresponding low pH values in surface waters throughout the year.

The length of time it takes for a lake to become acidic (alkalinity reduced to zero or less) and the rate of change of water quality are among the least well-defined aspects of the acidification phenomenon. To date, the evidence available, based on sediment cores taken from several areas (Section 6.3.4), suggests that acidification has occurred and is occurring on the scale of decades.

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* *It is the view of the U.S. members of the Work Group that the reliability of wet sulphate deposition values is uncertain and therefore, any attempt to use them for analysis must be done with great care. Examination of the data shows that: (1) limited deposition data are available, and (2) annual variability in wet sulphate deposition values can be large.*

Before the alkalinity of a lake or stream is totally depleted, it is very likely that the system experiences short-term pH depressions during periods of high runoff. Large temporal fluctuations in pH levels may represent a transition phase in the process of acidification.

The phenomenon of short-term pH declines is probably more common than long-term reductions in alkalinity (in terms of numbers of lakes and rivers affected in North America). The chemistry of these events is fairly well defined. The biological consequences of these events are known to be severe in some cases, but the relationship between short-term pH depressions and effects on aquatic biota are not fully understood.

"In the second stage, the bicarbonate buffer is lost during longer periods and severe pH fluctuations occur resulting in stress, reproductive inhibition and episodic mortalities in fish populations (transition lakes)" (Henriksen 1980). Damage to fish and other biota as a result of short-term exposures to low pH and associated high metal concentrations has been demonstrated to occur in both laboratory and field studies (Section 3.7). Thus, summertime or annual pH has questionable value for determining effects on organisms of H^+ or metals over a few days. The timing magnitude and duration of short-term increases in H^+, associated with spring melt and storm events must, therefore, be included in an evaluation of critical loading rate and episodic response relationships for streams and lakes.

In summary, the short-term acute exposure or "shock" effects (including responses to aluminum) can take place in two to four days of exposure, with pH decreases in the order of 0.5-1.5 units; and these shock exposures can be expected to occur in waters with a broad range of pH above the level at which chronic effects occur.

The second category, long-term acidification, has altered a large number of lakes in North America, but the percentage of lakes and rivers with mean annual alkalinity of zero or less remains small. The biological responses to long-term acidification are, however, more clearly defined and generally more severe than for short-term pH declines.

The acidity and chemical composition of aquatic environments are affected by: (1) the acid neutralizing capacity of the basin; (2) the geologic and morphologic characteristics of the basin; and (3) the acidity of the precipitation. Biological processes (e.g., production and decomposition) also have an effect on acidity. Models used to simulate the geochemical processes and aquatic ecosystem effects are not fully developed or validated at this time. Development and application of detailed models will require detailed information on basin geology, hydrology, and biotic interactions. These are unlikely to be available soon for widespread application. Therefore, at present, the relationships between acidic deposition and aquatic effects can be determined only in a general way. Some data and phenomenological models exist that relate the behaviour of lakes and streams to acid loading. These empirical observations and models are discussed below.

3.9.2.1 Empirical Observations

Observed sulphate loadings and corresponding chemical and biological observations for a series of study areas in North America and Scandinavia are available.

The information in this section is drawn from a number of study areas within eastern North America which are located on the Precambrian Shield or on weathering resistant bedrocks. The surface water studies have been initiated for several reasons, have started at different times and are operated by different agencies. However, each project contributes information relevant to the acidification problem by comparison of results among and within the studies themselves. In general, each project involves some highly detailed work on a small number of watersheds and surface waters and less detailed work on a larger study set. Within a given study area, the surface waters and watersheds are usually chosen to cover as wide a range of water quality and geology as is available.

The study area descriptions will give some appreciation for the extent of the data base used in the empirical derivation of SO_4^{2-} loading versus chemical and biological effects.

SASKATCHEWAN SHIELD LAKES

More than 300 lakes in Northern Saskatchewan's Shield and Fringe Shield regions have been sampled to assess the sensitivity of lakes.

Deposition (kg SO_4^{2-}/ha.yr)	Annual Precipitation (m)	Annual Runoff (m)
5[a] 1980	0.357	.100 - .200[b]

[a] CANSAP Measurement.

[b] Fisheries and Environment Canada 1978.

Observed Characteristics

1. Alkalinity = −18.20 + 0.92 (Ca + Mg) (n=281,r=0.97) Liaw (1982) indicating that the bicarbonate and Ca + Mg are related by a 1:1 relationship and sulphate contributes very little to the total ion balance.

2. pH values range from 5.56 to 8.2, 39% < 7.0 (Liaw 1982).

EXPERIMENTAL LAKES AREA, ONTARIO

The Experimental Lakes Area is situated in northwestern Ontario on Precambrian shield granite. Approximately one-half the area of Canada is Precambrian Shield. Within the study area there are about 1,000 lakes, of which 46 lakes in 17 drainage basins have been set aside solely for experimental research. The inflows and outflow of Rawson Lake (a control lake) are calibrated as well as 14 other watersheds. The project was initiated in 1969 and is continuing a wide range of whole-lake chemical manipulations including the acidification of lakes with monitoring of chemical and biological parameters including fish population studies. The results from this multi-faceted project are published in many scientific journals including two special issues of the Canadian Journal of Fisheries and Aquatic Sciences devoted entirely to the Experimental Lakes Area (1971, Volume 28, Number 2 and 1980, Volume 37, Number 3).

Deposition (kg SO_4^{2-}/ha.yr)	Fraction	Time Period	Annual Precipitation (m)	Annual Runoff (m)
9.07[a]	bulk	1972	0.69[a]	0.297[a]
10.8[a]	bulk	1973	0.73[a]	0.354[a]
5.9[b]	wet	1980	0.51[b]	0.223[a]
				0.234[a]
				0.15[d]

Sum of Cations for 31 lakes 217 µeq/L ± 25 (Standard Deviation)

[a] Schindler et al. 1976; see also Figure 3-16.
[b] Barrie and Sirois 1982.
[c] CANSAP measurement.
[d] Fisheries and Environment Canada 1978.

Observed Characteristics

1. No long term acidification or biological effects observed in ten years of study (Schindler pers. comm; Can. J. Fish. Aquat. Sci. 37(3); Can. J. Fish. Res. Board 28(2)).

2. Sulphate export from the watersheds is about equal to the measured wet deposition (Schindler et al. 1976).

3. Lake alkalinity distributions for lakes in the Rainy River district have fewer low alkalinity values than four other Precambrian Shield areas in Ontario (Dillon 1982).

4. Lake pH values for a 109 lake survey ranged from 4.8 to 7.4 and averaged 6.5 (Beamish et al. 1976).

5. Lake sulphate concentrations ranged from about one-half to about equal to the bicarbonate concentrations (Beamish et al. 1976, Dillon 1982).

6. Filamentous algae are common in July and August but do not dominate the algal population (Stockner and Armstrong 1971)

ALGOMA, ONTARIO

The Algoma region of Ontario is an area of 862,000 ha in northcentral Ontario. From a chemical survey of about 85 lakes, Kelso et al. (1982) report results from 75 headwater, nondystrophic lakes with watersheds undisturbed by recent logging, fire or human settlement. Sampling was done in 1979-80 and included physical parameters, lake chemistry and phytoplankton analyses on the entire lake set with benthic invertebrate, sediment and fish tissue analyses done on subsets of the 75 lakes.

The Turkey Lakes Project, situated within the Algoma region, is an ongoing calibrated watershed study of 5 lakes and 20 watersheds, plus the outlet of the entire Turkey Lakes watershed basin. Initiated in 1980, intensive chemical, hydrological and biological studies are in progress including monitoring of precipitation, air quality, forest effects, ground and soil water, stream and lake chemistry.

Deposition (kg SO_4^{2-}/ha.yr)	Fraction	Time Period	Annual Precipitation (m)	Annual Runoff (m)
25 APN Turkey Lakes Station, (Barrie, pers. comm.)	wet	1981	0.8[a]	0.50[b]
28		1976	calculated from ion concentration data from Kelso et al. (1982) and precipitation data from Barrie and Sirois (1982)	
22		1977		
32		1978		
23		1979		
Sum of Cations for 75 lakes		285 µeq/L ± 125 (Standard Deviation)		

[a] Barrie and Sirois 1982.
[b] Fisheries and Environment Canada 1978.

Observed Characteristics

1. pH depression in streams during spring runoff up to 2.1 pH units with minimum values as low as 5.0 in streams with summer alkalinities less than 400 µeq/L (Keller and Gale 1982).

2. Excess sulphate runoff is elevated about five times over the remote areas of northwestern Ontario and Labrador (Thompson and Hutton 1982). Sulphate export from watersheds exceeds wet deposition indicating possible dry deposition of sulphate.

3. Of 75 headwater lakes surveyed, six had pH values of 5.3 or less and the lowest value was 4.8 (Kelso et al. 1982).

4. Sulphate ions are the dominant anions (i.e., exceed bicarbonate) in lakes below pHs of about 6.5 (Kelso et al. 1982).

5. In a survey of 31 headwater lakes (1.6-110 ha), the number of lakes devoid of the 8 fish species reported in the area was observed to increase with decreasing alkalinity. The relationship between the presence of fish and pH in these same lakes was weaker although a greater proportion of

lakes of pH <5.5 were fishless than lakes of pH >5.5 (Kelso et al. 1982). These observations are consistent with the hypothesis that the biota in the surveyed lakes have been adversely affected by changes in lake chemistry but do not necessarily indicate causality (Kelso et al. 1982).

6. Aluminum and lead levels in 75 headwater lakes in Algoma were elevated in lakes of lower alkalinity; mean total aluminum levels of 53 µg/L was slightly greater than aluminum levels in Muskoka-Haliburton waters (Scheider et al. 1979a) and intermediate between concentrations found in severely affected and slightly affected systems in Canada and Norway (Kelso et al. 1982).

MUSKOKA-HALIBURTON ONTARIO

The study area in Muskoka and Haliburton counties of southcentral Ontario encompasses an area of about 490,000 hectares within which are its 8 intensive study lakes and 32 calibrated watersheds, some of which have been calibrated since 1976. The watersheds vary in water quality and from low to high pH. Twenty other lakes have been monitored on a seasonal basis for a varying number of years. Many concurrent chemical and biological studies are ongoing on the calibrated lakes as summarized in Harvey et al. (1981). The results of these studies have been reported in approximately thirty publications in the primary scientific literature.

Studies of precipitation, deposition, air quality, soils, groundwater, forests and precipitation throughfall are all being carried out. A stream acidification experiment was started in 1982.

Studies of pH effects on fish and fish populations have been intensified since 1979 by Harold Harvey of the University of Toronto.

Deposition (kg SO_4^{2-}/ha.yr)	Fraction	Time Period	Reference
31	bulk	Aug76-Jul77	Scheider et al. 1979a
32	bulk	Aug77-Jul78	Scheider et al. 1979a
23	wet	Aug76-Jul77	Scheider et al. 1979a; Harvey et al. 1981
29	wet	Aug77-Jul78	Scheider et al. 1979a; Harvey et al. 1981
37	bulk	Jun76-May80 (Mean)	Scheider & Dillon 1982
31	bulk	Jun76-May77	Unpublished[d]
35	bulk	Jun77-May78	Unpublished[d]
42	bulk	Jun78-May79	Unpublished[d]
38	bulk	Jun79-May80	Unpublished[d]

Annual Precipitation (m)	Annual Runoff (m)
0.8[a]	
0.8[a]	0.45[c]
1.2[a]	

Sum of Cations in Surface Waters 150-300 μeq/L[b]

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[a] Barrie and Sirois 1982.
[b] Dillon et al. 1980.
[c] Fisheries and Environment Canada 1978.
[d] Ontario Ministry of Environment, ongoing studies.

Observed Characteristics

1. Severe pH depressions in streams and lakes with values as low as 4.1 recorded (Jeffries et al. 1979).

2. Sulphate concentrations in lakes average about equal to the bicarbonate concentrations (Dillon et al. 1980).

3. Manganese concentrations are elevated to about 50 µg/L compared to about 3 µg/L at the ELA station (Dillon et al. 1980).

4. Aluminum concentrations (50 µg/L) are elevated over values at ELA (Dillon et al. 1980).

5. Clear Lake, for which there are historical records, has declined in alkalinity from 33 µeq/L in 1967 (Schindler and Nighswander 1970) to between 2 and 15 µeq/L in 1977 (Dillon et al. 1978), a reduction in alkalinity of greater than 50%.

6. Mercury concentrations are higher in fish from lakes with low pH than from higher pH lakes (Suns 1982).

7. Unusually dense and extensive masses of filamentous algae proliferate in the littoral zones of many lakes with pH values of 4.5-5.5 (Stokes 1981).

8. Chrysochromulina breviturrita, an odour causing alga has reached densities that have reduced the recreational use of lakes for periods of time during the summer (Nicholls et al. 1981). The species dominance appears to be a recent phenomenon (within the past decade). This alga has been shown to increase with decreasing pH in lake acidification experiments (Schindler and Turner 1982).

9. Elemental composition of fish bones reported by Fraser and Harvey (1982) showed the centrum calcium was reduced in white suckers from lakes of pH 5.08 (King) and 5.36 (Crosson) compared to lakes of higher pH in the same area.

10. The white sucker population in Crosson Lake (pH 5.1) showed a truncated age composition compared with the age composition of the less acidic Red Chalk (pH 6.3) and Harp (pH 6.3) lakes (Harvey 1980).

11. Adult pumpkinseeds (Lepomis gibbosus) and frogs have been killed around the edges of Plastic Lake during spring melt and acidification is the suspected cause. Inlet streams had pH values as low as 3.85 (Harvey and Lee 1981).

LAURENTIDE PARK, QUEBEC

Humid Alpine Lower Boreal Regions

Elevated dome dominating the surrounding plateau. Elevation varies from 500 to 1200 m asl with summit elevations of 1100 to 1200 m. It is comparable to the entire Laurentian plateau, although here there are very few lakes and the drainage pattern is characterized by deep dissecting river valleys such as the Jacques Cartier.

The frost-free season is generally 80 days or less with a growing season of about 140 days. Average annual rainfall, one of the most abundant in Quebec, ranges between 1200 and 1600 mm.

On the upper slopes and summits, 85% of the surface is covered with glacial till of which two-thirds is less than 1 m deep, while the other 15% consists of exposed bedrock (gneiss). Low-lying areas are, for the most part, blanketed by sandy fluvio-glacial outwash deposits. A few organic deposits exist and are generally shallow, digotrophic and treed. Ferro-humic podzols characterize the well-drained soils with little or no ortstein to be found on excessively to well-drained sand soils.

The region, as defined by Thibault (1980), confirms early work completed by Jurdant and others (1968, 1972). The limits include all areas above 518 m. Jurdant (1968) and Lafond and Ladouceur (1968) characterized a distinct peripheral-band in the central upland plateaus covered by balsam fir and black spruce moss forests and occasionally white birch stands. Forest regeneration after cutting or fire, is dominated by white birch rather than trembling aspen. The central plateau supports a black spruce moss forest cover, but after cutting, regenerates and develops into a balsam fir Hylocomium, Oxalis forest (Lafond 1968).

The more exposed summits in the region such as Mount Blie in the Malbaie watershed, support a scattered alpine cover dominated by a heath, moss, and sedge complex and occasionally lichens.

Humid Lower Boreal Region

This region, the Laurential foothills, is found between 47°30' and 50°00' N latitude and 67° and 75° W longitude. Mountainous topography characterizes the region.

Average growing season is about 150 days with a total annual rainfall between 900 to 1000 mm. Due to altitudinal variations, local climate conditions vary within the region. Lower altitudes, especially in the southern sectors are not as cold or as wet as conditions on the higher plateau, a difference of 200-300 degree days and an average rainfall 200-300 mm.

Near the foothills, crystalline Precambrian bedrock underlies the region. Hillsides are generally covered by a thin (less than 1 m) layer of till, with deeper deposits near the base and scattered deposits on the upper slopes and summits. Fluvio-glacial deposits characterize the valley floors of the region. Ferro-humic and humo-ferric podzols are the dominant soil formations.

Rowe (1972), Jurdant et al. (1972) and work completed using provincial cover maps (MER-Ministère d'Energie et des Resources) were used to define the region. The limits as defined by Thibault (1980) and Jurdant et al. (1972) regroup regions considered by Jurdant as part of a large balsam fir-white birch forest domaine. This domaine is characterized by a semi-dense forest cover (60% crown closure nature, tree height greater than 21 m) of balsam fir and black spruce associated with white birch and an absence of jack pine.

Rowe's forest region and the MER information confirmed the region's limits. Mesic hillside conditions support balsam fir-black spruce mass as well as black spruce-balsam fir mass forest covers with white birch and white spruce associations. Pure black spruce stands preferred either dry sites or poorly drained hollows. White birch and to a lesser extent trembling aspen associated with black spruce, balsam fir and white spruce characterize the regeneration.

Except for a few isolated areas, the meridional sugar maple, yellow birch, red maple, red pine, black ash and American elm are not to be found in the region.

Deposition (kg SO_4^{2-}/ha.yr)	Fraction	Time Period	Reference
40	wet	Apr79-Mar80	Interpolated* from Glass and Brydges 1982
30/6 mo	wet	Apr79-Oct79	Interpolated* from Glass and Brydges 1982
10/6 mo	wet	Nov79-Mar80	Interpolated* from Glass and Brydges 1982
35	wet	1980	Thompson and Hutton 1982; interpolated from Barrie and Sirois 1982
22.2	wet	28Sep81-27Sep82	Grimard 1982

Annual Precipitation (m)	Annual Runoff (m)
1.14[a]	0.95[a]

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[a] Ferland and Gagnon 1974.

* Interpolations from existing deposition isopleth maps as a basis for estimating deposition values can be in error.

Major Cations in μeq/L	Average	Standard Deviation
Ca	114.8	57.6
Mg	54.1	23.9
Na	37.3	12.5
K	8.3	3.7
Cond	22.5	8.7

Observed Characteristics

1. The surface water pH is higher than the precipitation pH. The pH of 152 lakes sampled in the last week of March 1981 and the first of April varied between 4.7 and 6.6 with an average of 5.9 (Richard 1982).

2. The average content of sulphate in the lakes is of the order of 80 μeq/L (Bobée et al. 1982; Richard 1982) and it is higher or equal to bicarbonate.

3. The highest sulphate concentrations in lakes in Quebec and the greatest alkalinity differences were observed in the southwest. The lake water concentrations of sulphate and the alkalinity deficits decrease to the north and east (Bobée et al. 1982).

4. There is a significant correlation ($r = 0.76$, $p \leq 0.001$) between pH and total aluminum of the 152 lakes of Richard (1982).

5. The Laurentide Park area is found in hydrographic regions 05 and 06 (Figure 3-13). Sulphate vs. Σ [Ca] + [Mg] - [alk] for these two hydrographic regions is found in Figure 3-14.

6. Compared to the pH of 1938-41, there is a greater proportion of the lakes sampled 1979-80 in the classes of pH 4.40-5.09, 5.10-5.79 and 6.50-7.19 amongst 5 pH classes (Jones et al. 1980). Lakes in the two lowest pH classes showed reductions in pH; the higher pH class increased because of road salt and nutrient additions. The decline in surface water pH tended to occur in the southern part of the park.

7. In lakes continuously open to fishing for nine years prior to 1982, average annual angling yield, angling effort, and mean weight of fish caught in years 1978-81 were not significantly related to lake pH. Management policies within the Park provide for closure of a lake to fishing

when angling success is reduced below projected levels. The 44 lakes which were closed to fishing over the nine year period included 43.5% of the most acidic lakes (Group 1, mean pH 5.2); as compared with 36.9% of Group 2 lakes (mean pH 5.9) and 17.5% of the Group 3 lakes (mean pH 6.4). Although a direct cause-and-effect relationship between fish productivity and pH has not been established, the greater number of closures in the more acidic lakes suggests a lower productivity in these waters (Richard 1982).

8. The concentrations of manganese, zinc and strontium in the opercula of *Salvelinus fontinalis* are respectively 1.6, 1.3 and 1.2 times higher in the population of the three more acidic group of lakes comparatively to the three non-acidic group of lakes (Moreau et al. 1982).

NOVA SCOTIA

The Nova Scotian River Study by Watt et al. (1983) encompassed the approximately 500 km long Atlantic coast of Nova Scotia which is underlain by granite on about one-half of the mainland. This study of 23 rivers which historically supported salmon fisheries reports results of monthly monitorings from June 1980 to May 1981, with certain rivers studied as long as 10 years. An historical comparison of five of these rivers with data collected in 1954-55 (Thomas 1960) pH, alkalinity, and major ion concentration data was made. Fisheries data for the past 45 years was available for 22 of the rivers and Watt et al. (1983) related angling success to current water chemistry and geological factors. Within Kejimkujik National Park, central Nova Scotia, an ongoing study involves three calibrated lakes. Kerekes (1980) reported results for these lakes for the June 1978 - May 1979 period. From this study a chemical budget is available for the Mersey River (the outflow of Kejimkujik Lake), which is included in the fisheries data set of Watt et al. (1983).

Deposition ($kg\ SO_4^{2-}/ha.yr$)	Fraction	Time Period	Location
44	total	Jun78-May79	Kejimkujik,
22	wet		Kerekes (1980)
19	wet excess		
22-29	wet and dry excess	1977-79	Interpolated* from Figure 3, Underwood (1981)
22		1981	Kejimkujik[a]
17		1980	Kejimkujik[b]
27		1980	Truro[c]
32		1979	Truro[c]
31		1978	Truro[c]
18.12		Feb78-Dec80	East River St. Marys[d]
13.18		Nov77-Dec80	Cobequid[d]
29.01		Oct77-Nov79	Bridgetown[d]
21.27		May78-Dec80	New Ross[d]
22.50		Oct77-Mar80	Kemptville[d]

Annual Precipitation (m)	Annual Runoff (m)
1.2[e] 1978	1 m[f]
1.6[e] 1979	
1.2[e] 1980	
1.40 June 1978 - May 1979	
1.46[f] long-term average	

Sum of Cations for 41 lakes and rivers 59 ± 17 μeq/L (Standard Deviation)

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[a] Barrie pers. comm.

[b] Barrie et al. 1982.

[c] Truro CANSAP received a fair rating in the siting assessment (Vet and Reid 1982) and the station is being moved (Barrie pers. comm.).

[d] Underwood 1981 and Underwood pers. comm.

[e] Barrie and Sirois 1982.

[f] Fisheries and Environment Canada 1978.

* Interpolations from existing deposition isopleth maps as a basis for estimating deposition values can be in error.

Observed Characteristics

1. Precipitation pH is generally lower than the pH of the runoff water. High runoff is associated with the lowest pH values in river waters. The lowest mean monthly values in rivers generally occur in winter (Watt et al. 1983).

2. Sulphate is the dominant anion in three study lakes of pH 5.4, 4.8 and 4.5 (Kerekes 1980) and was highest in the two coloured lakes with lowest pH.

3. Excess sulphate export from the watersheds are elevated above those of remote areas by a factor of about 4 (Thompson and Hutton 1982) and sulphate export exceeds the measured wet deposition indicating possible dry deposition.

4. pH data are available for four rivers (corrected for flow) and 1980-81 values are less than 1954-55 by 0.24 to 0.79 units. The current bicarbonate concentrations are lower and sulphate and aluminum concentrations are higher than historical values (Watt et al. 1983).

5. Two rivers (St. Mary's and Medway) had the lowest pH values and highest excess sulphate loads in 1973. Similar changes in pH and excess sulphate were noted for two Newfoundland rivers (see Figure 3-30).

6. Long-term (five years or greater) records for pH, calcium and sulphate from eleven rivers in Atlantic Canada were fitted by time series models. Five of eight sensitive rivers decreased in pH and the other three did not change, while none of four insensitive rivers decreased. Relationships between trends in pH and Calcium and sulphate indicate that, conceptual models applied satisfactorily for pH and in only a limited number of cases for calcium and sulphate (Clair and Whitfield 1983).

7. Salmon catch data for 22 rivers which have not been affected by watershed changes or salmon stocking, have been recorded from 1937 through 1980. As a group (n = 10), rivers in the pH range 4.6 - 5.0 have reduced salmon stocks as reflected by a significant decline in angling catches over this time. Collectively, rivers with current pH values >5.0 do not show any significant trend in salmon catch over the past 45 years (Watt et al. 1983). The absence or reduced abundance of Atlantic salmon in 17 rivers was corroborated by electrofishing surveys in 1980-82 (Watt et al. 1983).

8. Diatom assemblages in four Halifax study lakes shifted toward more acid tolerant species between 1971 and 1980 (Vaughan et al. 1982).

BOUNDARY WATERS CANOE AREA AND VOYAGEURS NATIONAL PARK, MINNESOTA

The Boundary Waters Canoe Area Wilderness (BWCA), a wilderness unit within the Superior National Forest (Minnesota) and located along 176 km of the Minnesota-Ontario border. The area varies from 16 to 48 km in width. Over 1,900 km of streams, portages, and foot trails connect the hundreds of pristine, island-studded lakes that make up approximately one-third of the total area.

Most of the BWCA is included within the Rainy Lake basin, except for the eastern section, which is part of the Lake Superior watershed. Of a park total of 88,800 ha, several thousand of the 34,700 ha of recreational water in the VNP were created by dams, leaving 54,080 ha of land. The park has 31 named lakes and 422 unnamed swampy ponds larger than 2 ha. The BWCA has a surface area of 439,093 ha patterned by 1,493 lakes greater than 2 ha, and over 480 km of major fishing and boating rivers in addition to numerous streams and creeks (Glass and Loucks 1980).

Filson Creek watershed is approximately 13 km southeast of Ely, Minnesota. Filson Creek drains 25.2 km^2 and flows north and west to the Kawishiwi River. Included in the watershed are Omaday and Bogberry Lakes and one tributary, designated South Filson Creek for this study. South Filson has a 6.3 km^2 drainage area and no significant lakes.

About 60% of Filson Creek watershed is covered by mixed upland forest, 30% by wetlands and lakes, and the remainder by planted or natural stands of pine. Wetlands surround the lakes.

The precambrian bedrock is mostly troctolite (a pyroxene-poor, calcic gabbro) and other igneous rocks of the Duluth Complex. The northern 10% of the watershed is underlain by the Giants Range granite. A mineralized zone along the contact between the granite and the Duluth Complex contains copper and nickel sulfide minerals. The watershed has no carbonate rocks. Bedrock is at the land surface in about 10% of the watershed.

Most of the watershed is covered by drift generally less than 1 m thick. Its mineral composition reflects the underlying bedrock types. The total thickness of drift and peat under the wetlands can exceed 15 m. The peat in most of the wetlands is fibric, herbaceous, and partly decomposed (sapric) below about 0.75 m (Seigel 1981).

Deposition ($kg\ SO_4^{2-}/ha.yr$)	Fraction	Time Period	Reference
10-15	wet	1976-78	Glass and Loucks 1980
13	wet	1981	NADP 1981-83 (Marcel site)
1.6	snow	1978 (snow season)	Glass 1980
17	bulk	Nov76-Oct77	Siegel 1981
17.2	wet	1980	NADP 1981-83 (Marcell site)
16.6	wet	Apr78-May79	Total NE Minn., Eisenreich et al. 1978
14.8	Wet	Apr78-May79	Heiskary et al. 1982 (Hovland site)

Observed Characteristics

1. No known chemical or biological effects in lakes (Glass 1980; Glass and Loucks 1980).
2. Most of BWCA lakes surveyed have pH values <6.0 and 36.5% had CSI >3 (Glass 1980; Glass and Loucks 1980).
3. Of the 290 sites sampled 50.5% had alkalinity values between 40-199 μeq/L no lakes had alkalinity values less than 40 μeq/L (Glass 1982; Glass and Loucks 1980).
4. Filson Creek watershed retained 10.6 kg SO_4^{2-}/ha.yr of 17 kg SO_4^{2-}/ha.yr bulk (Siegel 1981)
5. SO_4^{2-} increased from 2 to 14 mg/L and $[H^+]$ from pH values of 6.6 to 5.5 during snowmelt (Siegel 1981).

NORTHERN WISCONSIN

Northern Wisconsin is a region in which a collapsing glacial mass left deep outwash sands and coarse tills interspersed with ice-blocks. The study area encompasses portions of seven counties in the Upper Wisconsin River Basin. Water covers 17% of the area. The area has had a 30% increase in population over the last decade, much of which has occurred along lakeshores. Although only 3% of the total land area is developed, approximately 40% of the lake shoreline is in residential land use.

About 90% of the land surface in the region is now forested. A century ago the upland vegetation was dominated by white pine, hardwoods and hemlock, but most of it was removed during logging and subsequent burning in the late 1800s and early 1900s. Regrowth of aspen, birch, mixed hardwoods and a few conifers has taken place now, much of it since 1920. Black spruce is common on the wet, peat areas. The sands and sandy loams in the surface layers have produced mostly acid soils (commonly pH 4-5), with low cation exchange capacities (10 meq/100 g) and low base saturation (10-30%). The upland soils are primarily sands and sand loams with peatland soils in the depressions. Total concentrations of calcium and magnesium in these soils are typically 1-2 meq/100 g.

The igneous and metamorphic bedrock underlying these northern Wisconsin counties is part of a southern extension of the Precambrian Canadian Shield. The principal bedrock type is granite, with lesser amount of diorite, schist, gneiss, quartzite, slate and greenstone. The bedrock is overlain by the glacial drift, the most recent of which was deposited during the Wisconsin glaciation. Drift thickness ranges between 10 and 70 m with an average slightly greater than 30 m. The drift is low in calcareous material, calcareous pebbles are found only in the deeper, older drift. Essentially all groundwater contributions to lakes and streams follows a path through the glacial drift. Because most of the lakes occur in pitted glacial outwash or end moraines, they are generally shallow, averaging about 10 m in maximum depth and rarely exceeding 30 m. Consequently, virtually all of the lakes in this study area are situated well above bedrock, encased in thick glacial deposits.

The recent pH of the rainfall has averaged 4.6 annually compared with an estimated 5.6 in the middle 1950s. The climate is cool and wet, with mean July temperatures of 19°C and January temperatures of -11°C. The lakes commonly are ice-covered from late November to late April (Schnoor et al. 1982).

Deposition (kg SO_4^{2-}/ha.yr)	Fraction	Time Period	Reference
17	wet (68 cm)	1981	NADP 1981-83 (Trout Lake)
17	wet (71 cm)	1980	NADP 1981-83 (Trout Lake)
16	wet (84 cm)	1981	NADP 1981-83 (Spooner)
22	bulk	1981	Becker et al. 1982

Annual Precipitation (m)	Annual Runoff (m)
.80	.30

Observed Characteristics

1. Median alkalinity for 117 seepage lakes sampled was 39 μeq/L. Conductivity and colour for the same lakes was 21 μS/cm and 8 Pt units (Eilers et al. 1982). For 409 total sites, 25.4% had alkalinities <40 μeq/L and 22.7% had alkalinities between 40 and 199 μeq/L (Glass 1982).

2. Two separate comparisons of present chemistry with the 500 Wisconsin lake survey of Birge and Juday (1925-41) have found that most lakes have significantly higher pH, alkalinity and conductivity (Bowser et al. 1982; Schnoor et al. 1982). Approximately 20% of lakes sampled had pH declines but the differences were not statistically significant.

3. Hydrologic type appears to control alkalinity. Median values of pH (6.4) alkalinity (39 μeq/L) and conductivity (21 μmohs) were found in seepage lakes (no defined inlet or outlet) (Eilers et al. 1982; Schnoor et al. 1982).

ADIRONDACK MOUNTAINS OF NEW YORK

"As a result of extensive glacial activity, the Adirondack region of northeastern New York State contains a vast and varied ponded water resource. The most recent count adapted from a 1979 inventory of the Adirondack ecological zone (Pfeiffer 1979) reveals that there are approximately 2,877 individual lakes and ponds, encompassing some 282,154 surface acres. The New York State portion of Lake Champlain, 97,000 acres, is purposely excluded from this summary since its low elevation waters are not considered to be representative of the Adirondack uplands. Average size of ponded waters included in this inventory approaches 98 acres and ranges from those of less than one acre to 28,000 acre Lake George." (Pfeiffer and Festa 1980)

The Integrated Lake-Watershed Acidification Study (ILWAS) selected three forested watershed areas (Panther, Woods and Sagamore) in the Adirondack Park region of New York for field investigation. The watershed areas contain terrestrial and aquatic ecosystems having physical, chemical and biological characteristics which distinguish one area from another. Lake outlets are the hydrologic terminal points of all three watersheds. The study watersheds are within 30 km of each other. Runoff in Panther and Woods watersheds drains directly to the lakes without extensive steam development. Sagamore Lake receives the majority of its inflow through a drainage system of bogs and streams. All watersheds contain mixtures of coniferous and deciduous vegetation.

Panther Lake sits on thick till rather than bedrock. The stratigraphy of the till is typically, from top to bottom, sand, sandy till, silty till, and clay till overlying bedrock. The till in Woods Lake basin is primarily sandy till with an average depth of three metres. Panther Lake basin has two till units, a sandy unit and a clay-rich unit; the two units together may be 60 m deep in places. Sagamore Lake basin has four units - a loose sandy unit, a more compact sandy unit, a silt-rich unit, and a clay-rich till. A thick sand deposit greater than 30 m deep, at the site of a glacial meltwater channel, is present near the inlet to Sagamore Lake.

High runoff periods typically occur during snowmelt. A winter thaw has been observed in January and February. A larger spring melt occurs in March and April. During the summer and fall, occasional storms may also generate high runoff.

Deposition (kg SO_4^{2-}/ha.yr)	Fraction	Time Period	Annual Precipitation (m)	Reference
26.4	wet	1981	1.02	NADP 1981-83 (Huntington site)
29	wet	1980		NADP 1981-83 (Huntington site)
34-37	bulk	1965-78		Peters et al. 1981 (Canton site)
39-43	bulk	1965-78		(Hinckley site)
40.03	wet	Jun78-May79	1.25	Johannes et al. 1981
5.38	dry	Jun78-May79		(Wood's Lake - ILWAS)
39.40	wet	Jun78-May79	1.21	Johannes et al. 1981
6.19	dry	Jun78-May79		(Panther Lake - ILWAS)
32.92	wet	Jun78-May79	.98	Johannes et al. 1981
5.71	dry	Jun78-May79		(Sagamore Lake - ILWAS)

Summary of 13 Years (1965-1978) Precipitation Data (Mean + S.D.) (Peters et al. 1981)

Site	Precipitation (cm/yr)	SO_4^{2-} (μeq/L)	NO_3^- (μeq/L)
Canton	94 ± 8	0.104 ± 0.057	0.033 ± 0.034
Hinckley	129 ± 52	0.084 ± 0.039	0.027 ± 0.025

SO_4^{2-} concentration increased by 1-4%/yr, while H^+ has remained unchanged.

NO_3^- has increased by 4-13%/yr.

NO_3^- and SO_4^{2-} loads have increased [% slopes: 12-15% (NO_3^-) and 0.5-0.7% (SO_4^{2-}) for the Canton and Hinckley sites, respectively] due partially to an increase in the amount of precipitation.

Observed Characteristics

1. In the East Branch of the Sacandaga River, SO_4^{2-} concentrations exceed HCO_3^- concentrations. USGS monitoring of the river from 1965 to 1978 indicate an increase in NO_3^- (4 μeq/L.yr), a decrease in SO_4^{2-} (4 μeq/L.yr), and a decrease in alkalinity (83 μeq/L.yr) (Peters et al. 1981).

2. In a 1975 survey of 214 Adirondack lakes at high elevations, pH ranged from 4.3 to 7.4. Fifty-two percent of the lakes had pH <5.0; 7% pH 5.5-6.0 (Schofield 1976c).

3. For a subset of 40 of these 214 lakes, historic data on pH and fish populations are available from the 1930s. Over this period, the number of lakes with pH <5.0 increased from 3 (out of 40) to 19. Likewise the number of lakes without fish increased from 4 to 22. In both surveys, none of the lakes with pH <5.0 had fish.

4. For 138 Adirondack lakes, a comparison of colormetric pH measurements for the 1970s vs. 1930s indicated a general decrease in pH (Pfeiffer and Festa 1980).

5. pH depressions in streams during spring snowmelt and periods of heavy rainfall have been observed (Driscoll et al. 1980; Galloway et al. 1980b).

6. Based on a comparison between lakes in the Adirondack region and within a given lake or stream monitored over time for a one- or two-year period, elevated aluminum concentrations have been demonstrated to be associated with low pH (Driscoll et al. 1980; Schofield 1976).

7. Current status of fish populations (presence/absence) in Adirondack lakes and streams is clearly correlated with pH level. The occurrence of fish is reduced particularly at pH levels below 5.0 (Colquhoun et al. 1980; Pfeiffer and Festa 1980; Schofield 1976). In the 1975 survey of 214 high elevation lakes, in 82% of the lakes with pH < 5.0 no fish were collected. For lakes with pH >5.0, about 11% had no fish collected (Schofield 1976b).

8. The New York Department of Environmental Conservation reported (based on available data) that 180 lakes have lost their fish populations (Pfeiffer and Festa 1980). Although no alternative explanations for this loss of fish are readily apparent, historic records are not adequate to definitely establish acidic deposition as the cause.

9. Survival of brook trout stocked into Adirondack waters was inversely correlated ($p < 0.01$) with elevated aluminum concentrations and low pH (Schofield and Trojnar 1980).

THE HUBBARD BROOK ECOSYSTEM, NEW HAMPSHIRE

The Hubbard Brook Experimental Forest (HBEF) was established in 1955 by the United States Forest Service as the principal research area for the management of watersheds in New England. The name of the area is derived from the major drainage stream in the valley, Hubbard Brook. Hubbard Brook flows generally from west to east for about 13 km until it joins with the Pemigewasset River, which ultimately forms the Merrimack River and discharges into the Atlantic Ocean. Water from more than 20 tributaries enters Hubbard Brook along its course. Mirror Lake, a small oligotrophic lake, discharges into Hubbard Brook at the lower end of the valley. The HBEF is located within the White Mountain National Forest of north central New Hampshire. Although the climate varies with altitude, it is classified as humid continental with short, cool summers and long, cold winters. The climate may be characterized by: (1) changeability of the weather; (2) a large range in both daily and annual temperatures; and (3) equable distribution of precipitation. HBEF lies in the heart of the middle latitudes and the majority of the air masses therefore flow from west to east. During the winter months these are northwesterlies and during the summer the air generally flows from the southwest. Therefore, the air affecting HBEF is predominantly continental. However, during the autumn and winter, as the colder polar air moves south, cyclonic disturbances periodically move up the east coast of the United States providing an occasional source of maritime air. The mean air temperature in July is 19°C and in January is -9°C. A continuous snowpack develops each winter to a depth of about 1.5 m. Occasionally, mild temperatures in midwinter partly or wholly melt the snowpack. A significant microclimatologic feature of this area is that even the uppermost layer of the forest soils usually remains unfrozen during the coldest months because of the thick humus layer and a deep snow cover.

The HBEF covers an area of 3,076 ha and ranges in altitude from 229 to 1,015 m. The experimental watershed ecosystems range in size from 12 to 43 ha and in altitude from 500 to 800 m. These headwater watersheds are all steep (average slope of 20-30%) and face south. The experimental watersheds have relatively distinct topographic divides. The height of the land surrounding each watershed ecosystem and the area have been determined from ground surveys and aerial photography.

The geologic substrate, outcrops of bedrock and stoney till, in the Hubbard Brook Valley was exposed some 12,000-13,000 years ago when the glacial ice sheet retreated northward. Bedrock is derived from highly metamorphosed sedimentary rocks of the Littleton formation and the granitic rocks of the Kinsman formation. The bedrock of watersheds 1-6 is the Litleton formation, which in this area is made of highly metamorphosed and deformed mudstones and sandstones. It is medium to coarse grained and consists of quartz, plagioclase, and biotite with lesser amounts of sillimanite. Much of the area of the experimental watersheds is covered with glacial till derived locally from the Littleton formation. The geologic substrate is considered watertight and losses of water by deep seepage are minimal.

Soils are mostly well-drained spodosols (haplorthods) of sandy loam texture, with a thick (3-15 cm) organic layer at the surface. Most precipitation infiltrates into the soil at all times and there is very little overland flow (Pierce 1967). This is because the soil is very porous, the surface topography is very rough (pit and mound, mostly from wind-thrown trees), and normally there is little soil frost.

Soil depths are highly variable but average about 0.5 m from surface to bedrock or till. Soil on the ridges may consist of a thin accumulation of organic matter resting directly on the bedrock. In some places, impermeable pan layers at depths of about 0.6 m restrict vertical water movement and root development. The soils are acid (pH $\leq$ 4.5) and generally infertile.

The vegetation of the HBEF is part of the northern hardwood ecosystem, an extensive forest type that extends with variations for Nova Scotia to the western Lake Superior region and southward along the Blue Ridge Mountains. Classification of mature forest stands as northern hardwood ecosystems rests on a loosely defined combination of deciduous and coniferous species that may occur as deciduous or mixed deciduous-evergreen stands.

Deposition (kg SO_4^{2-}/ha.yr)	Fraction	Time Period	Annual Precipitation (m)	Reference
36.4	wet	1981	1.50	NADP 1981-83 (Hubbard Brook)
22	wet	1980	.87	NADP 1981-83 (Hubbard Brook)
38.4 ± 2.5	bulk	1964-74	1.30	Likens et al. 1977a
33.7	bulk	Jun63-May64		Likens et al. 1977a
30.0	bulk	Jun64-May65		
41.6	bulk	Jun64-May65		
42.0	bulk	Jun64-May65		
46.7	bulk	Jun64-May65		
31.2	bulk	Jun64-May65		
29.3	bulk	Jun64-May65		
34.6	bulk	Jun64-May65		
33.0	bulk	Jun64-May65		
43.4	bulk	1973-74		
52.8	bulk	1973-74		

Observed Characteristics

1. The external and internal generation of H^+ exerts nearly equal roles in driving the weathering reactions. Input of H^+ is mainly in the form of H_2SO_4 and HNO_3 (Likens et al. 1977a).

2. Average streamwater pH ~ 5. During snowmelt events pH depressions of 1.0 to 2.0 units have been reported (Likens et al. 1977a).

3. The Hubbard Brook ecosystem accumulated hydrogen, nitrate and ammonium ions over the period 1963-74. Over the same period there was a net loss of SO_4^{2-} (Likens et al. 1977a).

4. Ca^{2+} and SO_4^{2-} dominated the streamwater chemistry at the HBEF. SO_4^{2-} was more than 4 times as abundant as the next most abundant anion which was NO_3^- (Likens et al. 1977a).

5. Elevated levels of Al are found in the headwater portions of streams in the HBEF. These levels are 2-29 times above levels in downstream waters. This effect was attributed to leaching of Al hydroride compounds from soils by acidic deposition (N.M. Johnson 1979).

MAINE AND NEW ENGLAND

The 97 lakes sampled by Norton et al. (1981a) ranged in pH from 4.25 to 6.99 (median = 6.40), in elevation from 12 to 1307 m (median = 154 m), surface area from <0.1 to 1098 ha (median = 56 ha), Secchi disc transparency from 2.5 to >5.0 m (median = 6.3 m), and water colour from 0 to 110 Pt units (median = 8 Pt units). The bedrock of the study area was noncalcareous and mostly granitic. As a result, the lake waters were of low alkalinity (0-360 µeq/L, $CaCO_3$; median = 64) and specific conductance (0-68 µmhos/cm at 25°C; median = 29). The watersheds were almost completely forested; very little cutting had occurred in the few decades prior to sampling. Many of the lowland lakes ($\leq$500 m) had cottages along their shores and access roads in their watersheds; the high elevation lakes were pristine and accessible only on foot. In summary, the lakes were small to medium size, ologotrophic to mesotrophic with moderately to very transparent water, low to moderate concentrations of humic solutes, and low alkalinity and conductance, and with moderately disturbed to pristine watersheds. Haines and Akielaszek (1982) sampled a similar set of 226 headwater lakes and streams in the other New England states, including Maine.

Deposition (kg SO_4^{2-}/ ha.yr)	Fraction	Time Period	Annual Precipitation (m)	Reference
28.0	wet	1981	1.10	NADP 1981-83 (Acadia site)
25.31	wet	1981	.87	NADP 1981-83 (Bridgton site)
24.80	wet	1981	1.15	NADP 1981-83 (Caribou site)
17.22	wet	1981	1.10	NADP 1981-83 (Greenville site)
18	wet	1980		NADP 1981-83 (Greenville site)
36.4	wet	1981	1.50	NADP 1981-83 (Hubbard Brook)
22	wet	1980	.87	NADP 1981-83 (Hubbard Brook)
38.4$\pm$2.5	bulk (129.5 cm)	1963-74	1.30	Likens et al. 1976, 1980 (Hubbard Brook)
35	wet	1981	.74	NADP 1981-83 (Bennington VI site)

Observed Characteristics

1. Lakewater pH declines based on comparisons with historical information (Davis et al. 1978) where 85% of 94 lakes studied (Norton et al. 1981 and 64% of 95 lakes studied (Haines and Akielaszek 1982) were found to have lower pHs.

2. Loss of alkalinity from lakewater in the New England states averaging about 98 µeq/L for 56 lakes for which there was historical information (Haines and Akielaszek 1982).

3. Paleolimnological confirmation of pH declines in lakes (Davis et al. 1982). Cores from New England acidic clear water lakes (pH less than 5.5) with undisturbed drainage basins (5 of the 30 lake samples taken over at least the last 50 years) show declines in sediment concentrations of Zn, Ca, Mg and Mn starting as early as about 1880 suggesting increased leaching of sediment delutus prior to entry into the lakes (Davis et al. 1982; Kahl et al. 1982) or reduced sedimentation rate.

4. Accelerated cation leaching from watersheds (Kahl and Norton 1982).

5. Lakes of pH <5 are distributed throughout a range in elevation from 10 to 1000 m. High elevation lakes (>600 m) tend to have low pH and alkalinity. All but two lakes having pH <5.5 were also less than 20 ha in surface area. Alkalinity and pH also increased with stream order (Haines and Akielaszek 1982). Of 226 lakes and streams sampled 25% had alkalinity ≤20 µeq/L, 41% were ≤100 µeq/L and 50% were ≤200 µeq/L (Haines and Akielaszek 1982).

SUMMARY OF EMPIRICAL OBSERVATIONS

SUMMARY

Location	Deposition (kg SO_4^{2-}/ha.yr)	Summary Effects
NORTHERN SASKATCHEWAN	5 wet (1980)	No chemical effects
ELA, ONTARIO	5.9 wet (1980) 9 and 11 bulk (1972-73)	No effect
MINNESOTA	10-15 wet (Nov80) 17 bulk (1977)	No effect

NORTHERN WISCONSIN	16-17 wet (1981)	No effect
ALGOMA, ONTARIO	24.7 wet (1981)	pH depression 2.1 pH units Elevated excess sulphate relative to region not receiving acidic deposition More lakes of low pH than expected Relationship between fish and alkalinity
NOVA SCOTIA	22 wet (1981) APN (Kejimkujik) 17 wet (1980) APN (Kejimkujik) 22.5 wet (1977-80) (CANSAP-Kemptville) 13.2-32 (various years) (CANSAP - various N.S. sites)	Loss of Atlantic salmon populations (historic record). Historic record of decreased pH in river
MAINE	17-28 wet (1981)	Evidence of slight pH decrease in lakes (historic records) No effects on Atlantic salmon No evidence of effects on fish in inland lakes
HUBBARD BROOK, NEW HAMPSHIRE	36 wet (1981) 22 wet (1980) 33-53 bulk (1963-74)	Spring pH depressions No long term change in stream or lake pH 1963-present
MUSKOKA-HALIBURTON	23-29 wet (1976-78) 31-42 bulk	pH depressions Fish kill associated with pH depression in one lake Algal composition related to pH

LAURENTIDE PARK, QUEBEC	22.2-40 wet (1977-80)	Indications of decrease in pH in some lakes, especially in southern region of park (increases in some lakes, especially along roads); indication of decline in angling success in lower pH lakes; pH depression in lakes in spring (Moreau et al. 1982) and lower pH in lakes in spring than summer (Bobée et al. 1982)
ADIRONDACKS	32-40 wet (1978-79) 29 wet (1980) 34-37 bulk (1965-78)	Evidence of pH declines and loss of fish populations over time

Detailed studies of watersheds have been carried out in sensitive regions of North America and Scandinavia under a range of sulphate deposition rates. The results of watershed studies conducted in North America are described below.

For those regions currently experiencing sulphate in precipitation loading rates of ≤ 17 kg/ha.yr there have been no observed detrimental chemical or biological effects.

For regions currently experiencing between 20 and 30 kg/ha.yr sulphate in precipitation there is evidence of chemical alteration and acidification. In Nova Scotia rivers, historical records of salmon population reductions as documented by 40 years of catch records have occurred as well as reductions in stream pH. In Maine there is evidence of pH declines over time and loss of alkalinity from surface waters. In Muskoka-Haliburton there is historical evidence of loss of alkalinity for one lake. There is documentation of pH depressions in a number of lakes and streams. Fish kills were observed during spring melt in one lake. In the Algoma region there are elevated sulphate and aluminum levels in some headwater lakes.

For regions currently experiencing loading ≥ 30 kg/ha.yr there are documented long-term chemical and/or biological effects and short-term chemical effects in sensitive surface waters.

In Quebec, sulphate concentrations in surface waters decrease towards the east and north in parallel with the deposition pattern. Sulphate concentrations are equal to or greater than the bicarbonate concentration in lakes in the south west part of the Province.

In the Adirondack Mountains of New York, comparison of data from the 1930s with recent surveys has shown that more lakes have been acidified. Fish populations have been lost from 180 lakes. Elevated aluminum concentrations in surface waters have been associated with low pH and survival of stocked trout is reduced by the almuninum.

In the Hubbard Brook study area in New Hampshire there is pH depression in streams during snowmelt of 1 to 2 units. Elevated levels of aluminum were observed in headwater streams.

3.9.2.2 Short-Term or Episodic Effects

While current and historical survey data may imply long-term trends, the samples usually represent only one or a few measurements at any one location and are usually collected only during 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 short-term changes in water chemistry coincide with sensitive periods in the life cycle of fish, significant mortality and reduced reproduction can occur.

Severe pH depressions in streams and small lakes due to snowmelt have been documented in a number of locales (e.g., Kahl and Norton 1982; Schofield 1973). The depression may be as much as 1-2 pH units. Much of the metal content of the snowpack is also released in early melting stages. Thus critical hydrogen ion and trace metal levels may be reached temporarily, even in waters with relatively high summer pH values. Leaching of metals from soils and sediments may be especially severe during this period, resulting in pulses of high concentrations of potentially toxic metals (e.g., Al > several hundred ppb [Kahl and Norton 1982; Schofield and Trojnar 1980]).

The question has often been raised, "How long does it take before the lakes become acidic?" The previous sections have indicated relationships for lakes and streams which have already been acidified. However, the rate of change is one of the least well-defined aspects of the acidification phenomenon. The rate-of-change questions become less relevant in light of evidence that current acid loadings are causing damage to fisheries and other biota due to short-term exposures to low pH and associated high metal concentrations, as reviewed earlier in this report.

The pH of lakes or streams tends to fluctuate considerably during the year, and average annual pH is a composite of these patterns. Thus, summertime or annual pH has limited value for determining effects on organisms which may respond to extreme concentrations of H^+ or metals over a few days. This, plus the known significance of brief acute exposure (Spry et al. 1981), suggests that the magnitude and duration of short-term increases in H^+, associated with a defined "flushing event", could be used for further evaluating critical dose/ response relationships in stream ecosystems, and lakes.

Research on brook trout and white sucker by Baker (1981), Baker and Schofield (1980), on Atlantic salmon by Daye (1980) and Daye and Garside (1975, 1977, 1980), and related research by Beamish and Harvey (1972), Beamish (1974a, 1974b, 1976), and Harvey (1975, 1979, 1980) has provided a broad understanding of the response of several pH-sensitive fish species to both long-term and short-term elevated H^+ and aluminum exposures. Mortalities have been documented for chronic pH depression, and effects on egg viability, hatching success and adult survival for short-interval acute H^+ and aluminum exposures are reasonably well known (Baker and Schofield 1980).

Among the experimentally-based relationships developed by Daye, Garside, Baker and Schofield is a recurring pattern (Loucks et al. 1981):

1) the short-term acute exposure, or "shock", effects, including responses to aluminum, can take place in two to four days of exposure, with as little change as 0.5 to 1.5 units of the pH scale; and

2) these shock exposures can be expected to occur in waters with a broad range of pH above the level at which chronic effects occur.

Stream water chemistry studies from a number of locations (Table 3-26) show short-term pH depressions during snowmelt and storm events (e.g., 1.0 unit on the Shavers Fork River in West Virginia [Dunshie 1979]) and from 1.0 to 2.0 units in two watersheds being studied in the Adirondacks (Galloway et al. 1980b). A third lake studied by Galloway et al. (1980b) at the Adirondack site had a mean annual pH of about 4.8 and shows no pH depression during flushing event. Likens et al. (1977a) reported pH depressions of 1.0 to 2.0 units for Hubbard Brook, New Hampshire. Outside the regions with snow accumulation, the maximum pH decline during a flushing event appears to occur during major rainfall events following a rain free period (Dunshie 1979).

Sulphate loadings associated with observed short-term pH declines and resulting biological effects are summarized in Table 3-26. In the ELA, Ontario, annual loadings of sulphate in precipitation of about 10 kg SO_4^{2-}/ha.yr have generally resulted in pH declines of only 0.2-0.3 units and no apparent biological effects. Depressions in pH of 0.3-1.0 units have been observed in northern Minnesota streams receiving approximately 14 kg SO_4^{2-}/ha.yr. However,

TABLE 3-26. PERIODIC pH DEPRESSIONS OBSERVED IN STREAMS AND LAKES WITH DIFFERENT SULPHATE LOADINGS AND CORRESPONDING BIOLOGICAL EFFECTS. SURFACE WATER ALKALINITIES IN THESE AREAS ARE GENERALLY LESS THAN 200 μEQ/L.

Location	Annual Sulphate Loading (kg SO_4^{2-}/ha.yr by wet deposition)	Lowest pH Observed	pH Largest Difference Between Spring pH and summer or winter values	Observed Biological Effect
Tovdal R. Norway	40	pH shock suspected but no field measurements taken during the fish kill		Fish kill (sea trout)[a]
L. Timmevatten Sweden (1970)	40	4.2	0.8	Wild population of minnows have disappeared[b]
Sweden (1972)	40	4.3	1.1	Caged sea trout and minnows experienced 68% and 59% mortality[b]
Hubbard Brook Experimental Forest			1.2	No biological studies
Panther L. ILWAS Project New York	38	4.8	2.5	No biological data available; fish population lst from one lake[j]
Muskoka-Haliburton Ontario (4 streams)	30	4.1	1.1	Evidence of fish population damage in areas lakes[c] and actual algae species[d]
(lake outflows)	30	4.8	1.3	
Plastic Lake Ontario Inlet	30	4.0	1.7	100% mortality of caged rainbow trout[f]
Outlet	30	5.0	0.7	13% mortality of caged rainbow trout[f]
Shavers Fork W. Virginia (stream)	30	5.6	0.9	Conditions caused by heavy rain; no biological studies[e]
Algoma		5.0	2.1	No biological studies[h]
Filson Creek, Northern Minnesota	14	5.5	0.3-1	No biological studies[i]
Experimental Lakes Area Ontario	10	4.5 has been observed generally above 5	0.2-0.3	No apparent biological effect[g]

[a] Braekke 1976
[b] Hultberg 1977
[c] Harvey 1980
[d] Nicholls et al. 1981
[e] Dunshie 1979
[f] Harvey et al. 1982
[g] Mills pers. comm.
[h] Keller and Gale 1982
[i] Siegel 1981
[j] Church and Galloway 1983

the lowest pH reading recorded is 5.8 and no biological studies have been conducted.

Galloway and Dillon (1982) have examined the relative importance of sulphuric and nitric acids in causing alkalinity (and pH) reduction during snowmelt and conclude that a major portion of the reduction in alkalinity during snowmelt was attributable to nitric acid. Although SO_4^{2-} itself showed little variation during snowmelt, its continued large presence in the stream was responsible for the alkalinity reduction in an indirect manner, namely by causing long-term alkalinity reductions (as opposed to episodic). Thus, the episodic reduction of alkalinity due to NO_3^- is added to the long-term reduction in alkalinity due to SO_4^{2-}. Jeffries et al. (1981) demonstrated that in Muskoka-Haliburton the increase in hydrogen ion concentration in several streams during snowmelt was due to increases in both NO_3^- and SO_4^{2-}.

3.9.2.3 Sensitivity Mapping and Extrapolation to Other Areas of Eastern Canada

TERRESTRIAL

In order to identify the magnitude of the surface water acidification problem our ability to extrapolate the results of the detailed watershed study areas to the remainder of eastern North America must be determined. Within eastern North America are hundreds of thousands of lakes and streams and it is clearly impractical to establish detailed or regional hydrochemical monitoring for them all. However, there is an urgent need to determine if the watershed study areas currently being monitored are anomalous in terms of their geochemical characteristics or if, in fact, they are representative of conditions occurring over large areas of eastern North America.

An early approach to this problem in Canada was to consider all of the Precambrian Shield as "sensitive" and then assume any study area located anywhere on the Shield would be representative of over 75% of eastern Canada (Altshuller and McBean 1979). This approach implied that the Canadian Shield was a single granitic plate and not, as is the case, a number of complex geological provinces composed of a variety of rock types (including marble) and covered, in places, by unconsolidated material of varying texture and carbonate content (Section 3.5). Areas outside the Shield, where hydrochemical changes have occurred (e.g., the Maritime Provinces), also exhibit a range of soil and bedrock conditions.

A major drawback to more detailed analyses and extrapolation has been the lack of the analyses of information on surficial and bedrock geological conditions for all of eastern North America, in a regional but detailed form. This has recently been alleviated for Canada with bedrock sensitivity mapping of Shilts et al. (1981) which has been incorporated into the bedrock-soil mapping composite of Lucas and

Cowell (1982). This mapping is discussed in more detail in Section 3.5. In order to determine the representativeness of three of the detailed watershed study areas, (Algoma, Muskoka-Haliburton and southwest Nova Scotia), the 65 classes of soil and bedrock characteristics mapped by Lucas and Cowell (1982) will be utilized.

The basis for extrapolation is the 1:1,000,000 scale map shown in Figure 3-9 (in map folio). This mapping represents the most detailed compendium of soil and bedrock characteristics yet assembled for all of eastern Canada. Extrapolation has been carried out by reviewing the kinds of soil and bedrock terrains which form the geochemical templates of three of the watershed study areas and then determining how representative these areas are in eastern Canada.

The 65 classes of terrain characteristics are listed in Tables 3-27 and 3-28. Each class is identified according to a two or three character alpha-numeric code which is defined in Table 3-8. Table 3-27 lists the area and percent cover of each class north and south of 52°N latitude for each province. [Figure 3-9 shows only the areas south of 52°N.] Table 3-28 summarizes the area and percent cover of each class for all of eastern Canada. This table indicates that 54% of eastern Canada is composed of bedrock types in combination with soil types which have a low potential to reduce acidity. These are predominately noncalcareous sands and sandy tills overlaying granitic-type bedrock. Within the area south of 52°N, 51% or 911,089 km^2 is considered as having a low potential to reduce acidity of atmospheric deposition prior to entering surface waters.

Terrain Characteristics of Three Specific Study Areas

Terrain classes are based on bedrock geology, percent bedrock exposed, soil depth and soil texture or depth to carbonate (Table 3-8; Section 3.5). Table 3-29 shows the terrain classes for watersheds within which the study lakes and rivers occur. These results have been obtained by directly overlaying the watershed areas for Algoma, Muskoka-Haliburton and Nova Scotia onto Figure 3-9.

By far the greatest proportion of each area is composed of terrain classes interpreted as having a low potential to reduce the acidity of atmospheric deposition (69 to 98%). The most complex area and the one with the greatest range of terrain conditions is Algoma which has up to 69% has a low potential to reduce acidity, 25% interpreted as having a moderate potential, almost 5% with a high potential to reduce acidity and less than 1% organic terrain (which has not been interpreted).

Two low potential terrain classes dominate in each area. In Algoma and Muskoka-Haliburton these are the L3 (41.79% and 59.42%, respectively) and the L4c (21.05% and 32.25%, respectively) classes; in Nova Scotia these are the L4b (53.15%) and L4c (27.11%) classes.

TABLE 3-27. COVERAGE OF TERRAIN TYPES IN EASTERN CANADA INTERPRETED FOR THEIR POTENTIAL TO REDUCE ACIDITY (H = HIGH, M = MODERATE, L = LOW AND O = ORGANIC TERRAIN) AND SUMMARIZED BY PROVINCE

Terrain Class (Potential to Reduce Acidity)		Ontario (total area = 1,068,587 km^2)						Quebec (total area = 1,540,687 km^2)						Newfoundland/Labrador (total area = 393,173 km^2)						New Brunswick (total area = 73,437 km^2)		Nova Scotia (total area = 55,491 km^2)		Prince Edward Island (total area = 5,656 km^2)	
		South of 52°N Latitude		North of 52°N Latitude		Provincial Total		South of 52°N Latitude		North of 52°N Latitude		Provincial Total		South of 52°N Latitude		North of 52°N Latitude		Provincial Total		South of 52°N Latitude		South of 52°N Latitude		South of 52°N Latitude	
		km^2	% of Zone	km^2	% of Zone	km^2	% of Province	km^2	% of Zone	km^2	% of Zone	km^2	% of Province	km^2	% of Zone	km^2	% of Zone	km^2	% of Province	km^2	% of Zone	km^2	% of Zone	km^2	% of Zone
1. High	H1a	35,426	5.07	35,258	9.81	70,684	6.62	6,720	0.89			6,720	0.44	1,369	0.72			1,369	0.35	117	0.16				
	H1b	56,448	8.07			56,448	5.28	5,630	0.74			5,630	0.37	32	0.01			32	0.00	2,516	3.43	1,334	2.40		
	H1c	665	0.09			665	0.06	7,239	0.96			7,239	0.47	52	0.03			52	0.00	125	0.17	24	0.04		
	H1e	61	0.01			61	0.01	937	0.12			937	0.06									6	0.01		
	H1f	109	0.01			109	0.01																		
	H1g	4,118	0.58			4,118	0.39							3,865	2.04			3,865	0.98	6	0.01				
	H1h	1,261	0.18			1,261	0.12	3,481	0.46			3,481	0.23							249	0.34	314	0.57		
	H1i	4,984	0.71			4,984	0.47							410	0.22			410	0.10	1,603	2.18	1,962	3.54		
	H1j	641	0.09			641	0.06	764	0.10			764	0.05												
	H2a	880	0.13	3,034	0.84	3,914	0.37							403	0.21			403	0.10						
	H2b	20	0.01	2,230	0.62	2,250	0.21							1,082	0.57			1,082	0.28	2,135	2.91				
	H3a	8,885	1.27	2,018	0.56	10,903	1.02	6,776	0.90	2,616	0.33	9,392	0.61	272	0.14			272	0.07						
	H3b	26,802	3.83	1,964	0.55	28,766	2.69	30,573	4.04	1,951	0.25	32,524	2.21	2,223	1.17			2,223	0.57	1,957	2.66				
	H3c	48,703	6.96	13,520	3.76	62,223	5.82	34,735	4.60	3,986	0.51	38,721	2.51	476	0.25			476	0.12						
Total High Potential		189,003	27.04	58,024	5.43	247,027	23.13	96,855	12.80	8,553	1.09	105,408	6.85	10,184	5.37			10,184	2.59	8,708	11.86	3,640	6.56		
2. Moderate	M1a							86	0.01	7,018	0.90	7,104	0.46												
	M1c									83	0.01	83	0.01												
	M1d	20	0.01			20	0.01			5,523	0.70	5,523	0.36												
	M1f															9,615	4.72	9,615	2.45						
	M1i									2,325	0.30	2,325	0.15												
	M1j															489	0.24	489	0.12						
	M1n									1,038	0.13	1,038	0.07												
	M1o									3,114	0.40	3,114	0.20												
	M1p	68	0.01	566	0.16	634	0.06	106	0.01			106	0.01												
	M1q	48	0.01			48	0.01																		
	M1r	692	0.10			692	0.07	3,264	0.43	1,869	0.24	5,133	0.33			8,520	4.18	8,520	2.17						
	M1s									374	0.05	374	0.02												
	M1t	219	0.03	1,520	0.42	1,739	0.16	479	0.06			479	0.03												
	M1u									415	0.05	415	0.03												
	M1v			14	0.00																				
	M2a			82	0.01	82	0.01																		
	M2b	982	0.14			982	0.09																		
	M3	8,086	1.16	46,726	13.01	54,812	5.13	2,679	0.35			2,679	0.17							1,931	2.63	966	1.74		
	M4a	156	0.02			156	0.02			789	0.10	789	0.05	1,251	0.66	12,881	6.32	14,132	3.59	157	0.21				
	M4b	34,084	4.88			34,084	3.19	38,451	5.08	23,087	2.94	61,538	3.99	24,074	12.72	61,093	29.97	85,167	21.66	4,066	5.54	14,658	26.41	2,654	46.92
	M4c	9,382	1.34			9,382	0.88																		
	M5	6,737	0.96	6,027	1.68	12,764	1.20							789	0.42			789	0.20	223	0.30				
	M6a	566	0.08	1,684	0.47	2,250	0.21	9,538	1.26	2,367	0.30	11,905	0.77												
	M6b	1,820	0.26	5,523	1.54	7,343	0.69	23,629	3.12	13,537	1.73	37,116	2.41							3,409	4.64	3,429	6.18		
	M7a	9,021	1.29			9,021	0.84	7,537	0.10	17,523	2.23	25,060	1.63							1,465	1.99				
	M7b	13,569	1.94	2,420	0.67	15,989	1.50	36,654	4.84	20,513	2.62	57,167	3.81	886	0.47			886	0.23	21,967	29.91	8,397	15.13		
	M7c	33,403	4.78	17,973	5.00	51,376	4.81	9,840	1.30			9,840	0.64	111	0.06			111	0.03	2,910	3.96	567	1.02		
Total Moderata Potential		118,935	17.02	82,453	7.72	201,388	18.87	132,213	17.47	99,575	12.70	231,788	15.03	27,111	14.33	92,598	23.55	119,709	30.45	36,128	49.20	28,017	50.49	2,654	46.92
3. Low	L1b									3,322	0.42	3,322	0.22												
	L1c	143	0.02			143	0.01			6,395	0.82	6,395	0.42												
	L1d	4,971	0.71	18,395	5.12	23,366	2.19	93	0.01	27,655	3.53	27,748	1.80			29,686	14.56	29,686	7.55						
	L1e	212	0.03	730	0.20	942	0.09			233	0.03	233	0.02	469	0.25	8,761	4.30	9,230	2.35						
	L2a	273	0.04			273	0.03	423	0.06	46,755	5.96	47,187	3.06												
	L2b	525	0.08			525	0.05	1,585	0.21			1,585	0.10			40	0.02	40	0.01						
	L2c	273	0.04	11,632	3.24	11,905	1.11																		
	L2d	11,837	1.69			11,837	1.11	13,977	1.85	131,047	16.71	145,025	9.41												
	L3	157,075	22.48			157,075	14.70	152,865	20.20	121,746	15.53	274,612	17.82	48,643	25.69	35,977	17.65	84,620	21.52	3,875	5.27	7,009	12.63		
	L4a	1,207	0.17			1,207	0.11			4,277	0.55	4,277	0.28	10,019	5.29	92	0.05	10,111	2.57						
	L4b	29,194	4.18			29,194	2.73	53,661	4.45	32,222	4.11	65,883	4.28	23,109	12.21	20,025	9.82	43,134	10.97	11,253	15.32	9,043	16.30	3,002	53.08
	L4c	89,251	12.77			89,251	8.35	253,001	33.44	276,543	35.36	529,549	34.37	33,799	17.85	13,618	6.68	47,417	12.06	3,501	4.77	6,538	11.78		
	L4d	21	0.00			21	0.00																		
Total Low Potential		294,982	42.21	30,757	2.88	325,739	30.50	455,847	60.25	649,964	82.89	1,105,811	71.78	31,039	61.29	108,199	27.52	224,238	57.03	18,629	25.37	22,590	40.71	3,002	53.08
4. Organic Terrain	O1a	45,964	6.58	154,399	42.98	200,363	18.75	5,385	0.71			5,385	0.35												
	O1b	13,147	1.88	23,414	6.52	36,561	3.42	1,042	0.14	913	0.12	1,955	0.13	1,610	0.85	300	0.15	1,910	0.49						
	O1c	5,353	0.77	7,271	2.02	12,624	1.18	1,430	0.19	2,824	0.36	4,254	0.28	23,233	12.27	2,256	1.11	25,489	6.48	9,972	13.58	610	1.10		
	O1d	30,859	4.42	13,392	3.73	4,425	4.14	63,872	8.44	21,800	2.78	85,672	5.56	11,154	5.89	489	0.24	11,643	2.96			634	1.14		
	O2a	34	0.01			34	0.00																		
	O2c									207	0.03	207	0.01												
	O2d	170	0.02			170	0.02			207	0.03	207	0.01												
	O3a	48	0.01			48	0.01																		
	O3c	55	0.01			55	0.01																		
	O3d	327	0.05			327	0.03																		
Total Organic Terrain		95,957	13.73	198,476	18.57	294,433	27.56	71,729	9.48	25,951	3.32	97,680	6.34	35,997	19.01	3,045	0.77	39,042	9.93	9,972	13.58	1,244	2.24		
Total for Zone		698,877	100	369,710	100	1,068,587	100	756,644	100	784,043	100	1,540,684	100	189,331	100	203,842	100	393,173	100	73,437	100	55,491	100	5,656	100

TABLE 3-28. SUMMARY OF TERRAIN TYPES AND POTENTIAL TO REDUCE ACIDITY FOR ALL OF EASTERN CANADA

Terrain Types (Potential to Reduce Acidity)	South of 52°N Latitude (area = 1,779,436 km^2)		North of 52°N Latitude (area = 1,357,595 km^2)		Total for Eastern Canada (area = 3,137,031 km^2)	
	km^2	% of Zone	km^2	% of Zone	km^2	% of Eastern Canada
H1a	43,632	2.45	35,258	2.60	78,890	2.51
H1b	65,690	3.71			65,960	2.10
H1c	8,105	0.46			8,105	0.26
H1e	1,004	0.06			1,004	0.03
H1f	109	0.00			109	< 0.01
H1g	7,989	0.45			7,989	0.25
H1h	5,305	0.30			5,305	0.17
H1i	8,959	0.50			8,959	0.29
H1j	1,405	0.08			1,405	0.08
H2a	1,283	0.07	3,034	0.22	4,317	0.14
H2b	3,237	0.18	2,230	0.16	5,467	0.17
H3a	15,933	0.90	4,634	0.34	20,567	0.66
H3b	61,555	3.46	3,915	0.29	65,470	2.09
H3c	83,914	4.72	17,506	1.29	101,420	3.23
Total High Potential	308,390	17.33	66,577	4.90	374,967	11.95
M1a	86	<0.01	7,018	0.52	7,104	0.23
M1c			83	0.01	83	< 0.01
M1d	20	<0.01	5,523	0.41	5,543	0.18
M1f			9,615	0.71	9,615	0.31
M1i			2,325	0.17	2,325	0.07
M1j			489	0.04	489	0.02
M1n			1,038	0.08	1,038	0.03
M1o			3,114	0.23	3,114	0.10
M1p	174	0.01	566	0.04	740	0.02
M1q	48	<0.01			48	< 0.01
M1r	3,956	0.22	10,389	0.77	14,345	0.46
M1s			374	0.03	374	0.01
M1t	698	0.04	1,520	0.11	2,218	0.07

TABLE 3-28. CONTINUED

Terrain Types (Potential to Reduce Acidity)	South of 52°N Latitude (area = 1,779,436 km^2)		North of 52°N Latitude (area = 1,357,595 km^2)		Total for Eastern Canada (area = 3,137,031 km^2)	
	km^2	% of Zone	km^2	% of Zone	km^2	% of Eastern Canada
M1u			415	0.03	415	0.01
M1v			14	0.01	14	< 0.01
M2a	82	<0.01			82	< 0.01
M2b	982	0.06			982	0.03
M3	13,662	0.77	46,726	3.44	60,388	1.93
M4a	1,564	0.09	13,670	1.01	15,234	0.49
M4b	117,987	6.63	84,180	6.20	202,167	6.44
M4c	9,382	0.53			9,382	0.30
M5	7,749	0.44	6,027	0.44	13,776	0.44
M6a	10,104	0.57	4,051	0.30	14,155	0.45
M6b	32,237	1.81	19,060	1.40	51,297	1.64
M7a	18,023	1.01	17,523	1.29	35,546	1.13
M7b	83,473	4.58	22,933	1.69	104,406	3.33
M7c	46,831	2.63	17,973	1.32	64,804	2.07
Total Moderate Potential	345,058	19.39	274,626	20.23	619,684	19.76
L1b			3,322	0.24	3,322	0.11
L1c	143	0.01	6,395	0.47	6,538	0.21
L1d	5,064	0.28	75,736	5.58	80,800	2.58
L1e	914	0.05	9,491	0.70	10,405	0.33
L2a	705	0.04	46,755	3.44	47,460	1.51
L2b	2,110	0.12	40	<0.01	2,150	0.07
L3	369,467	20.76	157,723	11.62	527,190	16.80
L4a	11,226	0.63	4,369	0.32	15,595	0.50
L4b	109,262	6.14	52,247	3.85	161,509	5.15
L4c	386,090	21.70	290,162	21.37	676,252	21.55
L4d	21	< 0.01			21	<0.01
Total Low Potential	911,089	51,20	788,920	58.11	1,700,009	54.19

TABLE 3-28. CONTINUED

Terrain Types (Potential to Reduce Acidity)	South of 52°N Latitude (area = 1,779,436 km^2)		North of 52°N Latitude (area = 1,357,595 km^2)		Total for Eastern Canada (area = 3,137,031 km^2)	
	km^2	% of Zone	km^2	% of Zone	km^2	% of Eastern Canada
01a	51,349	2.89	154,399	11.37	205,748	6.56
01b	15,799	0.89	24,627	1.81	40,426	1.29
01c	40,598	2.28	12,351	0.91	52,949	1.70
01d	106,519	5.99	35,681	2.63	142,200	4.53
02a	34	<0.01			34	< 0.01
02c			207	0.02	207	< 0.01
02d	170	0.01	207	0.02	377	0.01
03a	48	<0.01			48	0.01
03c	55	<0.01			55	< 0.01
03d	327	0.02			327	0.01
Total Organic Terrain	214,899	12.08	227,472	16.76	442,371	14.10

TABLE 3-29. TERRAIN CHARACTERISTICS OF WATERSHEDS CONTAINING THE DETAILED STUDY AREAS OF EASTERN CANADA

Terrain Class	Algoma km^2	Algoma %	Muskoka-Haliburton km^2	Muskoka-Haliburton %	Southwest Nova Scotia km^2	Southwest Nova Scotia %
L2b			116.1	6.52		
L3	3,380.7	41.79	1,058.1	59.42	154.8	1.36
L4a	283.9	3.51				
L4b	225.8	2.79			6,045.2	53.15
L4c	1,703.2	21.05	574.2	32.25	3,083.9	27.11
Total L	5,593.6	69.14	1,748.4	98.19	9,283.9	81.62
M4b	1,838.7	22.73			1,419.4	12.48
M7a	109.7	1.36				
M7b	25.8	0.32				
M7c	116.1	1.44	19.4	1.09		
Total M	2,090.3	25.85	19.4	1.09	1,419.4	12.48
H1b	45.2	0.56				
H1c	264.5	3.27				
H1i	77.4	0.96				
Total H	387.1	4.79				
O1a	12.9	0.16				
O1c					509.7	4.48
O1d	6.5	0.08	12.9	0.72	161.3	1.42
Total O	19.4	0.24	12.9	0.72	671.0	5.90
Study Area	8,090.4		1,780.7		11,374.3	

It is assumed that these classes represent the terrestrial geochemical template for the three study areas. The other "low" potential classes are very minor in these watersheds and one would expect little or no effect of acidic deposition in basins dominated by "moderate" and "high" potential templates.

In the Muskoka-Haliburton watersheds, nine of the lakes and associated tributary streams which have been monitored closely occur entirely within the L3 class. Detailed lake basin mapping by Jeffries and Snyder (1983) for 6 of the lakes indicate that this L3 class is predominately composed of their "Minor Till Plain" and "Thin Till" classes overlaying gneiss bedrock. These two surficial types represent between 84.3 and 94.0% of the basins of Red Chalk, Blue Chalk, Chub, Dickie, Harp and Jerry lakes.

The three dominant terrain classes in these study areas (L3, L4b and L4c) are composed of the following: (1) L3 - shallow sands and acidic type rocks (granite, gneiss, quartzite or other alkalic rocks) which outcrop in 0-49% of the map area; (2) L4b - deep sands overlaying ultramafic, serpentine and noncalcareous sedimentary rocks outcropping in 0-49% of the unit; and (3) L4c - deep sands overlaying bedrock similar to L3. These classes represent dominant conditions in a map area. At this scale of mapping (1:1,000,000) other subdominant conditions probably occur. However, the evidence from more detailed mapping at Muskoka-Haliburton, as described above, indicates that the descriptions are representative. It should be noted further that the term "sands" refers to the matrix texture; the deposit it represents is most commonly a till or glacial-fluvial outwash which include larger sized fragments.

Results of Terrain Extrapolation

Table 3-27 provides the basis of extrapolation by province and Table 3-28 for all of eastern Canada. Terrain classes L3, L4b and L4c, which represent the major geochemical templates for the watershed study areas, are three of the four most common terrestrial types. In eastern Canada, they cover 17% (527,190 km^2), 5% (161,509 km^2) and 22% (676,252 km^2) respectively (Table 3-28). They represent over 80% of the sensitive terrain types in Eastern Canada. Other classes which cover significant areas but are not represented in the study areas are H3c (deep clay overlying granitic rocks), O1a (organic deposits overlying carbonate rocks), O1d (organic deposits overlying granitic rocks), and L2d (shallow sand overlying granitic rocks with 50-74% outcropping).

Approximately one-fifth of eastern Canada (690,117 km^2) currently receives loadings of about 20 kg/ha.yr or more of SO_4^{2-} in precipitation in 1980. Within this loading zone terrain classes L3, L4b and L4c cover 18% (127,237 km^2), 6% (40,222 km^2) and 22% (153,545 km^2) respectively. In total, the three terrain types cover 46.52% of eastern Canada within the 20 kg/ha.yr, or higher, loading of SO_4^{2-} in precipitation. This is an area of 321,004 km^2 (125,192 mi^2) which represents 99% of all those areas with the lowest potential to reduce acidity within this loading zone. These areas occur primarily on the Grenville Province of the Precambrian Shield in southern Quebec and Ontario as well as in the Appalachian Region of New Brunswick and Nova Scotia (Figure 3-9).

These results indicate that over one-half of eastern Canada, is representative of terrain characteristics (Table 3-8) under which aquatic acidification effects have been observed.

From these results, it is concluded that terrain characteristics in the three watershed study areas are correlated with measured acidification effects, especially as expressed by alkalinity measurements. These three study areas are not anomalous but are representative of larger portions of Eastern Canada as defined by these terrain characteristics.

AQUATIC

As shown in the previous section the bedrock and surficial geology of the study areas are typical of large areas of eastern Canada. However specific watersheds with varying glacial deposits (kame, spillway, till, etc.) rock component hardness (i.e., resistance to weathering) and varying hydrological characteristics result in surface waters of varying alkalinity and total cation concentrations within each study area.

Hydrochemical data from the Muskoka-Haliburton area of Ontario also compares closely with mapped terrain conditions. Average annual and spring T.I.P. alkalinity values for 9 lakes within the Muskoka-Haliburton study area are all lower than 71 µ eq/L (Table 3-30). Five of these lakes are considered very sensitive on the basis of their alkalinity regime (<40 µeq/L). The basins of all 9 lakes are composed primarily of shallow to deep ($\leq$2 m) sandy tills overlaying gneiss (class L3 and L4c). In addition there is a close correlation between terrain class and alkalinity regime for a population of 141 lakes sampled throughout Haliburton County and Muskoka District. Table 3-31 shows the occurrences of lake alkalinities grouped by sensitivity classes, in each of the mapped terrain types. There is clearly a strong relationship with 77.5% of the lowest alkalinity lakes (0-39.9 and 40-199.9 µeq/L) occurring in terrain classes L3 and L4c. It is not possible, at present, to extrapolate the results of Table 3-31 to all the areas of eastern Canada mapped in these two terrain classes.

Further support for the representativeness of the study areas is drawn from the water quality data. Figures 3-49 and 3-50 show the distribution of lake alkalinities for a series of geographical areas on sensitive and moderately sensitive terrain. The data are taken

TABLE 3-30. AVERAGE ANNUAL OR SPRING TOTAL INFLECTION POINT ALKALINITIES FOR NINE LAKES IN THE MUSKOKA-HALIBURTON WATERSHED STUDY AREA (data from Ontario Ministry of Environment)

Lake	Time of Record	Alkalinity mg/L	Alkalinity µeq/L
Harp	1979-80	3.32	66.4
Dickie	1979-80	0.762	15.24
Chub	1979-80	0.798	35.96
Red Chalk	1979-80	3.15	63.0
Blue Chalk	1979-80	3.53	70.6
Jerry	1979-80	3.31	66.2
Plastic	Spring/79	0.62 ± 0.5	12.4 ± 10.0
Heney	Spring/79	0.34 ± 0.5	6.4 ± 10.0
Crosson	Spring/80	0.49 ± 0.5	9.8 ± 10.0

TABLE 3-31. DISTRIBUTION OF 141 LAKE ALKALINITIES, GROUP BY SENSITIVITY CLASSES, IN VARIOUS TERRAIN TYPES OCCURRING IN HALIBURTON COUNTY AND MUSKOKA DISTRICT, ONTARIO

Terrain Class	Map Area (km^2)	Alkalinity Classes (μeq/L)			
		0-39.9 (%)	40-199.9 (%)	200-499.9 (%)	500 (%)
L3	4283.9	34 (24.1)	61 (43.4)	3 (2.1)	6 (4.4)
L4C	1645.2	5 (3.5)	9 (6.4)	7 (4.9)	
L2d	206.5	3 (2.1)	3 (2.1)		
L2b	141.9	4 (2.8)	3 (2.1)		
H1c	109.7		2 (1.4)		
H1i	51.6			1 (0.7)	
M4b	25.8				
M7c	45.2				
O1d	25.8				
Total	6535.6	46 (32.5)	78 (55.4)	11 (7.7)	6 (4.4)

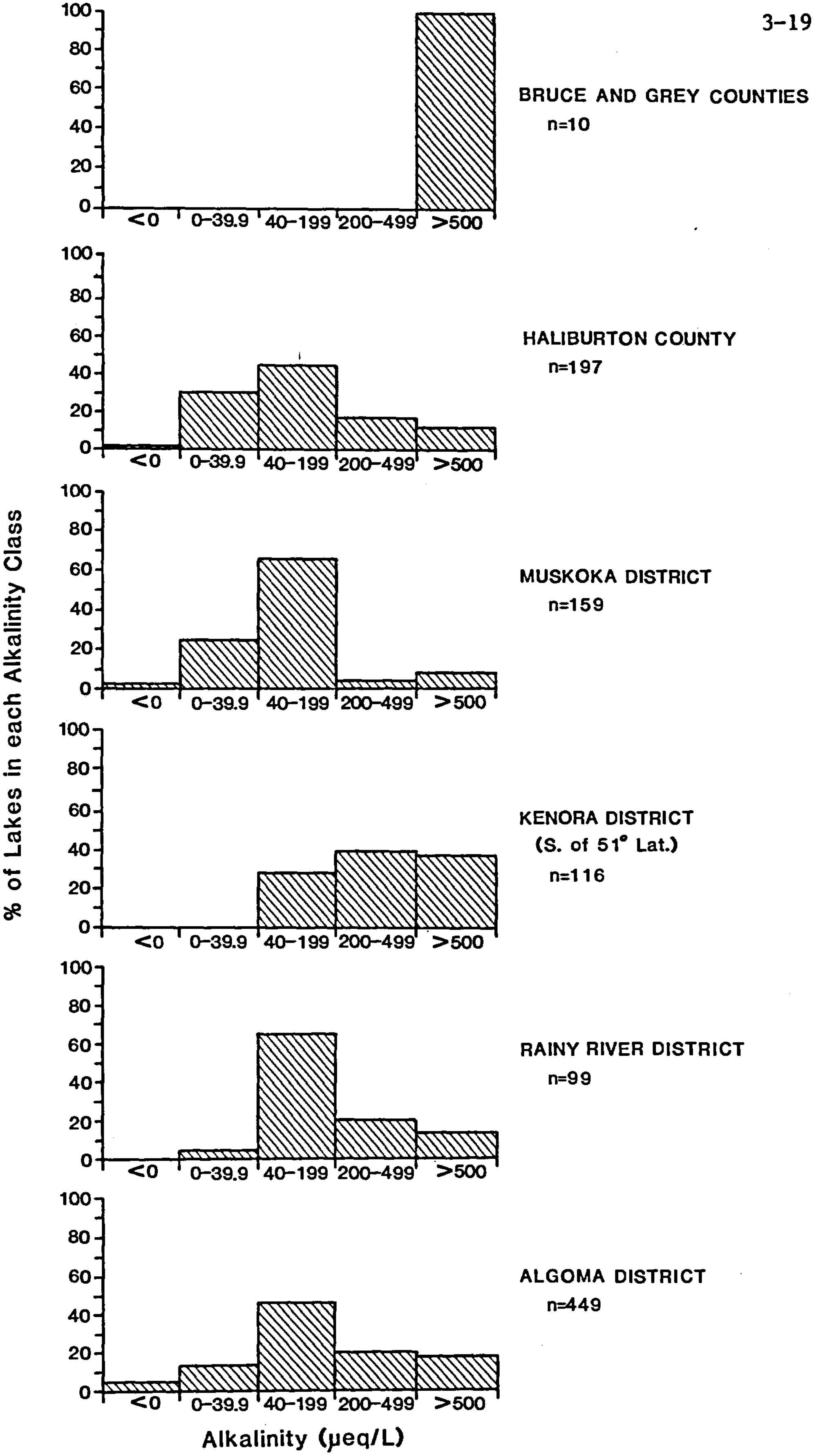


Figure 3-49. Distribution of alkalinity values for lakes in six regions on Ontario.

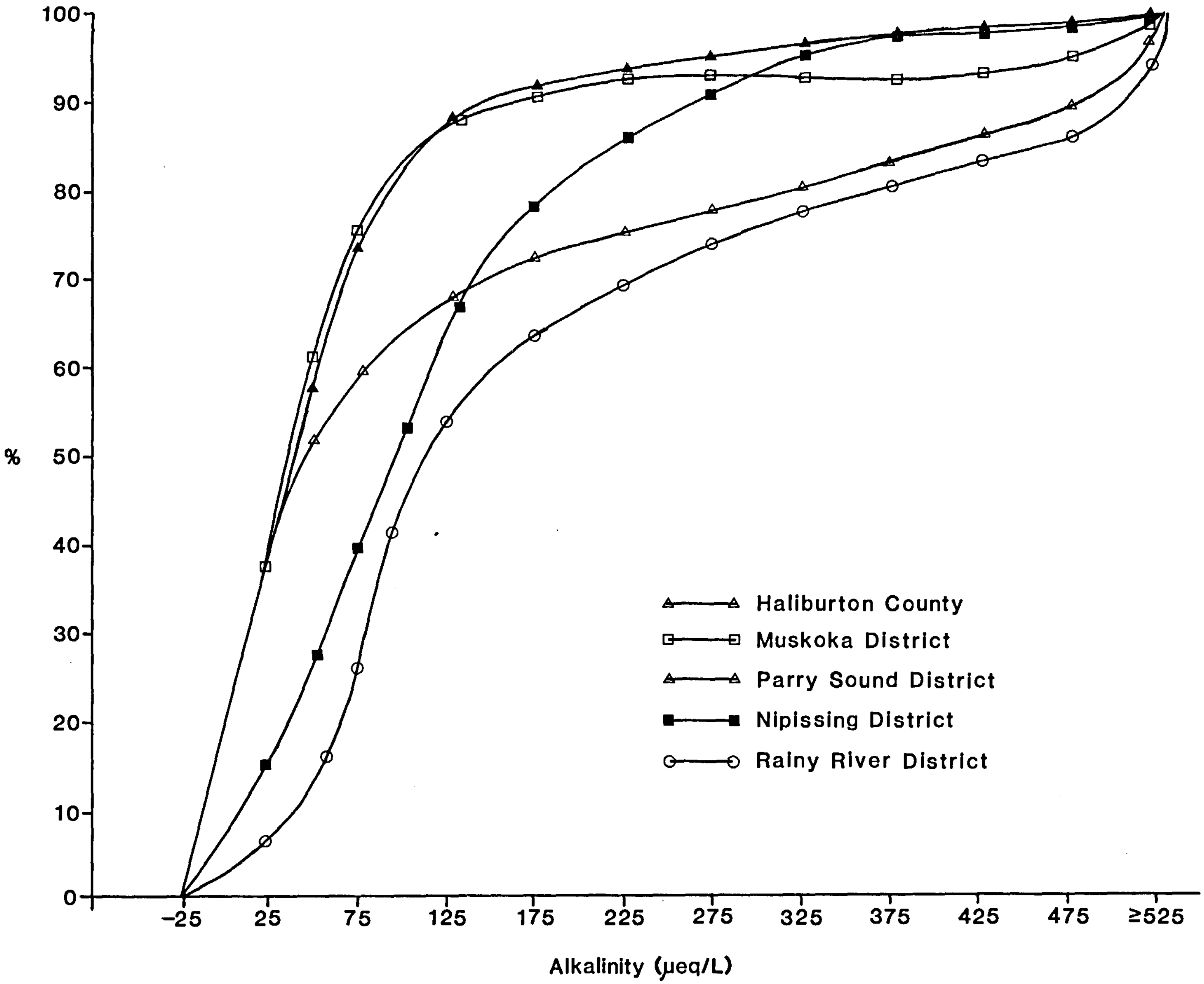


Figure 3-50. Cumulative distribution of alkalinity values for lakes in five regions of Ontario (Dillon 1982).

from Table 3-12. The percentage distribution of lake alkalinities are similar in all areas and contrast strongly with the alkalinities of 10 lakes in Bruce and Grey Counties which are located on calcareous till in southern Ontario (nonsensitive terrain)..

While the alkalinity distributions are similar, there are some important differences. The distributions for Haliburton, Muskoka, and Algoma have already been altered in that there is a greater number of lakes with low alkalinity than in the Kenora or Rainy River Districts or in background areas such as Northern Saskatchewan. Dillon (1982) further demonstrated the differences in alkalinity values for lakes in the areas of higher sulphate deposition (Muskoka-Haliburton and Parry Sound) by plotting the cumulative distributions (Figure 3-50). It is accepted that alkalinity distributions are already influenced by acid loadings in some areas and to reflect natural conditions the distributions should be shifted to the right as plotted in Figures 3-49.

Within each study area, the number of lakes for which detailed data are available is small relative to the total number of lakes. Therefore, it is important to show that the intensive study lakes and rivers themselves are representative of the surface waters of the sensitive areas. There are a total of 18 calibrated study lakes at ELA (1), Algoma (5), Muskoka-Haliburton (8), Quebec (1) and Nova Scotia (3). The current alkalinities show 2 less than 0 μeq/L, 7 in the 0-40 μeq/L range and 9 in the 40-200 μeq/L range. Lakes above 200 are not subjected to intensive studies since acidification effects are minimal. In addition, Ontario has extensive information on five calibrated lake studies near the point sources in Sudbury which is used to contrast effects of local sources and long range transport. Of the 22 rivers in Nova Scotia used in analysis of salmon catch data, current alkalinities range from less than zero (acidic) to 173 μeq/L (Figure 3-47).

The study lakes and streams are located in areas with terrain characteristics and have alkalinity values similar to other sensitive areas in Canada. Therefore, the effects observed in the study lakes and rivers in response to specific loading rates should be similar in other water bodies in these sensitive areas. Similarly, loading rates protective of these study lakes should be protective of other sensitive waterbodies.

Possible Magnitude of Effects

The Canadian members of the Work Group have concluded that an indication of the extent of the current water quality effects may be derived for all of Ontario using the information presented in Section 3.6.1. The Precambrian area east of Algoma contains some 50,000 lakes (Cox 1978). The distribution of alkalinity values for lakes in districts within the 20 kg/ha.yr wet SO_4^{2-} *deposition isopleth (from Table 3-12) indicates that about 20% or about 10,000 lakes have alkalinity values and acid loadings that are combining to* *currently cause pH depression to values (less than 5.5) likely to be causing biological damage.*

Cox (1978) has indicated that the lake counts underestimate the number of lakes with surface areas less than one hectare by as much as a factor of three so the 50,000 and 10,000 numbers are both underestimates.

The data for the 57 headwater streams in Muskoka-Haliburton show that 65% experience minimum pH values less than 5.5 and 26% have minimum pH values less than 4.5 (Figure 3-21). Although the total number of miles of streams within the 20 kg/ha.yr wet SO_4^{2-} *deposition isopleth is not known and quantitative extrapolations are not possible, it is clear that many miles of stream water must also currently experience pH depressions to levels that can potentially cause biological damage.*

There is a larger area of lakes underlain by Precambrian rock in Quebec and the Maritime provinces where the acid loadings are at least as much as those at Algoma. While specific lake count data are not available, it is likely that many thousands of lakes are currently receiving acidic deposition.

In both Ontario and Quebec many more thousands of lakes are slightly less sensitive to acidic deposition and may experience biological damage in the future if the acid deposition continues.

In general, the total number of lakes being affected now in all Precambrian areas of eastern North America is measured in the tens of thousands with even more sensitive to effects in the future.

The U.S. members of the Work Group believe the statements in this section cannot be supported by the facts. The combined analysis of lake survey data, terrestrial mapping data and deposition data is an interesting methodology. Pending validation, the U.S. members have too many concerns about the influence of uncontrolled variables to consider its use more than speculative. One important variable is the level of dry deposition from local sources which can affect the representativeness of the survey lakes. Other factors which may determine the overall neutralizing capacity of a watershed system in addition to terrain class include elevation, hydrologic routing time, lake morphometry and vegetative cover. We therefore cannot support the conclusions in this section in the absence of further methodological validation.

3.9.3 Use of Acidification Models

A number of process-oriented (mechanistic) models have been developed (or are under active development) that simulate in detail the flow of acidic precipitation through terrestrial systems and the resulting chemical response of surface waters. These models have the potential to predict stream and lake responses (e.g., pH depressions) to episodic events, but most of them are not suitable for predictions of long-term ecosystem responses. Examples of these process-oriented models include the ILWAS model (Chen et al. 1982), the Birkenes model (Christophersen et al. 1982), and the trickel-down model (Schnoor et al. 1982). Each of these models has achieved some success in relating short-term variations in water chemistry of small drainage basins to hydrology and chemistry of precipitation. These models, while calibrated for specific watersheds have not been validated on a temporal or spatial scale that permits their general application with significant confidence.

More global modeling efforts, such as those of Hough et al. (1982), and USFWS (1982) have formulated detailed mechanistic submodels but have not developed them to the level of working codes. Thus, prediction of the dynamic response at the aquatic regime to the atmospheric loading remains to be achieved at this time. However, several efforts towards development of empirical or semi-empirical steady state models relating aquatic chemistry to the atmospheric loading stress have advanced to the point that response estimates are possible within the limits of assumptions of the models.

Three important general points must be made about these models. First, validation (especially for surface waters in North America) remains to be achieved. Second, each of these models is based upon individual, specific sets of asumptions regarding their application. Application of these models is therefore limited by the degree to which these assumptions are met. Third, these models are not dynamic and therefore, determination of the rates of reaction between sulphate deposition and lake water pH based on the models is not possible. The models rely on steady state conditions. With these important points in mind, potential use of these models for quantitative estimates of the relationship of SO_4^{2-} deposition to lake pH is discussed below.

The earliest empirical acidification model was developed by Almer et al. (1978) and modified by Dickson (1980, 1982), who related lake pH and excess SO_4^{2-} load (concentration of excess SO_4^{2-} multiplied by annual runoff) for arbitrary classifications or groupings of Swedish lakes. Since this relationship is, in effect incorporated by Henriksen (1979, 1980, 1982) in his model, it will not be discussed in detail here.

3.9.3.1 The "Predictor Nomograph" of Henriksen

Henriksen (1979, 1980) has studied atmospheric and edaphic influences on the chemistry of oligotrophic lakes in Scandinavia and has developed empirical formulations relating these influences to acidification. He has derived an acidification "indicator," a quantitative acidification "estimator," and an acidification "predictor nomograph" (Henriksen 1979, 1980). Of these formulations, only the "predictor nomograph" is intended for use as a predictive tool.

Henriksen (1980) developed his "predictor nomograph" of freshwater acidification based on the hypothesis that "acidified waters are the result of a large scale acid base titration." He compared the concentration of "Ca* + Mg*" with lakewater SO_4* concentrations (* indicates "excess concentration" -- that above contributions from seasalts) in the pH range 5.2-5.4 and 4.6-4.8 using data from 719 lakes in southern Norway (Wright and Snekvik 1978) and obtained "highly significant" linear correlations. The line for the pH range 5.2-5.4 agreed very well with a theoretical titration nomograph of bicarbonate concentration vs. (H^+ added), assuming that bicarbonate concentration is directly proportional to (Ca* + Mg*) concentration and that (H^+ added) is proportional to SO_4* concentration. The line for the pH range 4.6-4.8 did not agree with such a theoretical bicarbonate titration nomograph, but Henriksen (1980) argued that his deviation was readily explained by the effects of dissolved aluminum leached from soils. To complete his predictor nomograph, Henriksen (1980) added a Ca* concentration axis parallel to the (Ca* + Mg*) axis and a precipitation pH axis parallel to the SO_4* axis (Figure 3-51). The former was derived from correlations of Ca* concentrations and (Ca* + Mg*) in lake waters; the latter was derived by combining: (1) a correlation of SO_4* concentration in lake water to SO_4* concentration in precipitation, and (2) a correlation of SO_4* concentration in precipitation to H^+ concentration in precipitation. Henriksen (1982) added an axis of SO_4* in precipitation parallel to the axis of SO_4* in lakewater based on his 1980 regression.

Henriksen (1979, 1980) derived his predictor nomograph for pristine, oligotrophic lakes in areas with granitic or siliceous bedrock types and thin podsolic soils. In these lakes that have been receiving acidic deposition, SO_4^{2-} is the major anion. Prior to the advent of acidic deposition, Ca^{2+} and HCO_3^- were the dominant ions in these lakes. Lakes used to develop the relationships had low concentration of organic acids. The lakes ranged in area from 0.1 to 30 km^2 and in 90% of the lakes the Ca^{+2} concentration was less than 80 µeq/L. None of the lakes was on a major river (i.e., had very large watersheds) (Wright and Snekvik 1978).

Henriksen (1980) verified the predictor nomograph with an independent data set from an October 1974 survey of 155 Norwegian lakes (Wright and Henriksen 1978). These lakes ranged in area from 0.25 to 1.0 km^2, occurred at the head of undisturbed watershed drainage basins, and constituted 5% or more of their watersheds (Wright and Henriksen 1978). Henriksen (1980) found that for over 85% of the lakes, the nomograph correctly predicted a pH "grouping" ($pH < 4.7$ -- "acid lakes", 4.7 pH <5.3 -- "transition lakes", $pH > 5.3$ -- "bicarbonate lakes"). He also found that the nomograph was valid for 18 "large lakes" in southern Norway.

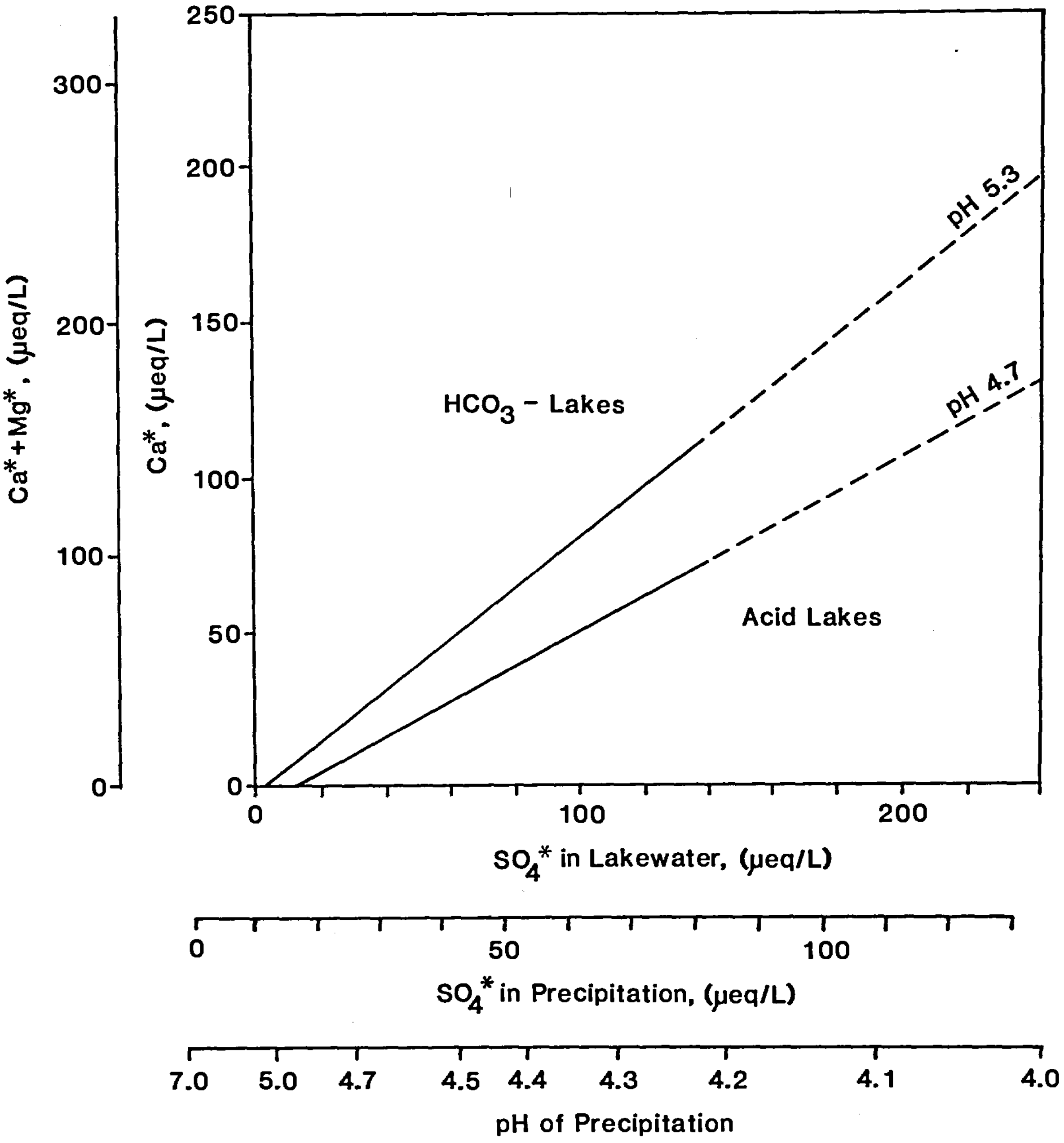


Figure 3-51. Nomograph to predict the pH of lakes given the sum of nonmarine calcium and magnesium concentrations (or nonmarine calcium concentration only) and the nonmarine sulphate concentrations in lake water (or the weighted-average hydrogen ion concentration in precipitation) (Henriksen 1982).

Henriksen (1980) concluded that the nomograph could successfully predict lake pH changes in response to changes in the pH of the precipitation of the particular composition for that area and, if the titration process of lake acidification is reversible, the nomograph could be used to indicate the amount of decrease in precipitation acidity necessary to restore acid lakes to bicarbonate lakes.

A number of assumptions and cautions pertain to the use of the predictor nomograph. One assumption initially inherent in the predictor nomograph was that increases or decreases in the acidity of precipitation do not affect the rate of leaching of Ca^{2+} or Mg^{2+} from soils. As Henriksen (1980) noted, this is a matter of debate (e.g., see Almer et al. 1978; Dillon et al. 1979) and a question that "certainly deserves further attention." If, for example, increased acidity of precipitation does cause increased cation leaching from soils (instead of decreased lake pH), then the titration hypothesis on which the nomograph is based is violated and extrapolations from the precipitation pH axis will be incorrect.

Henriksen (1982) has performed further research on this particular problem. Using data from lakes in Norway, Sweden, Canada, and the U.S., he: (1) compared historic and recent concentrations of (Ca* + Mg*), and (2) evaluated ranges of (Ca* + Mg*) concentrations in lakes in similar geologic settings over a gradient of acidic deposition. In some cases he found that (Ca* + Mg*) concentrations increased in conjunction with higher levels of acidic deposition. In other cases he found no such concurrent increases. For the data he examined the maximum value of a "base cation increase factor" for the lake waters would be about 0.4 μeq (Ca* + Mg*)/μeq SO_4* (Henriksen 1982). Thus, estimates of the effect of changes in acidic deposition on the chemistry of lake waters still require knowledge of the degree of increase of base cation concentrations, ranging from 0 μeq (Ca* + Mg*)/μeq SO_4* to roughly 0.4 μeq (Ca* + Mg*)/μeq SO_4*. This applied to certain lakes in Sweden, Norway, and North America where there was enough historical information to make an estimate. However, he does state (p.38, Henriksen 1982) for Lake Rishagerodvatten, Sweden, the factor was 0.63, and the Birkenes model (Christophersen et al. 1982) predicts an increase factor of about 0.55. Dickson (1980) showed increases greater than 0.4 for some Swedish west coast lakes.

The increase factor represents possible responses of the watershed system to acidic deposition. It reflects the geologic and hydrologic sensitivity of the system. The lowest limit of the increase factor is zero, which refers to a system with little base exchange capacity in the organic soil, quartz (SiO_2) sands for the mineral soil, and/or a lake in which precipitation does not flow through soils. Perfect seepage lakes without any drainage area other than lake area would qualify as systems with near-zero increase factors based on the lack of flow through neutralizing soils. The maximum upper limit would be a watershed with calcareous soils or bedrock which would serve as a perfect buffer and yield an increase factor of 1.0 μeq (Ca + Mg)/μeq SO_4^{2-}.

The leaching of aluminosilicate minerals in response to hydrogen ion attack has been studied in the laboratory. Wollast (1967) found a dissolution increase factor of 0.33 initially with respect to hydrogen ion attack in 5% K-feldspar solutions. Furrer and Stumm (1982) found a 0.4 increase factor in the dissolution of Al_2O_3. The factors that control a watershed's neutralizing capacity, and hence the cation increase factor, are not well known and are critical.

A second caution noted by Henriksen (1980) is that the predictor nomograph should not be applied to waters containing high concentrations of organic acids. Not only may the organic acids affect lake pH in a manner independent of precipitation acidity, but also ionic Ca^{2+} and Mg^{2+} may be overestimated inasmuch as analyses for these ions include Ca^{2+} and Mg^{2+} bound to organics (Henriksen 1980). A final point to note is that the derivation and verification of this model is based upon the premise that the observed data represent steady state conditions, both for concentrations and pH in deposition, and concentrations and pH in lake water.

A key question is whether the "predictor nomograph" is applicable to sensitive lakes in northeastern North America. Relationships between Ca* and (Ca* + Mg*) and between concentrations of these cations and SO_4* may be different in regions of varying geochemistry in North America. Furthermore, the empirical relationship between SO_4* in lake waters and SO_4* in precipitation (as well as the relationship between SO_4* in precipitation and pH of precipitation) may vary in different geographical regions. Therefore, for more accurate predictions it would be appropriate to develop region-specific regression relationships and predictor nomographs like Henriksen's from data bases for the regions of interest. Such studies would be a useful extension of Henriksen's model and should be pursued.

Church and Galloway (1983) examined data from two small oligotrophic headwater lakes in the Adirondacks and found, using only the (Ca* + Mg*) and lake water (SO_4*) axes, that the nomograph correctly predicted the pH for all 66 measurements in a "bicarbonate lake" and 71% of 78 measurements for an "acid-transition lake". However, they also found that the relationship between the precipitation pH axis and lake water (SO_4*) axis for the Adirondacks differs significantly from the relationship for southern Norway. This is possibly due to the different contributions of nitric and sulphuric acids to precipitation acidity or to the presence of other cations in precipitation in the two geographic regions. The variation of nitric and sulphuric acid contribution to acidity of precipitation has been further shown by Barrie (1982). Because as shown in Section 3.9.1, nitrate has only minor influences on long-term acidity of the aquatic regime in comparison with sulphate, only the relationships to sulphate loading are considered in this section. For water pH values less than 4.7, the presence of aluminum or of other buffering apparently becomes important as shown by Henriksen (1980, 1982) and may affect regression lines. However, we are more concerned with the "transition" sector of the Henriksen nomograph.

Haines and Akielaszek (1982) examined data from 122 New England lakes in relation to the predictor nomograph. The nomograph correctly predicted 6 of 7 lakes in the pH range <4.7 but incorrectly predicted that 19 other lakes with higher pH values fell in this grouping. The nomograph correctly predicted 5 of 14 lakes that fell in the pH range 4.7 - 5.3 but incorrectly predicted that 32 lakes not in this range had such pH values. Of the 101 lakes in the pH range >5.3, the nomograph correctly predicted 60%.

For those New England lakes the nomograph predicted the pH of acidic lakes correctly but frequently predicted lower pH values than were actually observed in higher pH lakes. These differences may occur because the relationships of calcium, magnesium, and sulphate are different in New England than they are in Norway, where the model was developed. Application of the predictor nomograph in New England should be based on empirical relationships that exist in this region. Presently the relationship between lake sulphate concentration and atmospheric sulphate deposition has not been established for this region.

Keeping in mind the important limitations and assumptions inherent in its use, we have attempted an application of this approach to estimating the effects of SO_4^{2-} deposition on the chemistry of lakes in northeastern North America. Numerous lakes in Norway have calcium concentrations less than 50 µeq/L, and Bobée et al. (1982) found that 7.5% (15) of 199 lakes sampled on the Precambrian Shield of the Province of Quebec had calcium concentrations less than 50 µeq/L. Haines and Akielaszek found that 11% (25) of 226 lakes and streams in New England had calcium concentrations less than 50 µeq/L. This indicates that such a limit would include all except the more sensitive waters. From the regressions given by Henriksen on: (1) the relationship of both (Ca* + Mg*) vs. alkalinity and (Ca*) vs. alkalinity I and thus (Ca*) vs. (Ca* + Mg*)I (Henriksen 1980), and (2) the relationship of strong acidity to SO_4* and (Ca* + Mg*)I both with and without increased leaching of base cations (Henriksen 1982)I, we can roughly estimate a SO_4* concentration that yields a pH of 5.3 in surface waters having initial Ca* concentrations of 50 µeq/L. Using the regression given by Henriksen (1980) on the relationship of lake SO_4* concentration to SO_4* concentration in precipitation and assuming an annual rainfall of 100 cm, we can then estimate loading rates consistent with maintenance of a pH of 5.3 or greater (pH 5.3 is the upper limit of Henriksen's transition zone). The results of such calculations and the regression equations used are given in Table 3-32. Estimated loading values of wet sulphate deposition that will maintain lakewater pH at values $\geq$5.3 range from approximately 26 kg/ha.yr (assuming no increased leaching of base cations) to approximately 43 kg/ha.yr (assuming leaching of base cations of 0.4 times the change in excess sulphate concentration (see Henriksen 1980) and an initial lake SO_4* concentration of 0 µeq/L).

TABLE 3-32. CALCULATION OF WET SULPHATE LOADINGS CONSISTENT WITH pH 5.3 OR GREATER IN LAKES WITH INITIAL CALCIUM CONCENTRATION OF 50 μeq/L OR GREATER (Regressions are from Henriksen [1980, 1982])

	Condition			
All Units (μeq/L) (except where noted)	No Leaching of Base Cations	Leaching of Base Cations (according to Eqn (4) below) .4	.2	.1
Ca^*_i	50	50	50	50
$(Ca^* + Mg^*)_i$	70	70	70	70
$(Ca^* + Mg^*)_p$	70	128	121	114
$(SO_4^*)_w$	81	146	138	130
$(SO_4^*)_p$	53	87	83	78
$(SO_4^*)_L$ (kg/ha.yr)	26	43	41	39

$SO_4{}^*{}_i$ - concentration of excess sulphate in lake water prior to "acidification" (i.e., initial SO_4^* concentration)
Ca^*_i - initial excess calcium concentration
$(Ca^* + Mg^*)_i$ - initial sum of excess calcium plus excess magnesium concentrations
$(Ca^* + Mg^*)_p$ - predicted sum of excess calcium plus excess magnesium concentration
$(SO_4^*)_w$ - final concentration of excess sulphate in lake water
$(SO_4^*)_p$ - concentration of excess sulphate in precipitation
$(SO_*)_L$ - areal wet sulphate loading assuming annual rainfall of 100 cm

Equations Used in Calculations

(1) $(Ca^* + Mg^*)_i = 1.32\ (Ca^*)_i + 4.3$ (adapted from Henriksen 1980)
(2) $(SO_4^*)_w = [1.01\ (Ca^* + Mg^*) + 1.8]/0.9$ (assuming no leaching of base cations; Henriksen 1982)
(3) $(SO_4^*)_w = [1.01\ (Ca^* + Mg^*)_p + 1.8]/0.9$ (assuming maximal leaching of base cations; Henriksen 1982)
(4) $(Ca^* + Mg^*)_p = (Ca^* + Mg^*)_i + 0.4\ (SO_4^*)_w$ (Henriksen 1982)
(5) $(Ca^* + Mg^*)_p = (Ca^* + Mg^*)_i + 0.4\ (SO_4{}^*{}_w - SO_4{}^*{}_i)$

Substituting Equation 5 into Equation 3 and solving for $(SO_4^*)_w$ yields

(6) $(SO_4^*)_w = 2.04\ (Ca^* + Mg^*)_i + 3.64 - 0.82\ (SO_4^*)_i$
(7) $(SO_4^*)_p = [(SO_4^*)_w + 19]/1.9$ (Henriksen 1980)
(8) $(SO_4^*)_L = (SO_4^*)_p/2$ (assuming 100 cm annual rainfall)

3.9.3.2 Cation Denudation Rate Model (CDR)

Thompson (1982) developed a model relating the pH of a river to the atmospheric loading of excess sulphate and the rate of cations from a watershed via runoff (the Cation Denudation Rate or CDR). This model is designed to apply to areas with acid-resistant bedrock, till, and soils and relatively unbuffered surface waters.

In most fresh waters the sum of base cations (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}) closely approximates the sum of anions HCO_3^- and SO_4^{2-} after correction for seasalt or road salt contributions. Thompson (1982) noted that if excess sulphate concentration is plotted against the sum of the cation concentrations, a series of lines can be generated, each line representing constant bicarbonate concentration. If the partial pressure of CO_2 (P_{CO2}) in the surface water in question is constant, then each line also represents constant pH. This model may be applied to either rivers or lakes (Thompson 1982; Thompson and Hutton 1982). If a runoff value of 1 m/yr is assumed and the concentrations of terms in the axes of Figure 3-52 are multiplied by this value, the axes become loading rates, and the figure becomes a plot of cation denudation rate (CDR, $meq/m^2.yr$) versus the discharge rate of excess sulphate (Thompson 1982). If all the atmospheric sulphate deposited on the watershed is contained in runoff and if we assume that all non-seasalt sulphate comes from atmospheric loading, then the abscissa is equivalent to atmospheric loading of acid sulphate. Note that if wind-blown dust has neutralized some of the sulphuric acid in atmospheric deposition, the loaing terms in Figure 3-52 must be corrected for these neutral salts. Thus, according to the model, if CDR, runoff, excess sulphate load, and P_{CO2} are known, mean pH can be estimated.

An example of how model calculations are made is given below. 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 estimates that the resultant runoff water (assuming a yield of 1 m/yr) will have a mean pH of 5.6 (Figure 3-52). As the rate of excess SO_4^{2-} loading approaches the CDR, the runoff water will approach a pH of 5.1 (at which HCO_3^- alkalinity is totally exhausted). Data for very soft water rivers in Nova Scotia and Newfoundland that have mean runoff rates near 1 m/yr are shown in Figure 3-52. These rivers have a total CDR ranging from 55 to 200 $meq/m^2.yr$. In 1973 at least three of these rivers received SO_4^{2-} loads exceeding their CDR and had median pH values less than 5.1.

At first glance the CDR model appears to be quite similar to the predictor nomograph of Henriksen. The CDR model is developed strictly from consideration of charge balance, however, whereas the predictor nomograph is strongly dependent on empirical observations. Thompson (1982) explicitly assumes that CDR is independent of acid loading; that it varies only with discharge. The recent data review by Henriksen (1982) shows that CDR cannot be considered to be

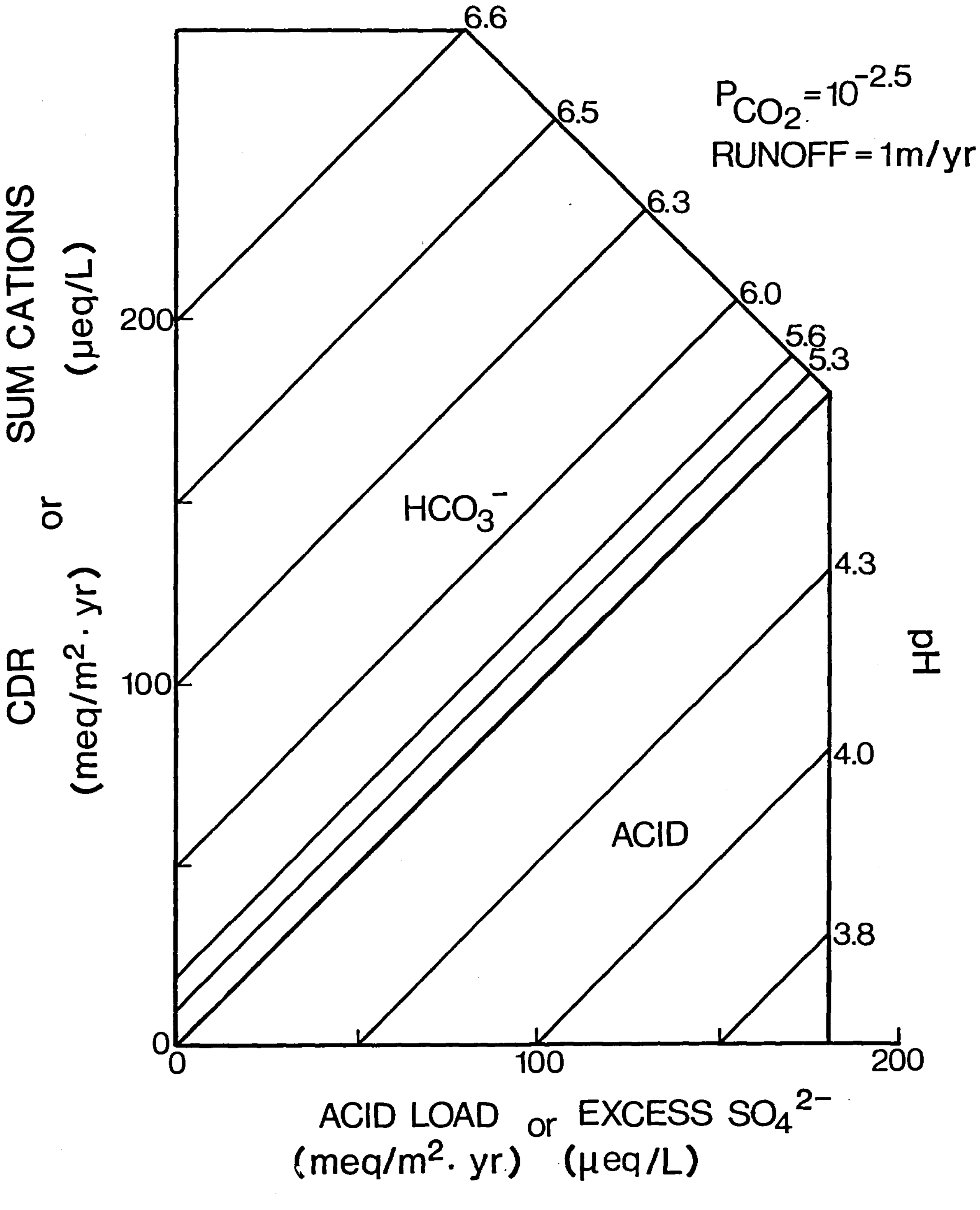


Figure 3-52. The model plot - pH predicted for consideration of the sum of cations and sulphate (modified from Thompson 1982).

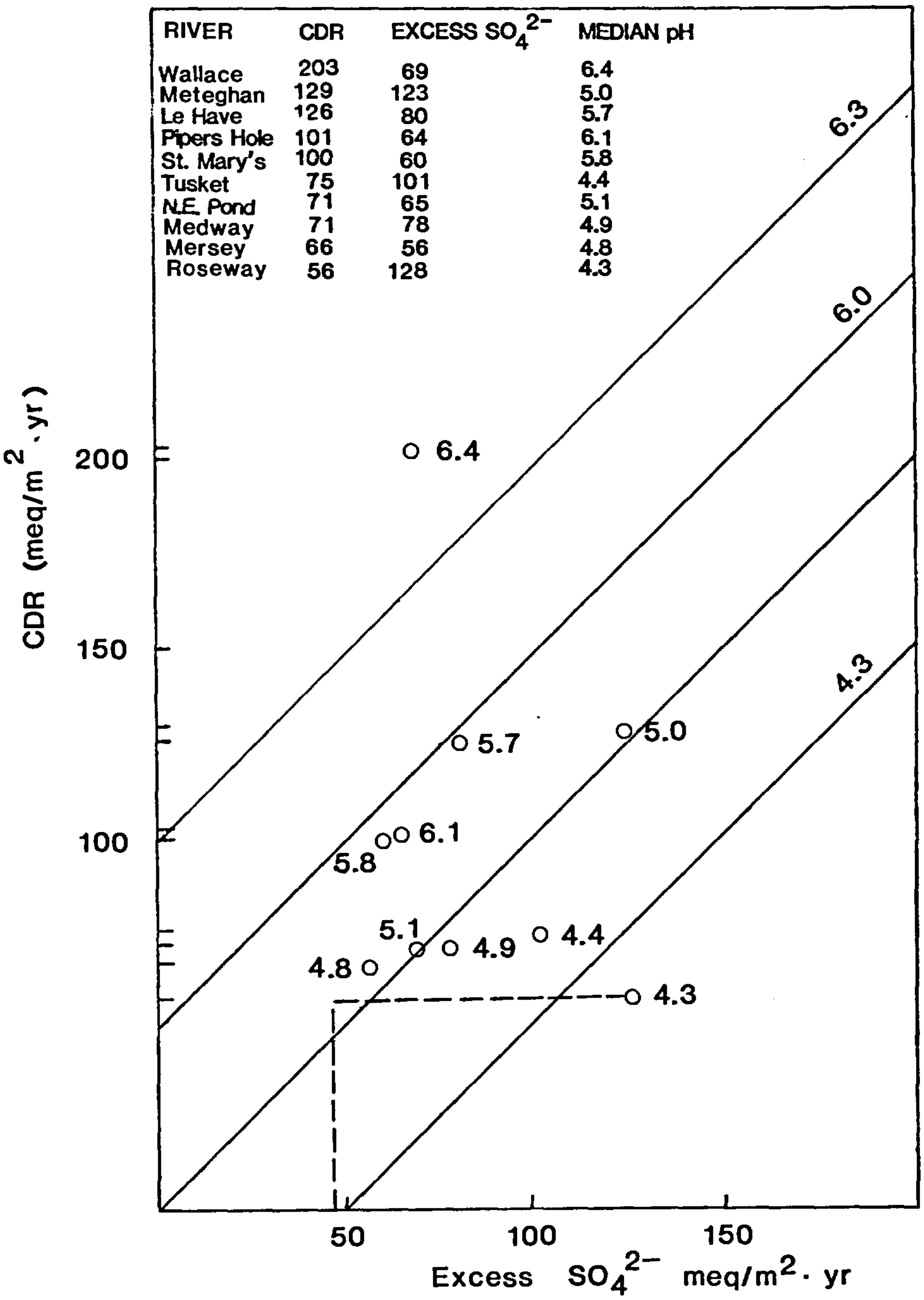
constant in all cases. Thompson et al. (1980) compared data from between 1954-55 and 1973 for very soft water rivers in southern Nova Scotia. They found a lower pH and higher excess SO_4^{2-} concentrations in the most recent data but did not find significant changes in major cation loads.

A way in which the CDR model is similar to Henriksen's predictor nomograph is that it does not apply in situations where organic acids strongly influence pH. The CDR differs, however, in that it does not consider the possible effects of buffers other than bicarbonate. Also, P_{CO2} must be known to estimate pH with the CDR model. As is commonly known, P_{CO2} varies significantly in surface waters.

Haines and Akielaszek (1982) applied the CDR model to data from 122 New England lakes. The CDR model gave better results than the predictor nomograph (discussed above). Predicted pH agreed very well with measured pH at values ≤ 6.3. However, this model also predicted lower pH than was measured for many lakes with pH >6.3.

As discussed above, estimates of the relationship between sulphate deposition rates and surface water pH may be made. As an example, the Roseway River, Nova Scotia (Figure 3-53) has a CDR of 56 meq/m^2.yr. If all of the assumptions noted above hold and if the acidification process is reversible, then a reduction of the sulphate loading rate to 40 meq/m^2.yr (20 kg SO_4^{2-}/ha.yr) might be expected to return the river to an annual pH of roughly 5.3. A significant problem exists with such a prediction. The Roseway River has strongly coloured waters, as do the Mersey and Medway Rivers (also shown in Figure 3-53). As Thompson (1982) notes, the pH values of these rivers "have been thought to be dominated by naturally- occurring organic acids." Thompson (1982) feels that "their low pHs can be explained quite well on the basis of simple inorganic chemistry." No chemical data (e.g., Gran titrations for weak and strong acids) were presented to confirm this. If the pH values of these rivers were controlled by naturally-occurring organic acids, reduction of excess sulphate deposition would not result in the increases in stream water pH predicted.

Figure 3-54 and Table 3-33 were calculated based on the Thompson (1982) model. If 80 μeq/L of cation concentration (roughly equivalent to 50 μeq/L Ca^{2+} as used in Table 3-33) is used as a criteria for basin sensitivity to acidification, maintenance of the basin water to a mean pH >5.3 should be possible with sulphate loadings of 35 kg SO_4^{2-}/ha.yr given a runoff of 100 cm/yr. Other combinations of sulphate deposition and runoff are shown on Table 3-33. It should be noted that any retention of sulphate within the watersheds or increased leaching of base cations would violate assumptions in the model, causing the above loading estimates to be too low.



RIVER	CDR	EXCESS SO_4^{2-}	MEDIAN pH
Wallace	203	69	6.4
Meteghan	129	123	5.0
Le 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 3-53. Cation Denudation Rate Model applied to rivers of Nova Scotia and Newfoundland (Thompson 1982).

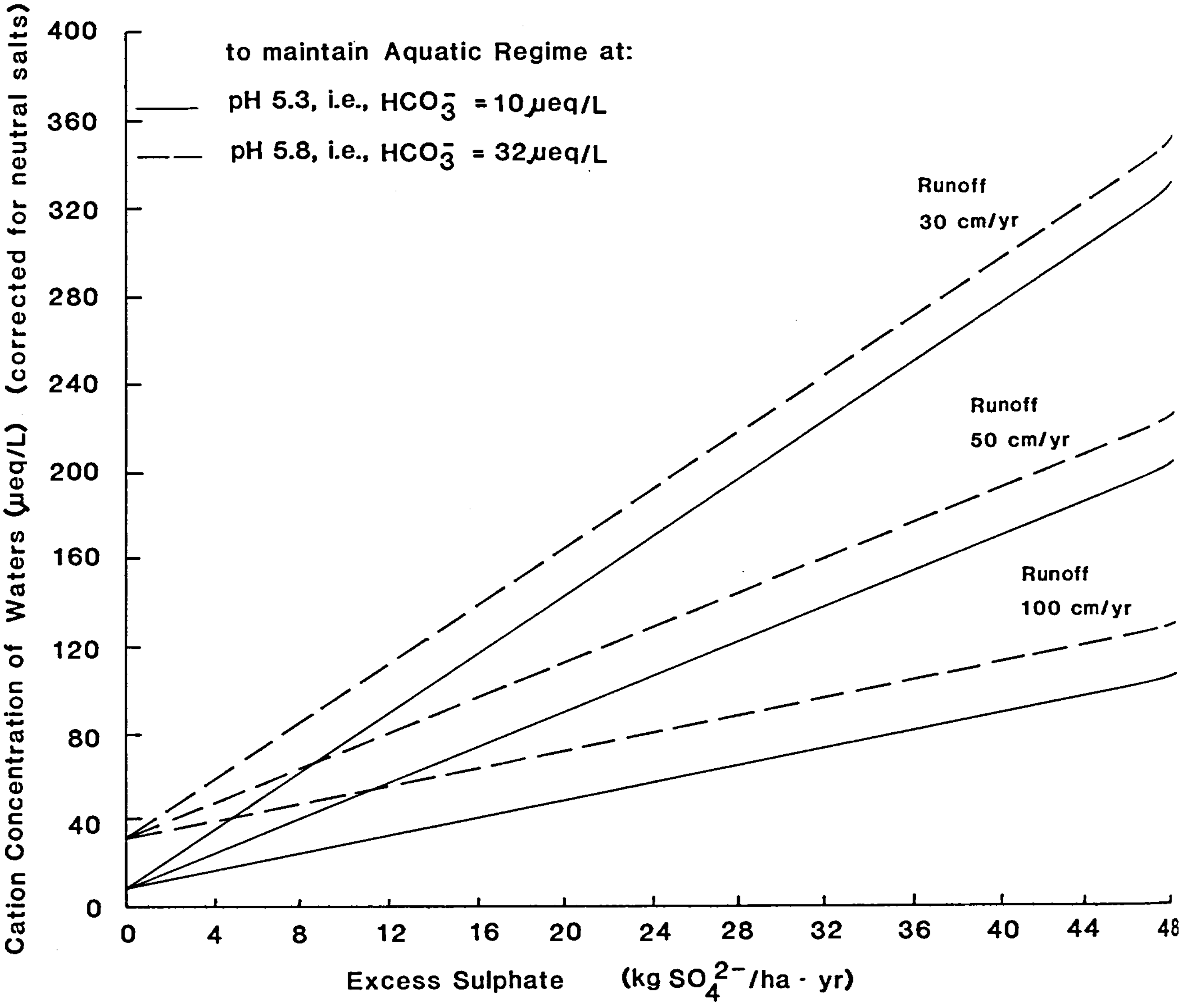


Figure 3-54. Relation of excess sulphate and cation concentration for pH 5.3 and 5.8 for basin runoff of 30, 50 and 100 cm/yr. The model was developed for an area with 100 cm runoff. It has not been corroborated for areas with lower runoff (derived by the Work Group from Thompson 1982).

TABLE 3-33. ACIDIFICATION SENSITIVITY OF SURFACE WATERS RELATED TO SULPHATE LOADING FOR TWO pH OBJECTIVES AND THREE RUNOFF VALUES [derived by the Working Group from CDR model, Thompson (1982)]

Cation Concentration of Waters (μeq/L)		Runoff (cm/yr)		
	pH Objective	30	50	100
300	5.3	44	50	50
	5.8	40	50	50
200	5.3	28	47	50
	5.8	25	42	50
100	5.3	13	22	45
	5.8	10	17	34
50	5.3	6	10	20
	5.8	3	5	9

The model was developed for an area with 100 cm runoff. It has not been corroborated for areas with lower runoff.

3.9.3.3 Summary

The application of two simplified models to the problem of relating wet deposition of sulphate to lake pH has been discussed in this section. Before any environmental or water quality model can be used to make estimates with specified confidence of future conditions in a particular geographic region, the applicability of that model for that region and conditions must be verified. This process of verification is just beginning for Henriksen's predictor nomograph and CDR model to northeastern North America. Until such verification (and perhaps, model adaptation) is achieved, quantitative predictions based on these models must be viewed with caution.

3.9.4 Summary of Empirical Observation and Modelling

Chapter 3 of this report has reviewed the hydro-geochemical reactions to normal or altered fluxes in the hydrologic regime; the regional responses in lake chemistry; the basin characteristic which influence sensitivity to acidification; evidence of changes or trends in surface water quality in sensitive regions; evidences of alteration of biological components; and finally, the methodologies which are available to assist in estimation of target loadings by atmospheric deposition which would be consistent with protection of the ecosystem to a degree acceptable to society. Because environmental concerns are of rather recent recognition and those which have been recognized are most often related to more intense urban contamination, long term records of verified significance are available in only a few cases from which firm conclusions can be drawn relating to acidification of remote ecosystems. A deterministic knowledge of the inter-relationships of the bio-hydrogeochemical system and of its responses to altered precipitation chemistry is not yet available, therefore rendering precise predictive modelling of system responses, as yet, unattainable. These limitations have been thoroughly reviewed in recent summaries of the Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada (Harvey et al. 1981) and by the Committee on the Atmosphere and the Biosphere, Board on Agriculture and Renewable Resources Commission on Natural Resources (NAS 1981) and are further detailed in this report. However, these learned summaries of present knowledge have all indicated strong evidence of significant ecosystem deterioration due to past and present levels of acid precipitation loading and thus indicate the urgent need to use this present knowledge to arrive at best estimates of levels of acid loadings which can be tolerated.

While this chapter has considered only the aquatic portions of the ecosystem, it would appear that because of the interactions with other components, protection of the aquatic regime would, to a large degree, result in protection of the total environment. This sub-section therefore, reviewed the information and methodologies presented earlier with respect to their utility in producing estimates of loading/response relationships.

As developed in previous sections, acidification of aquatic regimes can be related to proton (H^+) loading, concentration of H^+, i.e., of precipitation, or to the constituents of the loading which determine the acidity (i.e., the major ionic species). The anthropogenic loadings add to and interact with the natural components to an extent that also influences the factors available for effective control. Evans et al. (1981), after reviewing the extensive evidence of dose response acidification relationships and considering the empirical model approach of Henriksen (1980) have proposed that "an annual volume weighted H^+ concentration of 25 µeq/L (pH 4.6) in precipitation appears to be a critical threshold."

These authors have reached their conclusions through the basic consideration of H^+ exchange in the reaction processes and through general empirical observations of dose response in sensitive regimes. However, as reviewed in earlier sections, the biosystem response and ability to assimilate nitrate, ammonia or sulphate (the primary acidifying ions of precipitation) differ and therefore the acidifying potentials of these ions differ. In addition, Stensland (1979) and Barrie (1981) have shown that the ionic concentrations of precipitation over eastern North America varies as to relative contribution to its acidity in both space and time. Thus the H^+ concentration cannot be considered to have a unique relation to the acidity controlling ions nor has it a unique relation in its dose response in the bio-hydrogeosystem. Thus, neither H^+ concentration of precipitation nor H+ loading rates form acceptable criteria for target loadings in relation to protection of aquatic ecosystems from acidification.

Henricksen (1980) has argued that surface water acidification can be accounted for as the titration of bicarbonate waters and replacement of bicarbonate by sulphate in the ionic charge balance. He found good empirical agreement between sulphate loadings and observed acidification in widely diverse areas without consideration of any nitrogen species. His relationship to precipitation pH, as cited by Evans et al. (1981), was empirical and based upon Norwegian precipitation and was not an integral part of the argument. It should be stressed here, that while Henricksen's model has a basis in chemical equilibrium, as shown by Thompson (1982), it is in fact a "phenomenological" model which derives from actual dose response observations.

A range of sulphate loading vs bio-geo-system responses observed in eastern North America are summarized in Table 3-26 and Summary Table (p. 3-178). This includes several cases relating to episodic event pH changes. While the number of cases are small and statistical significance cannot be assigned, the identified cases of surface water acidification and observed biosystem effects all fall within regions of sulphate deposition of greater than 17 kg SO_4^{2-}/ha.yr. There appear to have been no reported cases of identified acidification which cannot be related to organic sources in areas of less than this level of sulphate deposition.

The Canadian members of the Work Group consider that this evidence, often circumstantial but not inconsistent with theory, leads to the approach best able to provide estimates of target loadings of sulphate in relation to surface water acidification. It is well recognized that this estimate is of limited accuracy in terms of predicted ecosystem response and must surely be subject to later re-evaluation as more information is developed from scientific study. The empirical observations presented in Table 3-26 and Summary Table (p. 3-178) immediately suggest a target loading of sulphate which could be accepted but is only poorly defined in terms of geosystem parameters. The Henricksen-Thompson model permits a quantification of the target loadings in terms of the geochemical basin sensitivity parameter CDR (Ca^{2+} + Mg^{2+}) as an approximation or unaltered alkalinity as suggested in Section 3.9.3 and further developed in this section. As pointed out by Henricksen (1980) this model will have, perhaps, significant errors below the titration end point for alkalinity due to other buffers but should apply with sufficient accuracy for estimates of the loadings of sulphate which would control the aquatic regime acidity above this transition pH. The CDR serves as the basic geosystem sensitivity criteria in this model and thereby links the basin hydrology and the sulphate loading to sensitivity to acidification. CDR and cation concentrations are related through the hydrological runoff.

Information derived from the Thompson (1982) model may, within the limitations cited, be used to estimate target loadings of sulphate (Figure 3-54 and Table 3-33). Thus if 200 µeq/L of cation concentration (also unal~~tered alkal~~inity) is used as a criteria for basin sensitivity to acidification, protection of the basin water to a mean pH of 5.3 would be indicated for sulphate loadings 47.5 kg SO_4^{2-}/ha.yr if runoff of 50 cm/yr occurred. For a 30 cm/yr runoff the protection would only tolerate a loading of 28 kg SO_4^{2-}/ha.yr. Thus the criteria of 200 µeq/L total cations or unaltered alkalinity is a reasonable choice of threshold of sensitivity to acidification over much of eastern North America where runoff may be near 50 cm and sulphate loadings exceed 40 kg SO_4^{2-}/ha.yr (see Figure 2-6b).

A target loading of 15-20 kg SO_4^{2-}/ha.yr would, by this model, serve to maintain surface water pH greater than 5.3 on an annual basis for basins having cation concentrations of 200 µeq/L or greater even in areas of low runoff. More sensitive basins in low runoff areas could not tolerate this level of loading and maintain a pH greater than 5.3.

The estimates of dose-response relationships presented here do not account for the episodic events discussed earlier which may, in some ecosystems, be cause for more concern than that based on the mean acidity. The estimates do not consider any time response and must therefore be limited to steady state conditions. Rate of response of *any basin to changes in precipitation loading, either quantity or quality, must relate in general to the water residence time. Other factors such as ionic migrations in the soils are not considered. Thus no response rates or equilibrium times are implied, in any sense, by these loading estimates.*

In the watershed studies summarized above, sulphate in precipitation was used as a surrogate for total acid loading. Sulphate in precipitation is reliably measured. It is recognized that dry deposition of sulphate and sulphur dioxide, and the wet and dry deposition of nitrogen oxides, nitric acid, particulate nitrate and ammonia, as well as other compounds also contribute to acidic deposition. Based on documented effects, wet and dry deposition of sulphur compounds dominate in long-term acidification.

Based on the results of the empirical studies, interpretation of long-term water quality data, studies of sediment cores and models that have been reviewed, we conclude that acidic deposition has caused long-term and short-term acidification of sensitive surface waters in Canada and the U.S. The work group also believes on the basis of our understanding of the acidification process that reductions from present levels of total sulphur deposition in some areas would reduce further damage to sensitive surface waters and would lead to eventual recovery of those waters that have already been altered chemically or biologically (Loss of genetic stock would not be reversible.)

The U.S. members conclude on the basis of modelling and empirical studies that reductions in pH, loss of alkalinity, and associated biological changes have occurred in areas receiving acidic deposition, but cause and effects relationships have often not been clearly established. The relative contributions of acidic inputs from the atmosphere, land use changes, and natural terrestrial processes are not known. The key terrestrial processes which provide acidity to the aquatic systems and/or ameliorate atmospheric acidic inputs are neither known nor quantified. The key chemical and biological processes which interact in aquatic ecosystems to determine the chemical environment are not known or quantified. Based on this status of the scientific knowledge, the U.S. Working Group concludes that it is not now possible to derive quantitative loading/effects relationships.

3.10 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.

3.10.1 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 long-term surface water acidification, even though it contributes to precipitation acidity and pH depression during snowmelt or runoff events. 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. Acidic deposition results in mobilization of metals, such as aluminum, iron, zinc 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.

3.10.2 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 geographical 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 throughout 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 acidic 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 spectrum 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.

3.10.3 Alteration of Biotic Components

Effects on the biological components of aquatic ecosystems are known only partially. Five research topics are identified:

1. It is essential that the biological responses to various water chemistry changes induced by acidic 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 sensitivity 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.

3.10.4 Irreversible Impacts

1. Geochemical and hydrologic principles suggest that the processes of sulphate accumulations, and associated acidification of soils and surface waters, represent a large-scale titration of available acid neutralizing capacity. 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.

3.10.5 Target Loadings and Model Validation

Much uncertainty remains as to the quantification of sulphate deposition level ("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 Henriksen 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:

Experimental Lakes Area - Ontario
Boundary Waters Canoe Area Wilderness - Minnesota
Algoma Area Watershed Study - Ontario
Dorset-Haliburton Study Area - Ontario
ILWAS Project - New York
Laurentide Park (Lac Laflamme) - Quebec
Kejimkujik Park - Nova Scotia
Hubbard Brook - New Hampshire

Northern Highlands Lakes - Wisconsin
Coweeta - North Carolina
Andrews - Washington
North Cascades - Washington

3.10.5.1 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 unaffected 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 verifications. 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 "tolerant" (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

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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 potentially harmful to terrestrial ecosystems are oxides of sulphur (SO_x), oxides of nitrogen (NO_x), particulates, and secondary products, such as oxidants and acidic deposition. There are also smaller amounts of heavy metals, several of which have potentially toxic significance after accumulation.

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 widely distributed in the atmosphere. 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) thus contributing to the formation of the secondary pollutant, acidic deposition. Similarly, NO_x gives rise to nitric acid (HNO_3) and are likewise precursors of acidic deposition. Ozone (O_3) is also an indirectly emitted secondary pollutant formed in the atmosphere in the presence of sunlight, after chemical transformations of nitrogen dioxide and reactive hydrocarbons.

In summary, acidic deposition and ozone, although secondary in nature, are usually considered to be long-range transported pollutants as they frequently occur in relatively high concentrations at distances hundreds of kilometres from the source of their primary precursors. Because ozone is a strong oxidizer, oxidative decay usually is rapid in polluted atmospheres and therefore decreases in concentration during late afternoon and evening as sunlight intensity decreases. However, ozone can persist overnight in rural areas or at altitudes where there are low concentrations of reactive components (Jacobson in press).

Improved understanding is needed of the ecological effects of the phytotoxic primary and secondary pollutants on terrestrial ecosystems. Field observations and laboratory studies have provided detailed descriptions of the visible injury symptom syndrome produced by ozone. Several review articles and chapters have provided excellent descriptions of these symptoms (Brandt and Heck 1968; Hill et al. 1970; USEPA 1978a). Field studies including the use of field chambers (Heagle et al. 1973; Thompson and Taylor 1966) and those with plots located in a natural ozone gradient have demonstrated that chronic ozone exposures suppress growth and reduce yield, often in the presence of little or no visible injury symptoms. A more detailed description of the response of plants to acute and chronic exposures to ozone is presented elsewhere (NAS 1977).

It has been more difficult to determine the adverse or beneficial effects of acidic deposition on plant communities. Although simulated rainfall experiments have produced some direct 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, some studies have demonstrated the direct effects of acidic deposition on soils (Cronan et al. 1978; Dickson 1978).

Indirect effects of acidic deposition (i.e., acting through soil, other organisms) and its implications are even less well known. Increases in acidic deposition could result in accelerated changes in the natural evolution of soils, leading to alterations in soil fertility over the long term. These changes in soil chemistry could have detrimental implications for long-term sustained forest productivity, and also must be considered in association with aquatic sensitivity.

This section on terrestrial effects of transboundary air pollutants is presented in four parts: (1) effects on vegetation; (2) effects on wildlife; (3) effects on soil; and (4) sensitivity assessment. Where possible, the information on acidic deposition and combinations of these pollutants has been partitioned and further subdivided into agricultural crop and forest effects.

4.2 EFFECTS ON VEGETATION

4.2.1 Sulphur Dioxide (SO_2)

4.2.1.1 Introduction

Sulphur dioxide is an air pollutant of concern to vegetation having most often been recognized for inducing direct foliar effects to plants growing proximal to major point sources of emission. The phytotoxicity of this gas has been studied extensively around long-term sources such as Sudbury, Ontario (Dreisinger and McGovern 1970; Linzon 1971) and the districts of Fox Creek and West Whitecourt, Alberta, (Legge et al. 1976). Controlled long-term exposure studies have recently been completed as part of the Montana Grasslands Studies (Lee et al. 1978; Preston 1979). This pollutant has also been considered of great importance to the vegetation within the heavily industrialized areas of Great Britain (Cowling and Koziol 1978) and central Europe (Guderian 1977).

Sulphur dioxide is not found on a regional basis at concentrations sufficient to cause direct injury to most plant species. Long-term, low-dose studies have demonstrated direct effects to lichen communities (Hawksworth 1971) and indirect effects to several plant species (Keller 1978, 1980; Laurence 1978). Likewise effects may result from lower doses of pollutants in combination with special reference to O_3 and SO_2 in mixtures (Heagle and Johnston 1979; Reinert and Nelson 1980). Several reviews of the effects of SO_2 on vegetation are available (Guderian 1977; Jacobson and Hill 1970; Linzon 1978; Rennie and Halstead 1977; Treshow 1970; USEPA 1973, 1978b).

4.2.1.2 Regional Doses of SO_2

As presented in Table 2-3 of Section 2 (Rasmussen et al. 1975), estimates of global background concentrations of SO_2 in gaseous form should be expected within a range of approximately 0.5-5.0 $\mu g/m^3$ (0.0002-0.002 ppm SO_2 at STP) with expected residency times of these concentrations to last from one to five days. Regional SO_2 emissions are shown in Figure 4-1.

Mueller et al. (1980) reported on atmospheric pollutant data collected during the period August 1977 - October 1978 for an area covering much of the eastern half of the United States (Figure 4-2). Monthly 1-hr averages varied from 5-40 $\mu g/m^3$ (0.002-0.015 ppm SO_2). The highest annual average SO_2 concentrations occurred along the Ohio River Valley; averages ranged from 0.019-0.029 ppm SO_2. The maximal 1-hr concentrations were from 0.11-0.19 ppm SO_2 and occurred in the same area during October 1978. Hourly deposition values of 1.5-2.3 ppm SO_2 are common near large emission sources (USEPA 1978a).

In the northeast alone, anthropogenic sources exceed all others by a factor of 12.5. Within this region, SO_2 levels annually average 16 $\mu g/m^3$ (0.006 ppm SO_2) (Shinn and Lynn 1979) which is several times that recorded in pristine areas. Therefore, it is reasonable to assume that at the present time concentrations of SO_2 seldom reach direct foliar injury thresholds for vegetation growing in forested areas or in areas of significant agricultural production. Duchelle and Skelly (1981) reported SO_2 concentration ranges of 0.001-0.002 ppm/hr SO_2 during the summer seasons of 1979 and 1980 within the Shenandoah National Park in Virginia and did not consider this pollutant of importance to vegetation in the area.

Distribution of even these low doses of SO_2 (and NO_2) over the major portion of eastern United States corresponds well with known ozone occurrences (USEPA 1978b).

4.2.1.3 SO_2 Effects to Agricultural Crops

There are several possible responses to SO_2 and related sulphur compounds: (1) fertilizer effects appearing as increased growth and

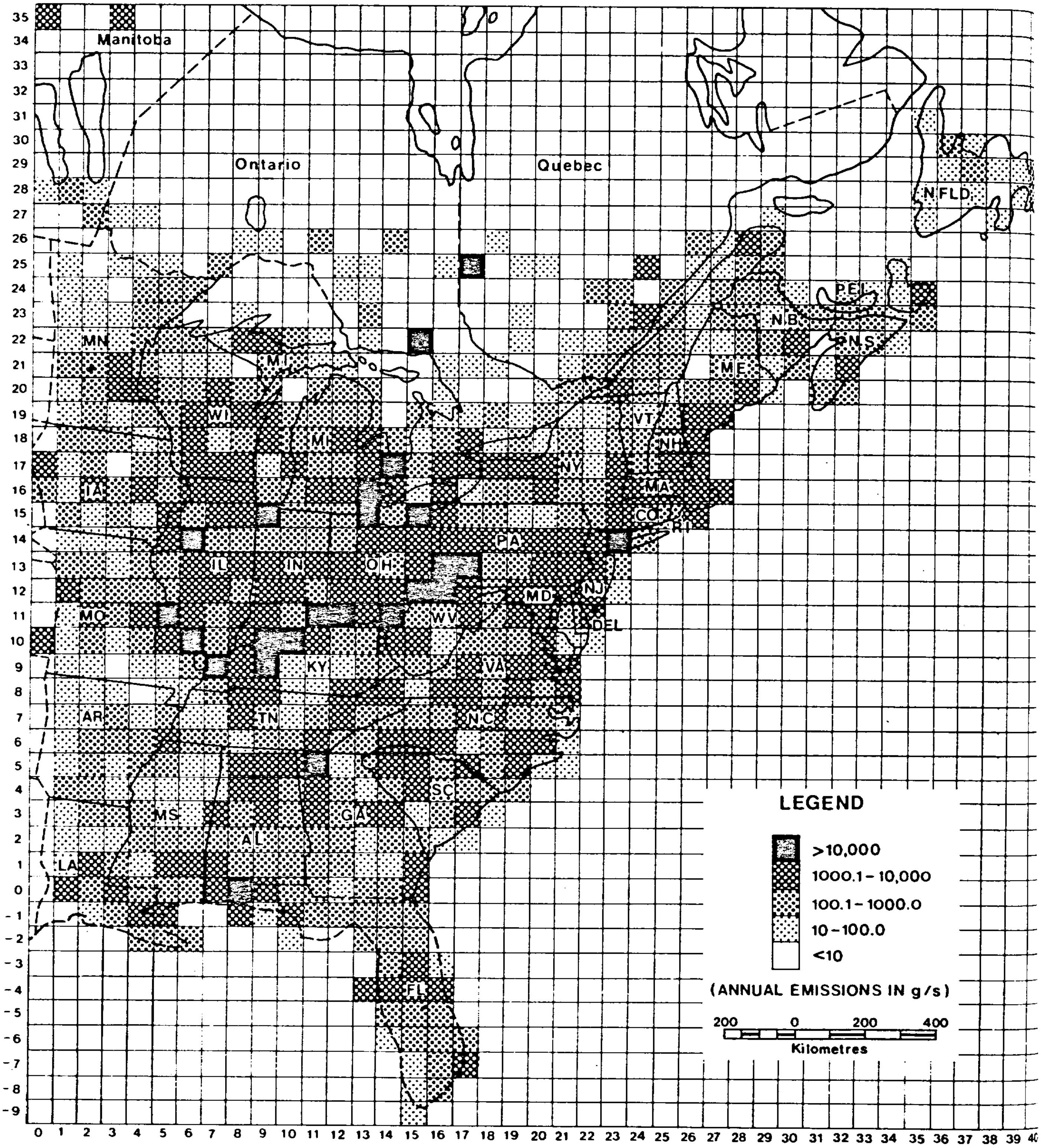


Figure 4-1. Magnitude and distribution of sulphur dioxide (SO_2) emissions in eastern North America. Data from SURE II data base and Environment Canada (Environment Canada 1981d).

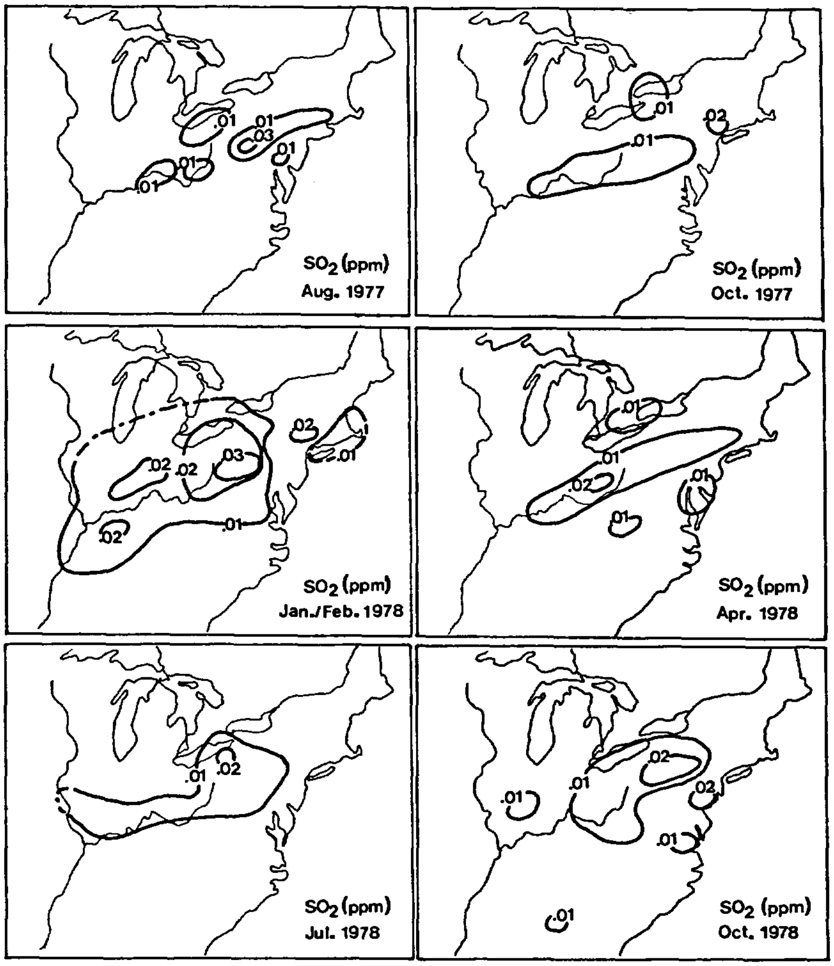


Figure 4-2. Geographic distribution of monthly arithmetic means for SO_2 (Mueller et al. 1980).

yields; (2) no detectable responses; (3) injury manifested as growth and yield reductions without visible symptom expressions on the foliage or with very mild foliar symptoms that would be difficult to perceive as air pollution incited without the presence of a control set of plants grown in pollution-free conditions; (4) injury exhibited as chronic or acute symptoms on foliage with or without associated reductions in growth and yield; and (5) death of plants and plant communities.

Sulphur dioxide passively enters plants via stomata as part of normal gas exchange during photosynthesis. Many factors govern stomatal opening and closing including light, relative humidity, CO_2 concentration and water stress. Sulphur dioxide uptake and ingress may also be limited according to plant genetics, previous exposure to SO_2 (Jensen and Kozlowski 1975) and subsequent biochemical and/or physiological alterations within exposed plants. Sulphur dioxide has been shown to increase or decrease stomatal resistance and this may directly affect potential for the photosynthetic performance (Hallgren 1978). Based on the available literature, it is difficult to assess the relationship of SO_2-induced biochemical and/or physiological changes at the cellular level in relation to subsequent effects on photosynthetic activity or resultant growth and yield.

Sulphur dioxide, upon absorption is further oxidized to SO_3 and SO_4^{2-} and subsequently is incorporated into S-containing amino acids and proteins. The rate of entry is particularly important to determining toxicity. Plants have an inherent, and apparently species dependent, capacity to absorb, detoxify, and metabolically incorporate SO_2 and some plants may absorb low concentrations of SO_2 over long time periods without injury.

Atmospheric SO_2 can have beneficial effects to agronomic vegetation (Noggle and Jones 1979). Sulphur is one of the elements required for plant growth and Coleman (1966) reported that crop deficiencies of S have been occurring with increasing frequency throughout the world. Several studies using SO_2 as a nutrient supply for S requirements of plants have been accomplished under varying degrees of soil-sulphur availability (Cowling et al. 1973; Faller 1970; Noggle and Jones 1979). The results of these and other studies leave little doubt that application of S as a nutrient via SO_2 fumigation of plants grown on borderline or S-deficient soils will lead to increased productivity.

The interpretation of studies demonstrating such beneficial effects must be evaluated in light of their single influence to one crop. Long-term natural ecosystem studies showing similar positive effects for the entire ecosystem have not been accomplished. Since these agronomic and natural ecosystems are often physically proximal to one another, further research is needed on the potential influence of S compounds to each singly and collectively.

Acute foliar injury occurs following high-dose exposures and the rapid absorption of a toxic dose of SO_2 results at first in marginal and interveinal areas having a dark-green, watersoaked appearance. After desiccation and bleaching of tissues, the affected areas become light ivory to white in most broadleaf plants. Some species show darker colours (brown or red), but there is characteristically an exact line of demarcation between symptomatic and asymptomatic portions of leaf tissues. Bifacial necrosis is common. In monocotyledons (e.g., corn, grasses) foliar injury occurs at the tips and in strips along the veins (Malhotra and Blauel 1980; USEPA 1976).

Plant injury that is visible but does not involve collapse and necrosis of tissues is termed chronic injury. This type of visible injury is usually the result of variable fumigations consisting of both short-term, high-concentration or long-term, low-concentration exposures to SO_2.

In broadleaf plants, chronic injury is usually expressed in tissues found between the veins, with various forms of chlorosis predominating. Chlorotic spots or chlorotic mottle may persist following exposure or may subside and disappear following pollutant removal or as a result of changing environmental conditions (Jacobson and Hill 1970).

The presence of acute or chronic foliar injury is not necessarily associated with growth or yield effects. Furthermore, when present, the degree of foliar injury may not always be a reliable indicator of subsequent growth or yield effects. The uniformity of exposure to even the low doses of SO_2 experienced by crops growing under field conditions presents difficulty in measuring 'treatment' effects due to the lack of a set of control (nonpollutant exposed) plants. Artificial systems must therefore be used under more controlled laboratory and field situations. The more ubiquitous exposure to known phytotoxic concentrations of O_3 must also be recognized and singly evaluated.

Yield effects in the absence of foliar symptoms have been reported for soybeans by Sprugel et al. (1980) and Reinert and Weber (1980) under field conditions using a zonal air pollution delivery system and using chamber exposures. Both reports, however, used doses more typical of point sources of emission and would therefore not be considered comparable to regional conditions of exposure. No studies consider all the potential variables that can effect plant response. This is not a possibility for a single study and is especially true for field studies (which are most relevant) where many environmental variables cannot be controlled. From the data available, we can conclude that growth and yield effects are not necessarily related to foliar injury. Depending upon the plant affected, the environmental conditions, and the pollutant exposure conditions, one may observe yield effects without injury, injury without yield effects or more direct correlations between injury and yield.

The primary focus of dose-response studies should be to develop useful generalizations of the relationship between meaningful parameters of plant response and measurable indices of exposure dose. The relationship between exposure dose and the amount of pollutant entering the plant may be significantly influenced by environmental factors controlling the rate of pollutant flux into plant leaf tissues (see Figure 4-3). The dose of SO_2 must be considered in relation to known concentrations under field conditions since both the regionally expected dose and the phytotoxicity of SO_2 are comparatively low (e.g., ozone dose and phytotoxicity are relatively high).

The role of short-term fluctuations in SO_2 may be of particular importance in areas proximal to point sources of SO_2 (McLaughlin and Lee 1974). Here concentrations may fluctuate widely during exposure and damage to vegetation may be closely associated with short-term averages (1 hr) or even peak concentrations. McLaughlin et al. (1979) studied the effects of varying the peak to mean SO_2 concentration ratio on kidney beans in short-term (3 hr) exposures to SO_2. They found that increasing the peak:mean ratio from 1.0 (steady state exposure at 0.5 ppm for 3 hr) to 2.0 (3 hr exposure with peak = 1.0 ppm) did not alter post fumigation photosynthetic depression. However, further increasing the ratio to 6.0 (1 hr exposure with peak = 2.0 ppm) tripled the post fumigation photosynthetic depression. Total dose delivered in the three exposures was 1.5, 1.8, and 1.1 ppm respectively. Clearly the quantity of SO_2 to which the plants are exposed may have a very different effective potential as the kinetics of the exposure are changed.

Data on SO_2 effects on plant growth and yield in most cases provide the most relevant basis for studying dose-response relationships. As a whole-plant measurement, plant productivity is an integrative parameter which considers the net effect of multiple factors over time. Productivity data are presently available for a wide range of species under a broad range of experimental conditions. Because results would not be expected to be closely comparable across these sometimes divergent experimental techniques, data have been tabulated separately for only controlled field exposures (Tables 4-1a and 4-1b).

Relatively few crops of economic importance have been studied under field conditions utilizing various field exposure systems. Of the seven "studies" reviewed in Tables 4-1a and 4-1b, dose exposure to induce a yield effect was 0.09 ppm SO_2 for 4.2 hr average fumigation period on 18 days scattered from July 19 through August 27 of the soybean growing season (Sprugel et al. 1980). Five studies indicated no effect following various exposure regimes, and one study (Neely and Wilhour pers. comm.) reported increased yields (27% and 8%) of winter wheat cv. Yamhill following exposure dose of 0.03 and 0.06 ppm SO_2 for 24 hr/day for the entire growing season, respectively.

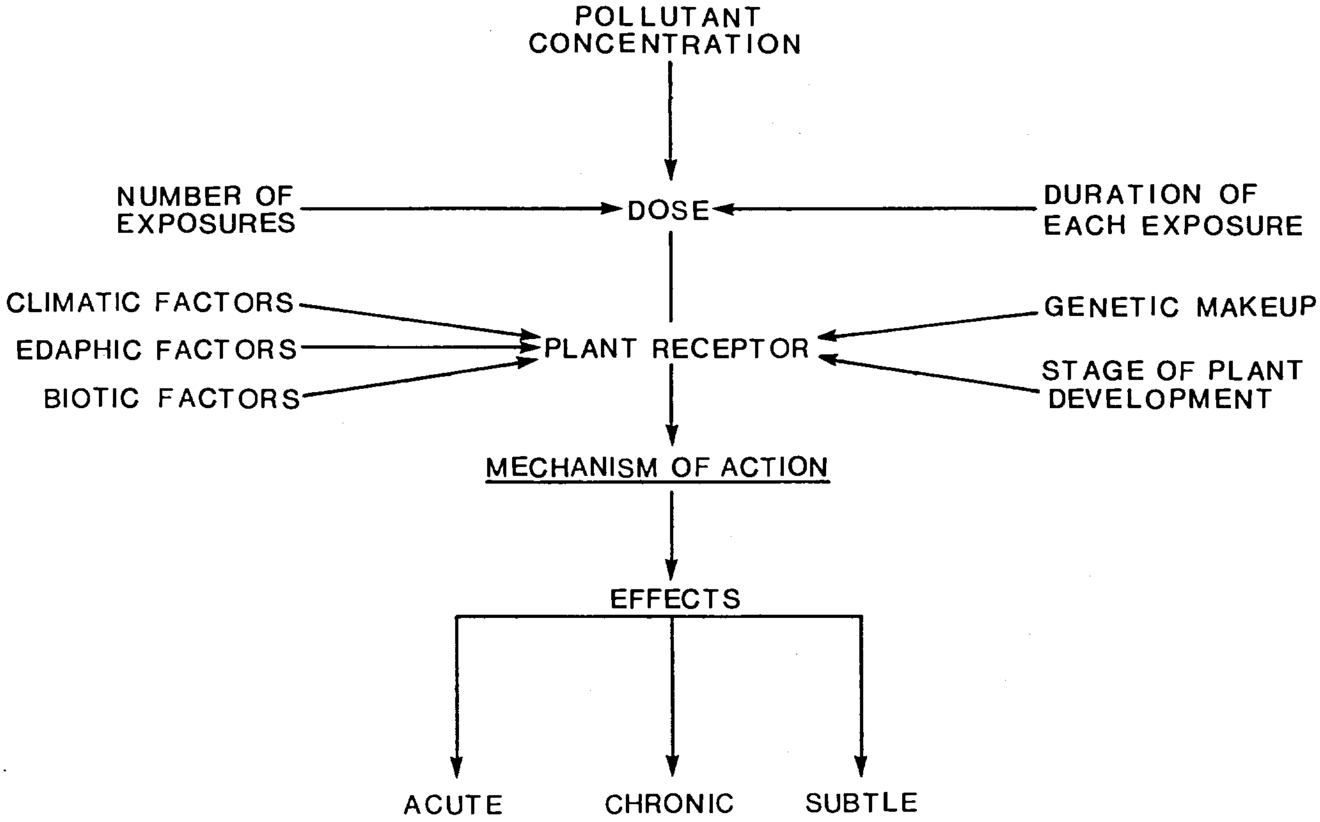


Figure 4-3. Conceptual model of the factors involved in air pollution effects (dose-response) on vegetation (Heck and Brandt 1977).

TABLE 4-1a. SUMMARY OF CROP EFFECTS FROM SO_2 EXPOSURE IN FIELD CLOSED CHAMBERS

Crop	Exposure	Significant Effects Reported	Reference
Soybean cv. Dare	260 $\mu g/m^3$ (0.10 ppm) 6 hr/day	No significant effect on foliage, fresh wt seeds/plant, or wt of seeds/plant until 92nd day (defoliation 12% > control) and 135th day (seed wt 1% < control)	Heagle et al. 1974
Wheat	100 $\mu g/m^3$ (0.04 ppm), 3 hr, 8 exposures during growing season	No effect on foliage or yield, no apparent effect on photosynthesis, no effect on the average head length or no. of grains/head	Heagle et al. 1979d
	1,180 $\mu g/m^3$ (0.45 ppm, 3 hr for 7 exposures during growing season	No accumulative effect on yield, no effect on average head length of no. grains/head	
Winter Wheat cv. Yamhill	80 (0.03), 140 (0.06), 260 (0.10), 390 (0.15), and 520 (0.20) $\mu g/m^3$ (ppm) for growing season	27%, 8%, 17%, and 70% reduced grain weight, respectively	Neely and Wilhour pers. comm.
cv. Hyslop	80 (0.03), 140 (0.06), 260 (0.10), 390 (0.15), and 520 (0.20) $\mu g/m^3$ (ppm) for 24 hr/day for growing season	No effect, 22%, 36%, 27%, and 56% reduced grain weight respectively	
Barley Durham Wheat Spring Wheat	80-260 $\mu g/m^3$ (0.03-0.10 ppm) 72 hr/wk for growing season	No effect on foliage or yield	Wilhour et al. 1978
	390 $\mu g/m^3$ (0.15 ppm), 72 hr/wk for growing season	Yield 44% less in Barley (N.S.)[a] Yield 42% less in Durham Wheat (N.S.) No effect on Spring Wheat	
	1,050 $\mu g/m^3$ (0.25 ppm), 2,100 $\mu g/m^3$ (0.80 ppm), and 3,140 $\mu g/m^3$ (1.20 ppm) from 3 hr once in 5 wk)	No effect on foliage or yield	
Alfalfa	630 $\mu g/m^3$ (0.25ppm) from 3 hr once a wk to 3 hr once in 5 wk	No effect on foliage or yield	

[a] N.S. = Results were not significant at 95% level of confidence.

	$\mu g/m^3$ (1.20 ppm) from 3 hr once in 5 wk)	
Alfalfa	630 $\mu g/m^3$ (0.25ppm) from 3 hr once a wk to 3 hr once in 5 wk	No effect on foliage or yield

[a] N.S. = Results were not significant at 95% level of confidence.

TABLE 4-1b. SUMMARY OF CROP EFFECTS FROM SO_2 EXPOSURE IN FIELD ZONAL AIR POLLUTION SYSTEMS

Crop	Exposure	Significant Effects Reported	Reference
Western wheat-grass, Prairie June Grass	50 $\mu g/m^3$ (G.M. + 58)[a], 130 $\mu g/m^3$ (G.M. = 100), and 260 $\mu g/m^3$ (G.M. = 178) during growing season	S content increased with increased SO_2 conc.; digestible dry matter was reduced by 2 yr treatment; crude protein content reduced significantly in wheat	Dodd et al. 1978
Soybean cv. Wells	2,100-5,240 $\mu g/m^3$ for 4 hr 20 min	Yield was reduced 4.5% at 3,760 $\mu g/m^3$,[d] 11% at 4,450 $\mu g/m^3$, and 15% at 5,240 $\mu g/m^3$[d]	Miller et al. 1979
Soybean cv. Wells	240, 260, 500, 660, and 940 $\mu g/m^3$ mean conc. 4.2 hr/18 fumigations from 19 July to 27 August	Yield was reduced by 6.4%, 5.2%, 12.2%, 19.2%, and 15.9%, respectively[b]	Sprugel et al. 1980
	310, 790, and 2,070 $\mu g/m^3$ mean conc. 4.7 hr/24 fumigations from 13 July to 29 August	Yield was reduced 12.3%, 20.5%, and 45.3% respectively[c]	

[a] G.M. = Geometric Mean.

[b] Standard geometric deviation of fumigation concentration ranged 44-45% of X.

[c] Standard geometric deviation of fumigation concentration ranged 41-64% of X.

[d] Pollutant average; no estimate on range of exposure doses.

Tables 4-1a and 4-1b also reviewed a large number of studies which were conducted using various greenhouse or exposure chamber techniques and exposure of agronomic or horticultural crop plants. Conclusions indicated difficulty in determining the significance of results of such studies in relation to actual similar fumigations under field conditions. Doses used for exposure treatments were usually considered to be in excess of expected doses for ambient field exposures. Acute foliar effects have not been reported in long-term studies using less than 0.15 ppm SO_2 for 24 hr/day for 7 days.

In greenhouse experiments conducted in England using ryegrasses, yield losses were measured following long-term exposure to low levels of SO_2. In one study (Bell and Clough 1973), perennial ryegrass experienced a 52% reduction in dry weight after exposure to a mean concentration of 0.067 ppm SO_2 over a 26-wk period. At the end of the study the plants were smaller and chlorotic in comparison to the control plants exposed to air that was purified by both activated charcoal and an absolute filter. In the other study (Crittenden and Read 1978), shoot dryweight of Italian ryegrass was reduced by 30 to 40% after 8-10 wk of exposure to 0.02 to 0.03 ppm SO_2, and was reduced about 10% after 5-wk exposure to air containing 0.004 to 0.02 ppm SO_2. The Italian ryegrass plants did not display visible symptoms of air pollution injury in either the exposure chamber or the control filtered air chamber.

In spite of differences due to exposure regimes, techniques, and species, certain generalizations can be made with respect to average and outer-limit responses of the plants under study. These have been made in the form of correlations of yield response with total exposure dose in part-per-million hours (ppmh). The latter data were calculated as the product of exposure time and SO_2 concentration and transformed to log values. For experiments employing controlled exposures under field conditions (Tables 4-1a and b), data are graphed in Figure 4-4 (McLaughlin 1980). For the 36 data points shown, exposure dose ranged from 0.24 to 259 ppmh. No effects on yield were detected in any of the six studies at doses $\geq$ 6 ppmh. Yield losses occurred in 26 cases at levels $\geq$ 6 ppmh, while no effects and positive effects were noted in two cases each at levels $\geq$ 6 ppmh. A linear regression of yield on dose for all studies reporting yield losses showed strong positive correlation (r = 0.75) of yield with dose and took the form:

$$\text{Yield loss} = -13.6 + 23.8\ (\log \text{dose})$$
$$r^2 = 0.53\ (\text{Significance} = \geq 0.001)$$

This correlation excludes four data points, two with no effects and two with positive responses. All were studies with wheat reported by Neely and Wilhour (pers. comm.). Data from studies reporting no effect or a positive effect are however all plotted in Figure 4-4.

Calculation of the phytotoxic potential for regional scale SO_2 exposures involves many assumptions regarding toxic and nontoxic

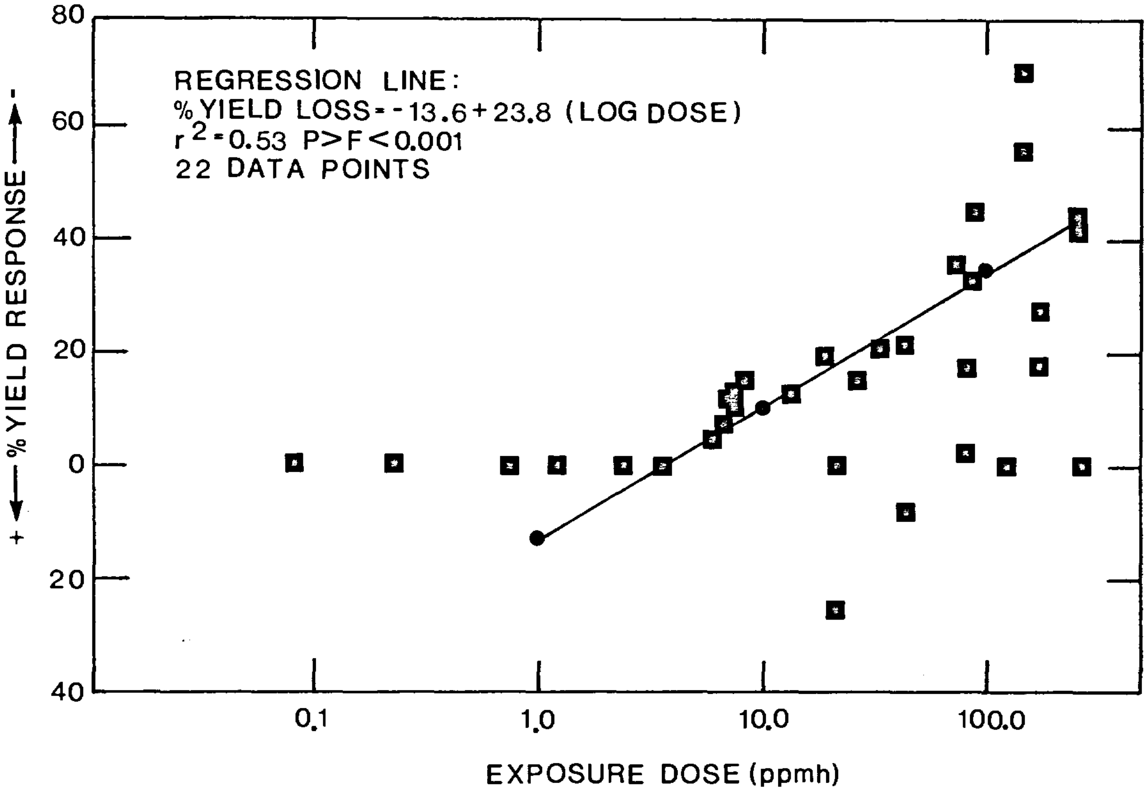


Figure 4-4. Regression of yield response vs. transformed dose (ppmh) for controlled exposures using field chambers (zero and positive effects excluded from regression analysis) (after McLaughlin 1980).

components of the total dose to which vegetation is exposed. Obviously not all, but probably most exposures to SO_2 on a regional scale are below levels producing phytotoxic reactions. An important aspect of evaluating the likelihood that plants will be negatively influenced by SO_2 exposures is the determination of what components within a plant's total exposure history are phytotoxic. McLaughlin (1980) recently examined USEPA (1978b) data on regional SO_2 concentration averages. Using the assumption that only the upper 10% of all SO_2 exposure days would have SO_2 concentrations high enough to cause stress to vegetation, and that only daylight exposure (8 hr/day) during the active growing season (6 mo/yr) would be effective, he calculated that the average potentially phytotoxic dose within designated air quality control regions would range from 0.9 ppmh (Region IX) to 5.5. ppmh (Region VIII). Maximum doses (highest reporting stations within regions) ranged from 2.6 ppmh to 27 ppmh, thus pointing once again to the potential injury to vegetation grown within smaller areas of high SO_2 point source emissions.

4.2.1.4 SO_2 Effects to Forest Vegetation

The effects of SO_2 on broadleaf tree species and similar types of native vegetation closely resemble those as described for agronomic crops.

In conifers, acute injury on foliage usually appears as a bright orange red tip necrosis on the current-year needles, often with a sharp line of demarcation between the injured tips and the normally green bases. Occasionally, the injury may occur as bands at the tip, middle, or base of the needles (Linzon 1972).

Recently incurred injury is light coloured but later bright orange or red colours are typical for the banded areas and tips. As needle tips die, they become brittle and break or whole needles drop from the tree. Pine needles are most sensitive to SO_2 during the period of rapid needle elongation but injury may also occur on mature needles (Davis 1972).

Chronic effects of SO_2 in conifers are generally first expressed on older needles (Linzon 1966). Chlorosis of tissues starting at the tips progresses down the needle towards the base (i.e., symptoms progress from the oldest to youngest tissues). Advanced symptoms may follow, involving reddening of affected tissues. Continued chronic injury to perennial foliage of coniferous trees results in premature needle abscission, reduced radial and volume growth, and early death of the trees (Linzon 1978).

Forest trees vary considerably in their sensitivity to SO_2 doses and Jones et al. (1973) evaluated the response of numerous species growing near point sources in southeastern U.S. (Table 4-2). Visible symptom expression only occurred on the most sensitive species at

TABLE 4-2. SULPHUR DIOXIDE CONCENTRATION CAUSING VISIBLE INJURY TO VARIOUS SENSITIVITY GROUPING OF VEGETATION[a] (Jones et al. 1973)

Maximum average concentration	Sensitivity grouping		
	Sensitive (ppm SO_2)	Intermediate (ppm SO_2)	Resistant (ppm SO_2)
Peak	1.0-1.5	1.5-2.0	2.0
1 hr	0.5-1.0	1.0-2.0	2.0
3 hr	0.3-0.6	0.6-0.8	8.0
	Ragweeds	Maples	White oaks
	Legumes	Locust	Potato
	Blackberry	Sweetgum	Upland cotton
	Southern pines	Cherry	Corn
	Red and black oaks	Elms	Dogwood
	White ash	Tuliptree	Peach
	Sumacs	Many crop and garden species	

[a] Based on observations over a 20-year period of visible injury occuring on over 120 species growing in the vicinities of coal-fired plants in the southeastern United States.

doses of 0.30 ppm/3 hr thus once again pointing to the smaller area of source influence on direct foliar injury. Dreisinger and McGovern (1970) indicated a somewhat similar injury threshold (i.e., 0.26 ppm SO_2/4 hr) for visible foliar injury to the most sensitive vegetation to SO_2, but doses were still above ambient concentrations as expected on a regional basis.

A few major investigations of the effects of SO_2 on tree species growing under natural conditions have been reported (Dreisinger 1965; Dreisinger and McGovern 1970; Linzon 1971, 1978). These reports indicated that a pollution (SO_2) gradient existed within the designated study area near Sudbury, Ontario, and effects correlated well with this gradient. Chronic effects on forest growth were prominent where SO_2 air concentrations during the growing season averaged 0.017 ppm SO_2, and were only slight in areas receiving 0.008 ppm SO_2 (Linzon 1978). In Czechoslovakia, Materna et al. (1969) reported the occurrence of moderate chronic injury to foliage of spruce trees at Celna, under the influence of an average annual concentration of SO_2 at 0.019 ppm.

Table 4-3 summarizes the results of tree studies that have utilized artificial exposure chamber systems under laboratory conditions. Only two studies (exposures) used doses close to ambient concentrations (Houston 1974); however, the use of selected clones of known sensitivity to SO_2 hinders further field speculation from this study. The remainder of the studies presented in Table 4-3 have used doses above expected occasional exposures under field conditions. Concentrations of 0.25 ppm SO_2 for 2 hr were required to induce slight injury to several pine species (Berry 1971), but overall trends for increasing foliar injury do not follow increasing dose for conifers *per se*. Smith and Davis (1978) exposed several conifers (pine, spruce, fir and Douglas fir) to doses of 1.0 ppm SO_2 for 4 hr or 2.0 ppm SO_2 for 2 hr and only pines developed necrotic tips at the 2.0 ppm dose. Likewise, Keller (1980) found only trends in reduced photosynthesis in Norway spruce at SO_2 doses of 0.05 ppm SO_2 for 10 wk exposure with significant effects noted at 0.10 and 0.20 ppm SO_2 over the same period.

4.2.1.5 SO_2 Effects to Natural Ecosystems

Ecosystems are basically energy processing systems whose components have evolved together over a long period of time. They are composed of living organisms together with their physical environmental conditions. Ecosystems respond to environmental changes or perturbations only through the response of the organisms of which they are composed (Smith 1980). The living (biotic) and nonliving (abiotic) units are linked together by functional interdependence. Processes necessary for the existence of all life, the flow of energy and cycling of nutrients are based on relationships that exist among the organisms within the system (Billings 1978; Odum 1971; Smith 1980). Because of these relationships, unique attributes emerge when

TABLE 4-3. SUMMARY OF STUDIES REPORTING RESULTS OF SO_2 EXPOSURES UNDER LABORATORY CONDITIONS FOR VARIOUS TREE SPECIES

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c] Foliage	Yield	Species effect[d]	Caveat[e]	Reference
E. white pine	0.25	2 hr	EC/SD	X		6.5% foliar injury	Plants maintained in sensitive condition	Berry 1971
Jack pine				X		4.5% foliar injury		
Red pine				X		0.5% foliar inury		
E. white pine	0.50	2 hr	EC/SD	X		12% foliar injury		
Jack pine				X		11% foliar injury		
Red pine				X		2% foliar injury		
Loblolly pine	0.25	2 hr	EC/SD	X		All equally sensitive; most sensitive period 8-10 wk of age or older	Plants maintained in sensitive condition	Berry 1974
Shortleaf pine				X				
Slash pine				X				
Virginia pine				X				
Sugar maple	0.50	24 hr/day	EC/SD			48% rate of photosynthesis, no symptoms		Carlson 1979
Black oak		1/wk				54% rate of photosynthesis, no symptoms		
White ash						20% rate of photosynthesis, no symptoms		

TABLE 4-3. CONTINUED

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c] Foliage	Yield	Species effect[d]	Caveat[e]	Reference
Sugar maple	0.50	24 hr/day	EC/SD			74% rate of photosynthesis, no symptoms		Carlson 1979
Black oak						33% rate of photosynthesis, no symptoms		
White ash						7% rate of photosynthesis, no symptoms		
American elm	2.00	6 hr	GC	X	X	Induce severe foliar injury; defoliation in older leaves; significant reduced expansion of new leaves; no. of emerging leaves and root dry wt reduced		Constantinidou and Kozlowski 1979a
American elm	2.00	6 hr	GC			No significant reduction in lipid content; significant in new leaf protein content; significant leaf, stem root carbohydrate content		Constantinidou and Kozlowski 1979b
Ponderosa pine	0.45	9 hr/day for 8 wk	EC	X		Severe needle tip chlorosis and necrosis		Evans and Miller 1975

TABLE 4-3. CONTINUED

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c]		Species effect[d]	Caveat[e]	Reference
				Foliage	Yield			
E. white pine	0.025	6 hr	EC/SD	X		Threshold dose for needle damage; most sensitive clones only		Houston 1974
E. white pine	0.05-0.15	6 hr	EC/SD	X		60% of tolerant clones developed foliar injury	Sensitive clones	
E. white pine	0.45	6 hr	EC/SD	X		All tolerant clones developed foliar injury		
Trembling aspen	0.35	3 hr	EC/SD	X		3 of 5 clones injured Up to 4.4% foliar injury		Karnosky 1976
Trembling aspen	0.50	3 hr	EC/SD	X		3 of 5 clones injured up to 45.2% foliar injury		
Trembling aspen	0.65	3 hr	EC/SD	X		5 of 5 clones injured up to 45.4% injury		

TABLE 4-3. CONTINUED

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c]		Species effect[d]	Caveat[e]	Reference
				Foliage	Yield			
Beech	0.05	16 wk Winter	EC/SD			Number of dead buds in spring at 0.10 ppm and higher; 10% kill at 0.20		Keller 1978
Norway spruce	0.05	10 wk	ES/SD	X	X	No foliar effects 25% vol. growth (avg.).	2 clones only	Keller 1980
	0.10			X	X	Foliar injury 38% vol. growth (avg.)		
	0.20			X	X	Foliar injury 53% vol. growth (avg.)		
Jack pine	0.18-0.20	24 hr	EC/SD			Inhibit foliar lipid synthesis, inhibition reversible; dose = recovery time		Malhotra and Kahn 1978
American elm	1.00	8 hr	EC			Inhibition of stomatal closing		Noland and Kozlowski 1979
Ginkgo	2.00	6.5 hr				Water stressed plant uptake of SO_2		

TABLE 4-3. CONTINUED

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c] Foliage	Yield	Species effect[d]	Caveat[e]	Reference
Scots pine	1.0	1 hr	EC	X		No injury, primary needles; slight injury, secondary needles		Smith and Davis 1977
		3 hr		X		14% maximum injury primary neeles; 52% maximum injury secondary needles		
		5 hr		X		37% maximum injury primary needles 60% maximum injury secondary needles		
Austrian pine Ponderosa pine Scotch pine Balsam, Fraser fir White fir Blue, White spruce Douglas fir	0.50	5 hr	GC	X		No injury		Smith and Davis 1978

TABLE 4-3. CONTINUED

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c] Foliage	Yield	Species effect[d]	Caveat[e]	Reference
Austrian pine Ponderosa pine Scotch pine	1.00	4 hr	GC	X		Less than 4% foliar injury for all species		Smith and Davis 1978
Balsam, Fraser fir, White fir Blue, White spruce Douglas fir	0.50							
Austrian pine Ponderosa pine Scotch pine Balsam, Fraser fir, White fir Blue, White spruce Douglas fir	2.00	2 hr	GC	X		No foliar injury on Douglas fir, firs, spruce Pine foliar injury threshold, necrotic tips		
Chinese elm	0.50	24 hr/day up to 30 days	GC	X		7 days to chlorosis		Temple 1972
Gingko				X		14 days to chlorosis		
Norway maple				X		12 days to chlorosis		
Pin oak				X		30 days to chlorosis		

TABLE 4-3. CONTINUED

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c]		Species effect[d]	Caveat[e]	Reference
				Foliage	Yield			
Chinese elm	2.00	6 hr	GC	X		100% leaf necrosis		Temple 1972
American elm	2.00	12 hr	GC			Induced stomatal closing; S content in plants fumigated in light		
Gingko	3.00	6 hr	GC	X		50% leaf necrosis		

[a] Doses within a single study that did not induce specifically different effects are listed along with the lowest SO_2 concentration that induced said effects.

[b] GC = growth chambers, EC = exposure chambers, EC/SD = exposure chamber, special design.

[c] X indicates study found foliar and/or yield effects.

[d] Most prominent or significant effect reported.

[e] Caveats for consideration about proper study design and interpretation.

ecosystems are studied that are not observable when individuals, populations or communities are studied.

Natural ecosystems are seldom, if ever, exposed to a single air pollutant. Therefore, the responses observed under ambient conditions cannot conclusively be attributed to a single substance such as sulphur dioxide alone. Consideration of low SO_2 doses on a regional basis presents even further difficulties in discerning effects induced by this pollutant.

Questions relating how sulphur deposition from anthropogenic emissions is incorporated and distributed by aquatic and terrestrial ecosystems is not fully resolved. The issue is critical since ecosystems subject to excess nutrients or toxic materials do not commonly distribute them uniformly throughout the system but rather preferentially sequester them in specific pools or compartments. In addition, sulphur dioxide as a gas can cause injury to the vegetative components of specific and local ecosystems so that energy flow and the cycling of other nutrients as well as sulphur may be disrupted if the pollutant is at sufficient concentrations.

Specific studies of the more detailed effects of SO_2 on natural systems have been conducted proximal to point sources of high SO_2 emissions and include studies in the vicinity of the Kaybob gas plants (Fox Creek, Alberta) (Winner et al. 1978), West Whitecourt gas plant (Whitecourt, Alberta) (Legge et al. 1976) and the Sudbury, Ontario smelter district (Dreisinger and McGovern 1970; Linzon 1971). Additionally, a series of designed studies using ariticial sources of SO_2 have been conducted in the Montana grasslands (Preston 1979).

The results of these studies, particularly the West Whitecourt and Montana grasslands studies, document the usefulness of addressing ecosystem level responses to SO_2 from a multidisciplinary approach incorporating investigations of physiology, autecology, synecology, geochemistry, meteorology and modelling. The results confirm that producers are sensitive to direct SO_2 effects as evidenced by SO_2-associated changes in cell biochemistry, physiology, growth, development, survival, fecundity, and community composition. Such responses are not unexpected. An equally important point of agreement among the different research efforts is the potential for ecological modification resulting from either direct SO_2 effects on nonproducer species or direct changes in habitat parameters, which in turn affect an organism's performance. Changes in biogeochemistry, particularly in the soil compartment, are notably responsive to low-dose SO_2 exposures. A major conclusion of the Montana grasslands studies indicated that at SO_2 levels above 0.02 ppm (52 $\mu g/m^3$), induced changes occur in the performance of producers, consumers, and decomposers. Many of the responses are individually small, but collectively over time they gradually modified the structure and function of the grasslands. The significance of these changes to the long-term persistence of the ecosystem remains controversial (Preston 1979).

Direct effects of SO_2 on individuals within natural plant communities are most noted within the lichens. Sulphur pollution not only has caused the depletion of lichen vegetation in certain areas, but also has resulted in changes in the distribution of different species (Hawksworth et al. 1973). Epiphytic lichen communities have been mapped within several regions of North America. In a rural area of Ohio surrounding a coal-consuming power station (emitting 1025 tons SO_2/day), the distribution of two corticolose lichens, Parmelia caperata and P. ruderta, was markedly affected by elevated SO_2 levels (Showman 1975). In regions experiencing an annual SO_2 average exceeding 0.020 ppm, both species were absent. The distribution of more resistant lichens was not noticeably affected until SO_2 levels exceeded 0.025 ppm (annual average). Somewhat lower levels were projected by LeBlanc and Rao (1973) to effect the ability of sensitive lichen species to survive and reproduce; acute and chronic symptoms of SO_2 toxicity in epiphytic lichens occurred when annual averages of SO_2 exceeded 0.03 and 0.006-0.03 ppm respectively.

The network of biotic-abiotic interactions, which is characteristic of managed and natural ecosystems, leads to the hypothesis that SO_2 effects on producers must have repercussions to other trophic levels. Demonstration of such responses, however, is difficult experimentally, and an accurate assessment of the specific importance of SO_2 in eliciting these responses is complicated by the often complex relationships between producers, consumers, and decomposers.

More subtle effects may occur in areas of low SO_2 (0.05 ppm annual average) deposition by shifts in soil microfloral populations thus further influencing plant rhizopheres leading to subsequent ecosystem alterations (Legge et al. 1976; Wainwright 1979).

Induced changes in natural ecosystems should not be evaluated on a positive or negative basis. Change as induced by anthropogenic sources of SO_2 must be considered as an alteration of natural processes. For example, natural ecosystems evolved on sulphur-deficient soils have done so within the imposed constraints per se. Although atmospherically derived sulphur may not be sufficient to cause injury, the prolonged input of sulphur may relax the constraints of a limited sulphur supply thereby inducing shifts in species composition.

4.2.2 Ozone (O_3)

Ozone air pollution injury was first reported by Richards et al. (1958) and during the subsequent years a diverse array of visible injury symptoms was described on a wide variety of crop, ornamental and native vegetation. Numerous review chapters and journal articles contain detailed descriptions of these symptoms (Brandt and Heck 1968; Hill et al. 1970; NAS 1977; USEPA 1978a). Characteristics of the injury symptoms and extent of injury are influenced by climatic and edaphic conditions, genetic variability, characteristics of the pollutant dose, and by interactions between the pollutant and other air pollutants or other environmental factors (NAS 1977). Injury symptoms described by the various researchers have included: bleaching, bifacial necrosis, general chlorosis, chlorotic mottling, chlorotic streaking, topical necrosis such as "fleck" and "stipple," and pigmented leaf tissue (Hill et al. 1970; NAS 1977; USEPA 1978a). In addition to the development of visible injury symptoms, exposure to atmospheric ozone can: (1) suppress photosynthesis; (2) stimulate respiration; (3) inhibit carbohydrate transport; (4) change membrane properties; (5) alter metabolite concentrations; (6) alter symbiotic associations; and (7) alter host-parasite interactions.

Prior to 1970 most O_3 research dealt with observed foliar symptoms resulting from acute (short-term), artificially controlled, dose-response studies. In the 1970s, the research approach shifted toward chronic (long-term) studies providing a more realistic estimate of natural plant response. The results of several such studies are summarized in Table 4-4. These studies formed the foundation for quantification of dose-response relationships that provided a more realistic basis for the assessment of losses under field conditions. A number of assessment techniques (e.g., open-top chambers, protective sprays) were utilized in several major studies designed to pursue this objective.

The National Crop Loss Assessment Network (NCLAN) (Heck et al. 1982) utilized open-top chambers and controlled O_3 concentrations. Its purpose was to provide standardized crop dose-response data which could be utilized in the development of reliable regional scale loss assessment calculations.

4.2.2.1 O_3 Effects to Agricultural Crops

Foliar responses of crops to artificial O_3 exposure have been well documented and used in the development of species and varietal sensitivity listings and the preparation of predictive dose-response curves (Larsen and Heck 1976; Linzon et al. 1975). However, these data may not be reliable for estimating the total effect on crop productivity (e.g., yield, quality). Most information now indicates that the severity of foliar symptoms is not a reliable index of crop growth or yield effects (Reinert 1980) as there is uneven competition among several sinks that receive photosynthate. Also, compensatory responses to ozone can produce rapid recovery from injury (Jacobson in press). Studies with soybeans (Tingey et al. 1973), tomatoes (Oshima et al. 1975) and alfalfa (Tingey and Reinert 1975) all support this concept. The exceptions to this general finding are cases where the harvested product is the foliage and where foliar injury development coincides with the rapid growth of the harvested product (Linzon et al. 1975).

TABLE 4-4. EFFECTS OF LONG-TERM CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD AND FOLIAR INJURY TO SELECTED PLANTS (USEPA 1978)

Plant species	Ozone Concentration $\mu g/m^3$ (ppm)	Exposure time, hr	Plant response percent reduction from control	Reference
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/wk 10 wk	39, bract size	Craker & Feder 1972
E. white pine	196 (0.10)	4/day, 5 days/wk 4 wk (mixture of O_3 and SO_2 for same periods)	3, needle mottle (over 2-3 days of exposure)	Dochinger & Seliskar 1970
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 vegatative growth)	
Lemma, duckweed	196 (0.10)	5/day, 14 days	100, flowering; 36, flowering (1 wk after exposure completed) 50, frond doubling rate	Feder & Sullivan 1969
Sweet corn cv. 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	
Soybean cv. 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	
Wheat	196 (0.10)	7/day, 54 days	16, yield	Heagle et al. 1979a
	255 (0.13)	7/day, 54 days	33, yield	
Field corn cv. Open-pedigree	294 (0.15)	7/day, 88 days	40, seed yield	Heagle et al. 1979b
cv. Coker 16	294 (0.15)	7/day, 88 days	12, seed yield	

TABLE 4-4. CONTINUED

Plant species	Ozone Concentration µg/m^3 (ppm)	Exposure time, hr	Plant response percent reduction from control	Reference
Spinach	255 (0.13)	7/day, 38 days	69, fresh wt	Heagle et al. 1979c
	196 (0.1)	7/day, 38 days	37, fresh wt	
	117 (0.06)	7/day, 38 days	18, fresh wt	
Bean cv. 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	
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	
Yellow poplar	588 (0.30)	8/day, 5 days/wk 13 wk	82, leaf drop; 0, height	Jensen 1973
Silver maple	588 (0.30)	8/day, 5 days/wk 13 wk	50, leaf drop; 78, height	
White ash	588 (0.30)	8/day, 5 days/wk 13 wk	66, leaf drop; 0, height	
Sycamore	588 (0.30)	8/day, 5 days/wk 13 wk	0, leaf drop; 22, height	
Sugar maple	588 (0.30)	8/day, 5 days/wk 13 wk	28, leaf drop; 64, height	
Poplar, hybrid	290 (0.15)	8/day, 5 days/wk 6 wk	50, shoot dry wt; 56, leaf dry wt 47, root dry wt	Jensen & Dochinger 1974
Wheat cv. Arthur 71	392 (0.20)	4/day, 7 days (anthesis)	30, yield	Kochhar 1974

TABLE 4-4. CONTINUED

Plant species	Ozone Concentration $\mu g/m^3$ (ppm)	Exposure time, hr	Plant response percent reduction from control	Reference
Bean cv. 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	
	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)	
	588 (0.30)	1/day, 14 days	40, leaf dry wt	
	558 (0.30)	3/day, 14 days	76, leaf dry wt	
Bean cv. Pinto	255 (0.13)	8/day, 28 days	79, top fresh wt 73, root fresh wt 70, height	Manning et al. 1971
Ponderosa pine	290 (0.15)	9/day, 10 days	4, photosynthesis	Miller et al. 1969
	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	
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
	98 (0.05)	7/day, 68 days	30, top dry wt, harvest 1 50, top dry wt, harvest 2	
Beet, garden	392 (0.20)	3/day, 38 days	50, top dry wt	Ogata & Maas 1973
Sweet corn cv. Golden Jubilee	393 (0.20)	3/day, 3 days/wk until harvest	13, kernel dry wt; 20, top dry wt; 24, root dry wt	Oshima 1973
	686 (0.35)	3/day, 3 days/wk until harvest	20, kernel dry wt; 48, top dry wt; 54, root dry wt	

TABLE 4-4. CONTINUED

Plant species	Ozone Concentration µg/m^3 (ppm)	Exposure time, hr	Plant response percent reduction from control	Reference
Tomato	392 (0.20)	2.5/day, 3 days/wk 14 wk	1, yield; 32, top dry wt; 11, root dry wt	Oshima et al. 1975
	686 (0.35)	2.5/day, 3 days/wk 14 wk	45, yield; 72, top dry wt; 59, root dry wt	
Brome grass	290-647 (0.15-0.33) (Varied)	4/day, 5 days/wk growing season	83, biomass	Price & Treshow 1972
Radish	98 (0.5)	8/day, 5 days/wk 5 wk	54, root fresh wt 20, leaf fresh wt	Tingey et al. 1971
		8/day, 5 days/wk (mixture of O_3 and SO_2 for same periods)	63, root fresh wt 22, leaf fresh wt	
Soybean	98 (0.05)	8/day, 5 days/wk 3 wk	13, foliar injury	Tingey et al. 1973
		8/day, 5 days/wk (mixture of O_3 and SO_2 for same periods)	16, foliar injury; 20, root dry wt	
	196 (0.10)	8/day, 5 days/wk 3 wk	21, top dry wt; 9, root dry wt	
Alfalfa	98 (0.05)	8/day, 5 days/wk 12 wk	18, top dry wt	Tingey & Reinert 1975
Ponderosa pine	196 (0.10)	6/day, 126 days	12, root length 21, stem dry wt; 26, root dry wt	Wilhour & Neely 1977
W. white pine	196 (0.10)	6/day, 126 days	13, foliage dry wt; 9, stem dry wt	

Although the adverse effects of O_3 exposure on crop yield or productivity have not been as extensively documented as has been the case with foliar injury, there are nevertheless numerous reports on this topic. Any assessment of yield or quality parameters under field conditions is complicated by the ubiquity of ozone exposure, the effect of meteorological variables on ozone distribution within crop canopies, and the difficulty in establishing ozone-free control plots. Numerous biotic (pathogen, genetics) and abiotic factors (i.e., RH, light, and soil moisture) within the environment must also be taken into account. These difficulties have been partially overcome by recent progress which has been made in the development of field assessment techniques for plant growth and productivity (Reinert 1980). These include open-top field chambers, pollutant exclusion methods, open-air fumigations, ambient air pollutant gradients and chemical protectants.

Experimental studies with field grown crops have demonstrated yield reductions in a large number of ozone-sensitive crops: beans (Heggestad et al. 1980), potatoes (Heggestad 1973), grapes (Thompson et al. 1969), corn (Heagle et al. 1972) and others (Heggestad 1980; Jacobson in press; Reinert 1975). In general the studies have shown that decreased yield of susceptible species occurs with average ozone concentrations of between 0.05 and 0.1 ppm for 6-8 hr/day during the growing season (Heck et al. 1977). In a 5-yr study in Maryland (1972-79), typical yield reductions were 4, 9, 10, 17 and 20% respectively for field grown (open-top chambers) snap beans, sweet corn, potatoes, tomatoes and soybeans (Heggestad 1980).

The first report from the NCLAN project (Heck et al. 1982) appears to provide good agreement with earlier dose-yield response data (Heagle and Heck 1980) and with yield losses in the various crops as follows: soybean 10%, peanut 14-17%, a single turnip 7%, head lettuce 53-56% and red kidney bean 2%. The yield reductions were equated with seasonal 7 hr/day mean O_3 concentrations of 0.06-0.07 ppm compared to the 0.025 control value. In the earlier study (Heagle and Heck 1980) employing open-top chambers with O_3 dispensing capabilities, an annual U.S. crop loss estimate assuming a seasonal 7 hr/day mean O_3 concentation of 0.06 ppm in all crop production areas was calculated at $3.02 billion (5.6% of the national production). In a subsequent manuscript Heck (1981) pointed out that it is a weak assumption that crops in all parts of the United States are in a sensitive state during much of the growing season and the values should be reduced by 50%. This would bring the estimate of O_3 crop losses in the U.S. to between $1 billion and $2 billion or 2-4% of total production assuming all areas were at concentrations of 0.12 ppm for 1 hr. As most sections of the country are above the current standard, the national losses are probably higher than the above values (Heck 1981).

There are limitations in assessing O_3 impact on crop species, in that a majority of presently operating O_3 monitors in both the U.S. and Canada are in urban locations. They therefore may not represent levels to which rural vegetation is exposed. However, some indication of the occurrence of O_3 in rural areas along the U.S./Canada border is given in Table 4-5. The Ontario rural data (Table 4-6) have been summarized to provide some indication of the potential for adverse crop effects (growing season daytime basis) and can be compared directly with the O_3 data (Table 4-7) for urban locations in the National Air Pollution Surveillance Network (NAPS) in Ontario, Quebec and New Brunswick.

It is apparent from these urban and rural data that the southern portion of the Province of Ontario is most adversely affected by ozone in Eastern Canada. This finding is corroborated by numerous reports of ozone-related crop injuries in this area (Cole and Katz 1966; Curtis et al. 1975; Hofstra et al. 1978; Ormrod et al. 1980) and by the absence of any documented injurious effects to sensitive agronomic or forest species in Quebec or the Maritime provinces.

In Ontario the first indication of transboundary ozone movement across Lake Erie was documented (Mukammal 1960) following extensive work on the relationship between the incidence of weather fleck on tobacco and meteorological conditions associated with the buildup of ozone. Since then a number of large-scale meteorological investigations (Anlauf et al. 1975; Yap and Chung 1977) have documented these early findings and have shown that high ozone levels generally are associated with regional southerly air flows which have passed over numerous urban and industrialized areas of the U.S. and which, as they move across the lower Great Lakes, undergo rapid dispersion as they encounter unstable conditions near the northern shore of Lake Erie. Contributing to these influx patterns are the more localized downwind urban effects which can add to the already high background levels.

In an effort to estimate the severity and extent of plant injury or yield loss resulting from exposure to ambient ozone in southern Ontario, a summary has been prepared for all major crop species on the basis of documented research reports of yield or productivity losses in Ontario or the northeastern U.S. and on unpublished documents by government agencies or university departments working under assessment mandates or research contracts. On the basis of these findings and 1980 economic values it is estimated that the average annual loss for ozone-sensitive Ontario crops based on 1980 economic values is in excess of $20 million (Pearson 1982). An example of the types of work which were considered in the assessment of crop loss is shown for one of the most sensitive species, white bean.

In 1961, bronzing and rusting of white bean foliage was reported (Clark and Wensley 1961) throughout southwestern Ontario and the resultant defoliation and pod abortion was estimated to have resulted in a loss of approximately 600 pounds of beans per acre (45% yield loss) in severely affected fields. Following extensive field work in 1965 and 1967 the disorder was found to be associated with the

TABLE 4-5. THE NUMBER OF TIMES IN 1980 and 1981 THAT OZONE CONCENTRATIONS EXCEEDED THE USEPA STANDARD OF 0.12 ppm ALONG THE U.S./CANADA BORDER[a]

Station	State	1980	1981
Allen Park	MI	1	1
Detroit	MI	2	0
Detroit	MI	6	4
Essexville	MI	1	–
Livonia	MI	1	1
Macomb Co.	MI	6	6
Marquette Co.	MI	0	0
Port Huron	MI	5	7
Port Huron	MI	–	7
Southfield	MI	0	0
Warren	MI	0	0
Lake Co.	MI	0	0
St. Louis Co.	MI	–	0
Berlin	NH	–	0
Amherst	NY	0	0
Erie Co.	NY	–	1
Essex Co.	NY	5	7
Monroe Co.	NY	1	0
Niagara Co.	NY	5	1
Niagara Falls	NY	2	0
Rochester	NY	1	1
Wayne Co.	NY	2	1
Berea	OH	0	1
Cleveland	OH	0	0
Conneaut	OH	1	2
Elyria	OH	0	–
Elyria	OH	2	1
Painesville	OH	1	–
Toledo	OH	0	5
Toledo	OH	3	2
Westlake	OH	0	0
Burlington	VT	0	0
Burlington	VT	0	0

[a] Only data from the U.S. counties touching the international boundary were used. Data were compiled by Rambo and Patent (pers. comm.). SAROAD data base covers all of calendar year 1980, but only includes January to September of 1981.

TABLE 4-6. SUMMARY OF GROWING SEASON: DAYLIGHT OZONE TRENDS IN RURAL LOCATIONS IN SOUTHERN ONTARIO, 1976-81

		All Values Based on Hourly O_3 Data from 9 a.m. - 6 p.m. Inclusive (10 hr/day) During June, July and August Each Year						
Location	Year	% Valid Data	Maximum Hourly O_3 Concentration (ppmh)	% of Time O_3 Concentration 8.0	10.0 (ppmh)	12.0	No. of Days O_3 8.0 for 4 Consecutive Hours	No. of Days O_3 10.0 for 2 or more Consecutive Hours
Simcoe Ontario	1976	98.2	13.9	17.9	6.6	2.0	22	9
	1977	96.1	13.3	10.7	2.8	0.3	12	6
	1978	96.7	13.2	13.5	4.3	0.4	18	9
	1979	96.5	14.8	7.1	0.7	0.1	6	1
	1980	92.0	9.9	3.4	0.0	0.0	3	0
	1981	94.3	11.0	6.9	1.3	0.0	5	4
Huron Park Ontario	1976	-	-	-	-	-	-	-
	1977	97.4	11.7	6.4	0.9	0.0	7	3
	1978	99.0	13.0	9.5	1.1	0.2	14	3
	1979	91.6	12.3	4.5	1.9	0.3	6	2
	1980	99.0	11.7	3.5	0.3	0.0	4	1
	1981	96.1	14.2	8.4	2.1	0.2	9	5
Petrolia Ontario	1976	-	-	-	-	-	-	-
	1977	87.7	14.6	10.4	1.7	0.6	13	3
	1978	89.3	14.8	15.7	5.4	1.1	17	10
	1979	97.2	14.8	10.6	3.6	0.7	12	9
	1980	98.0	12.5	3.8	1.1	0.2	3	2
	1981	89.3	13.2	5.6	1.1	0.7	6	2
Merlin Ontario	1976	-	-	-	-	-	-	-
	1977	67.0	16.7	23.7	10.6	3.1	23	14
	1978	99.7	13.2	10.6	2.5	0.3	13	7
	1979	23.8	15.8	10.5	5.9	1.8	2	3
	1980	97.6	12.5	4.9	0.7	0.1	6	2
	1981	71.4	10.2	4.3	0.2	0.0	4	0

TABLE 4-7. SUMMARY OF GROWING SEASON: DAYLIGHT OZONE TRENDS IN URBAN LOCATIONS IN EASTERN CANADA, 1976-80

TABLE 4-7. SUMMARY OF GROWING SEASON: DAYLIGHT OZONE TRENDS IN URBAN LOCATIONS IN EASTERN CANADA, 1976-80

Location (NAPS Station No.)	Year	All Values Based on Hourly O_3 Data from 9 a.m. - 6 p.m. Inclusive (10 hr/day) During June, July and August Each Year						
		% Valid Data	Maximum Hourly O_3 Concentration (ppmh)	% of Time O_3 Concentration 8.0 (ppmh)	10.0 (ppmh)	12.0 (ppmh)	No. of Days O_3 8.0 for 4 Consecutive Hours	No. of Days O_3 10.0 for 2 or more Consecutive Hours
Halifax	1976	-	-	-	-	-	-	-
Nova Scotia	1977	96.1	12	0.8	0.5	0.2	1	1
(030115)	1978	96.1	10	0.9	0.0	0.0	2	0
	1979	99.0	10	1.4	0.1	0.0	1	0
	1980	67.4	9	2.7	0.0	0.0	2	0
St. John	1976	-	-	-	-	-	-	-
New Brunswick	1977	-	-	-	-	-	-	-
(040202)	1978	-	-	-	-	-	-	-
	1979	-	-	-	-	-	-	-
	1980	51.2	8	0.0	0.0	0.0	0	0
Quebec	1976	97.7	7	0.0	0.0	0.0	0	0
Quebec	1977	76.5	9	1.4	0.0	0.0	2	0
(050304)	1978	96.4	9	0.7	0.0	0.0	2	0
	1979	92.6	7	0.0	0.0	0.0	0	0
	1980	89.3	7	0.0	0.0	0.0	0	0
Montreal[a]	1976	95.4	13	4.9	1.3	0.5	7	6
Quebec	1977	94.3	12	2.3	0.5	0.1	4	2
(050102)(050111)	1976	91.4	12	7.1	2.8	1.0	11	7
(050103)(050112)	1979	90.8	11	2.3	0.4	0.1	5	2
(050104)(050113)	1980	87.9	10	0.9	0.1	0.1	2	1
(050109)(050115)								
Ottawa[a]	1976	82.3	9	0.5	0.0	0.0	1	0
Ontario	1977	96.9	11	1.3	0.4	0.1	2	1
(060101)	1978	80.7	11	2.8	0.5	0.2	3	1
(060104)	1979	96.4	10	0.9	0.0	0.0	1	0
	1980	81.0	9	0.7	0.0	0.0	1	0

TABLE 4-7. CONTINUED

		All Values Based on Hourly O_3 Data from 9 a.m. - 6 p.m. Inclusive (10 hr/day) During June, July and August Each Year						
Location (NAPS Station No.)	Year	% Valid Data	Maximum Hourly O_3 Concentration (ppmh)	% of Time O_3 Concentration 8.0 (ppmh)	% of Time O_3 Concentration 10.0 (ppmh)	% of Time O_3 Concentration 12.0 (ppmh)	No. of Days O_3 8.0 for 4 Consecutive Hours	No. of Days O_3 10.0 for 2 or more Consecutive Hours
Cornwall	1976	95.3	11	0.6	0.2	0.0	1	1
Ontario	1977	94.3	6	0.0	0.0	0.0	0	0
(061201)	1978	97.2	11	7.9	2.3	0.0	8	4
	1979	79.5	11	4.4	0.7	0.0	5	2
	1980	80.7	10	4.0	0.0	0.0	4	0
Toronto[a]	1976	90.7	12	5.6	2.0	0.4	5	4
Ontario	1977	87.1	10	1.4	0.5	0.1	2	1
(060401)	1978	85.3	12	8.4	2.4	0.4	7	4
(060402)	1979	94.9	12	3.8	0.8	0.2	4	2
(060403)	1980	91.7	11	3.3	0.6	0.1	3	1
(060410)								
(060413)(060415)								
St. Catharines	1976	97.7	13	12.7	3.7	0.7	18	9
Ontario	1977	93.0	12	4.2	1.4	0.2	4	3
(061301)	1978	98.6	12	11.7	2.1	0.0	14	6
	1979	90.2	12	1.3	0.1	0.1	0	0
	1980	94.8	13	4.6	0.8	0.2	5	3
Kitchener	1976	27.9	11	13.2	2.3	0.0	4	1
Ontario	1977	90.4	10	2.3	0.1	0.0	3	0
(061501)	1978	99.0	12	13.5	3.2	0.2	16	6
	1979	96.9	10	3.7	0.2	0.0	3	0
	1980	96.3	9	3.7	0.0	0.0	6	0
London	1976	95.6	11	6.6	0.7	0.0	8	2
Ontario	1977	94.5	10	3.2	0.3	0.0	3	1
(060901)	1978	97.7	11	6.3	0.4	0.0	8	1
	1979	96.4	10	3.8	0.2	0.0	3	1
	1980	95.2	11	4.5	0.5	0.0	3	1

TABLE 4-7. CONTINUED

		All Values Based on Hourly O_3 Data from 9 a.m. - 6 p.m. Inclusive (10 hr/day) During June, July and August Each Year						
Location (NAPS Station No.)	Year	% Valid Data	Maximum Hourly O_3 Concentration (ppmh)	% of Time O_3 Concentration 8.0 (ppmh)	% of Time O_3 Concentration 10.0 (ppmh)	% of Time O_3 Concentration 12.0 (ppmh)	No. of Days O_3 8.0 for 4 Consecutive Hours	No. of Days O_3 10.0 for 2 or more Consecutive Hours
Windsor Ontario (060204)	1976	90.5	17	18.0	7.6	1.9	19	14
	1977	92.6	14	15.8	4.1	0.7	19	10
	1978	95.4	11	10.1	2.6	0.2	10	7
	1979	89.8	12	6.0	1.3	0.0	6	3
	1980	93.0	13	12.0	1.5	0.4	7	4

[a] Values shown are averages for several stations.

occurrence of elevated levels of atmospheric ozone pollution (Weaver and Jackson 1968). The symptoms first appear sometime between flowering and normal senescence, a critical period in the development of yield potential. They appear as a bronze-coloured necrotic stipple which, as it becomes more severe, results in premature leaf drop and reduced seed set.

In an effort to assess and compare the annual severity of ozone injury on sensitive white beans, Ontario government personnel have conducted visual assessment surveys throughout the major production areas in southern and southwestern Ontario since 1971. These studies ruled out any varietal resistance and confirmed that the bronzing disorder was widespread throughout all the bean production areas (Pearson 1980).

Studies utilizing chemical protectants against ozone injury have helped to provide information on the economic relevance of the bronzing disorder in Ontario. In one case a 13% yield increase was associated with the reduction in bronzing severity (Curtis et al. 1975), while in another study, yield increases of up to 36% (27% yield reduction) were realized (Hofstra et al. 1978).

In 1977 and 1978 yield increases with antioxidant protection were not as high (Toivonen et al. 1980) due to climatic problems. The overall response in these years was 16% and 4% increase in yield respectively due to antioxidant protection. On the basis of these values and considering the uniformity of cultivar sensitivity, the average annual loss for this crop was estimated at 12% (Pearson 1982).

4.2.2.2 O_3 Effects to Forest Vegetation

As in the case of agricultural crops, economic evaluation of the effect of pollutants on forest productivity is ultimately contingent upon the establishment of dose-response relationships. Consideration must be given to pollutant loadings and then quantitative measure of growth-suppression or yield-depression.

There are different considerations in evaluating the effects of O_3 and acidic deposition on forest trees than for agricultural crops. Most forest tree species are long-lived, perennial plants that are not subjected to fertilization, soil amendments, cultivation, extensive pest control or other cultural practices that agricultural crops receive. Their size also precludes pollutant exclusion (chambers) studies or protective sprays limiting the assessment of growth or productivity losses to visual observations of growth characteristics. This must then be related to ozone dose information (i.e., pollution gradients) where available.

In general, many tree species indigenous to North America are classified as susceptible to O_3 damage (Davis and Wilhour 1976; Skelly 1980). Direct injury to tree foliage by O_3 has been demonstrated repeatedly in experiment situations (Table 4-4), and in nature as well. Concentrations of O_3, at least in some forested areas, are sufficient to cause injury (Miller and McBride 1975; Skelly 1980). These effects of O_3 can alter the productivity, successional patterns, and species composition of forests (Smith 1980) and enhance activity of insect pests and some diseases (Woodwell 1970).

The current status concerning O_3-induced effects on Temperate and Mediterranean forest tree species, communities and ecosystems has been summarized (Skelly 1980). It is possible that primary productivity, energy resource flow patterns, biogeochemical patterns and species successional patterns may all be challenged by oxidant air pollution.

4.2.3 Acidic Deposition

Various types of injury listed below may result from direct exposure of plants to acidic deposition (Cowling 1979; Cowling and Dochinger 1980; Tamm and Cowling 1977):

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 reproductive processes;
7) Synergistic 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; and
11) Alteration of host-parasite interactions.

In contrast to results with O_3, experimental studies with simulated acidic deposition 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. These results depend upon 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. 1980). Each species may thus have unique patterns of physiological and genetic responses to the potentially beneficial and detrimental components of acidic deposition.

4.2.3.1 Acidic Deposition Effects to Agricultural Crops

Experimental studies with plants grown under controlled (or semicontrolled) conditions have demonstrated that visible foliar symptoms can be produced on certain crops, when pH of applied simulated rain is 3.5 or less (Table 4-8). Field-grown plants may be less susceptible to the development of foliar symptoms than plants grown under controlled or semicontrolled conditions (Jacobson 1980; Shriner 1978). Further, as with O_3 and SO_2, foliar symptoms may not correlate closely with yield reductions (Lee et al. 1980). However, recent evidence suggests that generalizations concerning effects on crops from experiments with O_3 alone or with acidic deposition alone, may underestimate the interactive effects of sequential exposures to these two pollutants (Jacobson et al. 1980). Further research is needed to determine if acidic deposition 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 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 events. The one (or several) most acidic event(s) 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 from acidic deposition 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.

To evaluate the economic cost of acidic deposition on agricultural crops, answers to several questions are needed. Which crops are actually benefited by components of acidic deposition? Which crops are most susceptible to reductions in yield by exposure to acidic

TABLE 4-8. REPRESENTATIVE TOLERANCE LIMITS OF SELECTED PLANTS TO SIMULATED ACID PRECIPITATION[a]

Plant Species	Pollutant Concentration	Species Effect	Reference
Birch Willow herb Scots pine	pH 2.0 - 2.5	Foliar lesions	Abrahamsen et al. 1976
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
Radish	pH 3.5	Foliar damage	Lee et al. 1980
Beet	pH 4.0	Foliar damage	
Carrot	pH 4.0	Reduced yield	
Mustard greens Spinach Swiss chard	pH 3.5	Foliar damage and reduced marketability	
Tobacco Lettuce Cauliflower Broccoli	pH 3.5	Foliar damage	
Cabbage	pH 3.0		
Broccoli	pH 3.0	Reduced yield	
Potatoes	pH 3.0	Foliar damage reduced yield	
Potatoes	pH 3.5	Increased yield	
Alfalfa	pH 3.5	Foliar damage Increased yield	
Kidney beans Oak	pH 3.2	Inhibition of parasitic organisms	Shriner 1976
Conifer seedlings	pH 2.0	Foliar damage	Strifler and Kuehn 1976
Mosses	pH 2.0 - 3.0	Desiccation, death	Teigen et al. 1976
Chrysanthemums Juniper	pH 3.0 pH 4.0+	Foliar damage and increased phosphate uptake Growth decreased	Tukey 1980
Yellow birch	pH 2.3 - 3.0	Foliar damage	Wood and Bormann 1976

[a] 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.

deposition? Unfortunately, only preliminary indications are available in response to these questions (Lee et al. 1980). Accordingly, the dose-response function needs to be provided with many more quantitative dose descriptions that relate to yield effects under actual growing conditions. Information on the influence of other parameters on these dose-response functions also needs to be provided. These factors include patterns of rainfall occurring as they interact with stage of crop development, soil nutrient and water supplies, and deposition of particulate matter from the atmosphere. Further clarification also is needed of the possible modifying influence of NO_3^- and SO_4^{2-} as nutrients in leaf tissue in response to acidic rainfall events. Finally, the critical factors determining plant susceptibility, expressed as yield reductions, need further definition to enhance extrapolation from a few of the most economically important crop species and cultivars to describe the response of the entire ecosystem.

When this information is provided, it may then be possible to make reasonable and reliable estimates of the economic impact of acidic deposition on agricultural productivity.

4.2.3.2 Acidic Deposition Effects to Forest Vegetation

Effects of acidic deposition on forest trees involves several considerations differing from those relating to agricultural crops. Trees are perennial plants with long lifetimes. Thus, there is greater concern with the cumulative impact or repeated exposures to acidic deposition. 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 partially affected by the nature, age, and condition of forests. Consequently, the effect of acidic deposition on forests could also have important secondary impacts which are initiated by direct effects on trees.

The historic pattern of forest growth as revealed in the growth rings may show "direct" evidence of the effects of acidic deposition. Based on substantial analysis of growth rings of Scots pine and Norway spruce trees that grow 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." This is a controversial study because other Scandinavian researchers have not been able to uncover similar trends. For example, in a large study in Norway, Strand (1980) was unable to "find definite evidence that acidic deposition has had an effect on the growth of the trees". Studies of a similar type in North America have been limited in scope. Cogbill (1976), having examined historic patterns of growth rings in two forest stands (one a beech-birch-maple woods in New Hampshire and the other a spruce woods in Tennessee) observed that "no regional, synchronized decrease in radial increment was evident in the two mature stands studied." However, Johnson et al. (1981) 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. The relationship of these findings to other possible incitants (i.e., disease, insects, ozone) should be more fully explored.

Experimental evidence from studies of the action of simulated acidic deposition on tree parts does indicate that under regimes of high acid dosing, direct damage (i.e., foliar lesions) can be produced (Table 4-8).

A potential impact of acidic deposition may occur indirectly through the soil and may become involved in the complex natural circulation of elements upon which forest vegetation depends, (i.e., 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 for agricultural use. In contrast to agricultural practice, amendments (i.e., fertilizers or lime) are rarely used in forestry practice.

Deficiencies of nitrogen (N) are common in forests of the temperate and boreal regions. Appreciable responses to N-fertilizer have been reported frequently, particularly for conifers on upland sites in both the acidic deposition 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. 1977a,b).

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 acidic deposition sensitive, including cation exchange capacity (CEC), exchangeable K and percent base saturation. Also, in northern Ontario Chrosciewicz (1963) associated better growth of jack pine with soils rich in basic minerals (and presumably richer in exchangeable bases). Hoyle and Mader (1964) noted a high degree of correlation between Ca content in foliage and height growth of red pine in western Massachusetts. Lowry (1972) across a wide range of sites in eastern Canada noted with black spruce relationships between site index and foliage content (including N, P, Ca, and to a lesser extent Mg concentrations).

Studies of forest soils (Lea et al. 1979) indicate that Ca and Mg levels can be leached following applications of acidic deposition simulants. Leaching of these elements from forest soils, as a result of high SO_4^{2-} mobility (Mellitor and Raynal 1981), may lead to 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 acidic deposition will interfere with uptake and cycling of various elements. First, acidic deposition may promote increased leaching of essential foliar constituents (e.g., K, Ca and Mg) as a function of both acid-related surface disintegration and mass exchange by H^+ ions.

Both wet and dry deposition undergo chemical alteration directly on the surface of the leaves and indirectly within the cellular tissue. The nature of the leachate or throughfall depends upon plant characteristics such as tree species, leaf morphology, stand characteristics (e.g., age and stocking), and site conditions (e.g., precipitation rate, distribution and chemical composition). Input/output analyses and element budgets with particular reference to acidic deposition, 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 (i.e., soil, water, and 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 (e.g., K) leach readily from both living and dead parts, while others (e.g., Ca) leach more slowly.

Some researchers have found that throughfall from deciduous forests exhibit 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 (i.e., 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 even though 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% and 70% 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 partially attributed 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 for part of the difference in chemical composition of the throughfall.

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 with both acidic and nonacidic deposition. Certain elements are leached more rapidly than others, especially when rainfall is acidic. There are also differences 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 enhance acidity and the concentration 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.

Acidic deposition may affect health and/or productivity of forest or other vegetation through indirect channels, or through effects on nutrition. Research efforts are just beginning to evaluate the possible role of acidic deposition in the predisposition of trees to disease infection and insect attacks. Further, the behaviour of plant litter and soil-occurring facultative saprobes, which may exhibit plant pathogenic tendencies under acidification, requires evaluation.

4.2.4 Pollutant Combinations

For much of the northeast and midwest sections of the United States where acidic rainfall events and low dose SO_2 trends have been recorded, ozone air pollution also occurs on a concomitant basis.

Sulphur dioxide, NO_x, and particulate emissions may be of "local" importance to vegetation, but mesoscale background concentrations of these pollutants are well below known thresholds for inducement of direct vegetation effects. From these background concentrations, long-term accumulation by plants of sulphates and nitrates and the related potentially beneficial or detrimental effects are poorly defined.

Extrapolation from results of single pollutant effects on vegetation under ambient field conditions must be approached with caution. Reactions in pollutant combinations may be additive (sum of effects), less than additive (antagonistic), or more than additive (synergistic). In addition to pollutant combinations under controlled conditions, the interaction of constantly changing environmental factors and fluctuating pollutant doses must be further evaluated before a conclusive statement of the importance of such interactions can be made. Reinert (1975) and Reinert et al. (1975) have prepared the most recent reviews of this area of investigation.

4.2.4.1 SO_2 - O_3 Effects

The most frequently occurring pollutant combination of significance to plant life must be considered as O_3 and SO_2. However, few studies have utilized doses which would be considered as even close to ambient except as they pertain to areas affected by point sources of emission of SO_2. Studies using combinations of O_3 and SO_2 are presented in Table 4-9. As indicated, only the study of Houston (1974) used doses of SO_2 approaching regional expected averages. He used mixtures of SO_2 and O_3 in doses to simulate actual field conditions and reported that even the lowest concentrations of O_3 (0.05 ppm) and SO_2 (0.05 ppm) for 6 hr in mixture caused more serious damage than that resulting from either pollutant alone at similar concentrations. Studies by Tingey et al. (1971a,b, 1973), Tingey and Reinert (1975), and Neely et al. (1977) used doses reasonably expected in smaller areas such as the Ohio Valley (Mueller et al. 1980). Doses used in other studies used less realistic doses for either SO_2 or O_3 and the results are of little value in estimating field effects on a regional basis.

A recent study by Reich et al. (1982) utilized a linear gradient field exposure system of SO_2 and O_3 over soybeans exposed during pod fill. Low dose exposure combinations averaged SO_2 at 0.040 ppm and O_3 at 0.034 ppm for 5.5 hr per day for 12 days. Yield

TABLE 4-9. EFFECTS OF MIXTURES OF SO_2 AND O_3 ON SELECTED PLANTS

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c] Foliage	Yield	Species effect[d]	Caveat[e]	Reference
Soybean	0.10 SO_2 + 0.10 O_3	6 hr/day 133 days	F/CC	X	X	SO_2 alone and in the mix did not significantly affect the yield and injury responses		Heagie et al. 1974
White bean	0.075 - 0.060 SO_2 + 0.15 O_3	5 or 10 days	EC/SD	X	X	Less than additive growth reductions and foliar injury		Hofstra and Ormrod 1977
Soybean				X		Less than additive foliar injury		
E. white pine	0.025 SO_2 + 0.05 O_3	6 hr	EC/SD	X	X	No effect to needle elongation Foliar injury on sensitive clones only; 10 trees with 75-100% of needles with tip necrosis SO_2 alone caused tip necrosis on 75-100% of the needles on one tree O_3 alone caused no injury		Houston 1974
Trembling Aspen (five clones)	0.20 SO_2 + 0.05 O_3	3 hr	EC/SD	X		Greater than additive injury to three clones; no injury due to SO_2 alone		Karnosky 1976
Trembling Aspen (five clones)	0.35 SO_2 + 0.05 O_3	3 hr	EC/SD	X		Greater than additive injury to four clones		
Tobacco Bel-W3 Bel-B Consolidation 402	0.24 SO_2 + 0.27 O_3	2 hr	GC	X		9-38% foliar injury-no injury due to either pollutant singly		Menser and Heggestad 1966
Tobacco Bel-W3 Bel-B Consolidation 402	0.28 SO_2 + 0.28 O_3	4 hr	GC	X		23-76% foliar injury-no injury due to either pollutant singly		

TABLE 4-9. CONTINUED

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c] Foliage	Yield	[d] Species effect	[e] Caveat	Reference
Alfalfa	0.06 SO_2 + 0.05 O_3	7 hr/day 68 days	F/CC		X	No significant alteration of plant reponses (carbohydrate, protein, dry weight) compared to the effects of single pollutants	Potted plants set on soil surface; grown hydroponically	Neely et al. 1977
Scotch pine	0.25 SO_2 + 0.14 O_3	10 - 6 hr/day 68 hr 5 days/wk 154 164	EC/SD	X		Less than additive effects-no effects due to O_3 alone		Nielsen et al. 1977
Scotch pine	0.25 SO + 0.29 O_3	10 - 6 hr/day 68 hr 5 days/wk 154 164	EC/SD	X		Less than additive effects-no effect due to O_3 alone		
Begonia (five cultivars)	0.50 SO_2 + 0.25 O_3	4 hr/day 4 times, 6 days apart	EC/SD	X	X	Less than additive effects for flower weight of one cultivar; 0.50 SO_2 alone significantly reduced flower production in the absence of foliar injury for one cultivar		Reinert and Nelson 1980
Soybean	0.25 SO_2 + 0.25 O_3	4 hr/day, 3 days/wk 11 wk	EC/SD	X	X	Additive growth effects		Reinert and Weber 1980
Radish	0.025 SO_2 + 0.05 O_3	8 hr/day, 5 days/wk 5 wk	EC/SD	X	X	Plant weight reductions additive (leaf fresh and dry wt) or significantly less than additive (plant fresh wt, root fresh and dry wt)		Tingey et al. 1971b

TABLE 4-9. CONTINUED

Plant Species	Conc.[a] ppm	Exposure[a] Time	Exposure[b] Condition	Effects on[c] Foliage	Effects on[c] Yield	Species effect[d]	Caveat[e]	Reference
Alfalfa Onion Soybean Tobacco Bel-B Tobacco White gold	0.25 SO_2 + 0.05 O_3	4 hr	EC/SD	X		Only tobacco Bel-W_3 showed greater than additive foliar injury	Bel-W_3 tobacco very sensitive	Tingey et al. 1973a
Tobacco Bel-W_3 Lima bean Broccoli Brome grass Cabbage Radish Spinach Tomato	1.00 SO_2 + 0.10 O_3					At 1.00 ppm SO_2 tobacco Bel-B and Bel-W_3 exhibited greater than additive effects, and there were less than additive effects for brome grass, cabbage, spinach and tomato		
Soybean	0.05 SO_2 + 0.05 O_3	8 hr/day, 5 days/wk 18 days	EC/SD	X	X	Additive foliar injury effects, greater than additive root dry weight	–	Tingey et al. 1973b
Tobacco	0.05 SO_2 + 0.05 O_3	8 hr/day, 5 days/wk 4 wk	EC/SD		X	Additive growth reductions		Tingey and Reinert 1975
Alfalfa		8 hr/day, 5 days/wk until control plants 40-45 cm high			X	Less than additive growth reductions		
Radish	0.45 SO_2 + 0.15 or 0.45 O_3	4 hr	EC/SD		X	Additive growth effects		

[a] Doses within a single study that did not induce specifically different effects are listed along with the lowest SO_2 concentration that induced said effects.

[b] GC = growth chambers, EC = exposure chambers, EC/SD = exposure chamber, special design.

[c] X indicates study found foliar and/or yield effects.

[d] Most prominent or significant effect reported.

[e] Caveats for consideration about proper study design and interpretation.

expressed as dry mass/seed was 9% less than that of plants exposed to ambient air; higher doses reduced yield by 10% and 15%.

4.2.4.2 SO_2 - NO_2 Effects

The possibility of adverse effects occurring on plant life due to the interaction between atmospheric SO_2 and NO_2 needs consideration. Tingey et al. (1971a) demonstrated experimentally that a gaseous mixture of 0.10 ppm SO_2 and 0.10 ppm NO_2 caused synergistic effects with more than 5% leaf injury being induced on 5 of 6 plant species treated in 4-hr exposure periods. The symptoms of injury produced by a mixture of SO_2 and NO_2 can resemble those caused by ozone which may make diagnoses in the field difficult.

4.2.4.3 SO_2 - O_3 - Acidic Deposition Effects

The currently available literature concerning the interactive effects of acidic deposition and gaseous air pollutants on terrestrial vegetation is extremely limited, consisting of only three separate studies. Shriner (1978) examined the interaction of acidic deposition and SO_2 or O_3 on red kidney bean (Phaseolus vulgaris) under greenhouse conditions. Treatments with simulated rain at pH 4.0 and multiple O_3 exposures resulted in a significant reduction in foliage dry weight. Simulated precipitation and sulphur dioxide in combination did not affect either photosynthesis or biomass production. Troiano et al. (1981) exposed two cultivars of soybean to ambient photochemical oxidant and simulated rain at pH 4.0, 3.4, and 2.8 in a field chamber system. The interactive effects of oxidant and acidic deposition were inconclusive with seed germination being greater in plants grown in the absence of oxidant at each acidity level. Irving and Miller (1980) also examined the response of field-grown soybeans to simulated acidic deposition at pH 5.3 and 3.1 in combination with sulphur dioxide and ambient ozone concentrations. No interactive effects of acid treatments with SO_2 on soybean yield occurred. However, sulphur dioxide alone resulted in a substantial yield reduction.

Changes in such things as soil chemical properties nutrient recycling resulting from acidic deposition do not occur rapidly. After more than a decade of research in Scandinavia, the observed changes in chemical properties of forest soils that can be attributed to acidic deposition still remain undetermined (Overrein et al. 1980). It is therefore unlikely that interactive effects of acidic deposition and gaseous pollutants on plants involving changes in soil properties will become evident within a single growing season.

A physical and chemical potential exists for interaction of various forms of wet fall and dry fall (including gases and trace metals) at, on, or within leaf surfaces. However, very few studies have addressed these interactions and the significance of the observed phenomena remain inconclusive (Fuzzi 1978; Gravenhorst et al. 1978; Penkett et al. 1979).

4.3 EFFECTS OF ACIDIC DEPOSITION ON TERRESTRIAL WILDLIFE

Although direct effects of acidic deposition are not likely, terrestrial wildlife may be indirectly affected in three ways: (1) contamination by heavy metals mobilized under acidic conditions; (2) loss of essential nutritional components from food; and (3) reduction in food resources.

While the sensitivity of organisms such as plankton and fish to metals released in acid waters has been established (Baker and Schofield 1980; Marshall et al. 1981; Muniz and Leivestad 1980), the potential for accumulation and subsequent effects on terrestrial animals is less well understood. Metal contamination and reduced size of roe deer (*Capreolus capreolus*) antlers from an industrialized area of Poland has been reported recently (Jop 1979; Sawicka-Kapusta 1978). Acidification and sulphurization of roe deer browse (Sawicka-Kapusta 1978) was suggested as the cause of the high metal levels (Jop 1979). Such a means of contamination has been demonstrated in southeastern Denmark where cadmium and copper in epiphytic lichens and mosses were compared with those from northwestern Denmark (Gydesen et al. 1981). Epiphytes from the southeastern areas of Denmark which received elevated metal deposition in bulk precipitation showed metal levels 1.5 times higher on average. The same trend was found in the kidneys of cattle feeding in these areas. While direct deposition to plant surfaces may be partially responsible, plant uptake of some metals such as cadmium increases as soil pH decreases (Andersson and Nilsson 1974), and high plant metal content is another route of contamination. In Sweden, moose (*Alces alces*) closer to sources of anthropogenic sulphur supported higher tissue levels of cadmium and the body burden increased with age (Frank et al. 1981; Mattson et al. 1981). The mechanism of contamination was not explored and could be via terrestrial or aquatic vegetation.

The availability of essential elements in wildlife nutrition may be affected by sulphur deposition and soil pH. Selenium, for example, is an essential element for vertebrates (Stadtman 1977). Selenium deficient conditions lead to degeneration of major body organs such as the liver, kidney and heart (Harr 1978; Schwarz and Foltz 1957). Most importantly from the viewpoint of ranchers, muscular dystrophy (known as white muscle disease) has been caused by selenium deficiency and reported in sheep, cattle, swine and horses (Harr 1978; Hidiroglou et al. 1965; Muth et al. 1958). The occurrence of white muscle disease in North American livestock is correlated to the concentration of selenium in forage (Allaway and Hodgson 1964). Lameness and poor growth and reproduction in domestic animals have resulted from selenium-deficient diets (Harr 1978). In poultry, edema (abnormal excess accumulation of fluid in connective tissue or body cavities) has been related to selenium deficiency (Harr 1978; Patterson et al. 1957).

Many of the soils in the temperate region of eastern North America are low in selenium and hence produce forages which contain low selenium concentrations, frequently less than the 0.1 ppm minimum level for animal health (Kubota et al. 1967; Levesque 1974; Winter and Gupta 1979). Although selenium deficiencies in livestock have been associated with forages grown on soils naturally low in selenium, many incidences of deficiency have been attributed to the high agricultural use of sulphate fertilizers (Allaway 1970; Davies and Watkinson 1966). Calves reared on hay grown in Kapuskasing, Ontario, developed muscular dystrophy due to selenium deficient conditions in the soil there (Lessard et al. 1968).

Due to the correlation between soil selenium levels and concentrations in plants grown on these soils (Muth and Allaway 1963), there is evidence that wildlife forage plants are similarly selenium deficient. This was the finding in a study of moose browse plants in Alaska (Kubota et al. 1970). Moreover, selenium deficiency symptoms have been reported for several wildlife species, (e.g., the pronghorn; Antelocapra americana) (Stoszek et al. 1978). Mountain goats (Oreamnos americanus) from an area where selenium levels in forage are low and where white muscle disease occurs in livestock, revealed symptoms of white muscle disease upon being stressed by handling (Herbert and Cowan 1971). It is suggested that the symptoms in wild populations may well be masked by predation (Herbert and Cowan 1971). The net effect of selenium deficiency diseases in wildlife would be an increased susceptibility to predation as well as reduced productivity and survival of young.

Recent increases in anthropogenic sulphur emissions have caused concern regarding the influence on selenium availability in vegetation. Selenium concentrations in plants in heavily industrialized Denmark have decreased over the past decades (Gissel-Nielsen 1975). Experimental applications of SO_2 and SO_4^{2-} to plants and soils have demonstrated that selenium levels are depressed by both the presence of sulphur and reduced soil pH (Shaw 1981a,b). Because excessive sulphur and sulphate cause uptake of selenium to be reduced in plants (Davies and Watkinson 1966; Gissel-Nielsen 1973; Shaw 1981a), the impact in areas of low selenium soils could be substantial. Furthermore, the solubility of selenium declines with pH, rendering selenium less available to be taken up by plants in acid soils (Geering et al. 1968; Johnson 1975).

Sulphur and its compounds have a further depressing effect upon selenium in the animal itself. Excessive sulphur in the diet can lead to increased elimination of selenium from the body (Harr 1978), compounding deficiency conditions.

Other essential elements in animal nutrition such as calcium, magnesium and sodium are similarly released from soils upon acidification (Abrahamsen 1980; Rorison 1980; Stuanes 1980). Accordingly, such elements will be less available for uptake by plants, resulting in lowered concentrations in plant tissues (Beeson 1941). Soil acidification similarly causes leaching of phosphorous which, if reflected in the vegetation (Rorison 1980), could have significant effects on wildlife nutrition. Lucas and Davis (1961) summarize the influence of pH on the availability of 12 plant nutrients.

Aside from nutrient content, the availability of food resources may decline due to acidic deposition affecting the entire food web including wildlife. For example, caribou (Rangifer sp.) may be affected due to the sensitivity of lichens to sulphur and acid compounds (Lechowicz 1981; Puckett 1980; Sundstrom and Hallgren 1973). The importance of lichens in the winter diet of Canadian caribou herds is well documented (Kelsall 1960, 1968; Thompson and McCourt 1981). Thompson and McCourt (1981) reported that 67% of the diet of the Porcupine Caribou Herd of the Yukon consists of lichens. The George River caribou herd of Nouveau Quebec and Labrador is the largest in North America (Juniper 1979; Juniper and Mercer 1979; Mallory 1980) and may rely heavily on the carrying capacity of their winter range. Much of this area lies in the zone of acidic deposition (Figure 8-1b). Exposure of the primary caribou lichen (Cladina stellaris) to simulated acidic deposition with pH 4.0, reduced maximum photosynthesis by 27% and slowed recovery from dormancy after wetting by 14% (Lechowicz 1981). These results suggest that acidic deposition reduces the growth and productivity of this lichen (Lechowicz 1981). The significance of reduced lichen productivity to the population dynamics of these caribou herds is uncertain, because the degree to which they are food-limited is unknown.

Another example of potential food loss involves herbaceous ground cover. Trees have tap roots in deep soil layers that are less susceptible to acidification, while plants draw their moisture and nutrients from the upper layers of soil making them more exposed to the effects of acidic deposition (Clark and Fischer 1981). Application of sulphuric acid in quantities corresponding to 100 kg/ha.yr killed much of the ground vegetation consisting mainly of mosses, lichens, and a species of dwarf shrub (Tamm et al. 1977). Therefore animals which feed on such vegetation may be affected by food loss.

4.4 EFFECTS ON SOIL

Soils vary widely with respect to their properties (i.e., 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 making it difficult to generalize from findings indicated in this report. Further, there are various offsetting mechanisms, influencing effects of increased precipitation acidity which vary with soil properties, vegetation types, climatic regimes and cultural practices. Water moves through soils by uniform capillarity and gravitational processes. Also, considerable moisture flow may be directed overland or may be channelized in the soil in root channels reducing the opportunity for equilibration. A high stone content can concentrate leaching effects to a smaller soil volume than in nonstony soils. Thus, theoretical calculations have to take into account particular _in situ_ characteristics.

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.

4.4.1 Effects on Soil pH and Acidity

It has been clearly demonstrated that the continued application of acidifying sulphate fertilizers brings about appreciable soil acidification, along with other changes in soil chemical and biological properties (Glass et al. 1980). The more striking of these changes are reductions in exchangeable bases, increases in soluble aluminum and manganese levels, shifts in optimum conditions for bacteria and mycorrhizal fungi, and reductions in soil microfaunal populations. Some of these undesirable changes have also been shown to occur in the proximity of strong point emitters of sulphur dioxide (Freedman and Hutchinson 1980; Nyborg et al. 1976; Strojan 1978), so concern is well-founded that the range of soil changes outlined in Table 4-10 could occur to a greater or lesser extent over more widespread geographical areas.

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, at least in states other than strong

TABLE 4-10. ACIDITY RELATED REACTIONS INFLUENCING AVAILABILITY OF SEVERAL ELEMENTS

Element(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^{3+} 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.

acid as described by Jenny (1961), Wiklander (1973/74, 1975, 1980a), Bolt and Bruggenwert (1978), Bache (1980), and Nilsson (1980). In the most strongly acid soils, there is evidence that aluminum becomes very mobile without there being any associated notable change in pH (Cronan and Schofield 1979; Norton et al. 1981; Ouellet 1981; Ulrich et al. 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 pHs in the range 3.5 to 4.5.

The numbers of field situations where investigators have been able to compare present with former soil pH values are extremely limited. However, Linzon and Temple (1980) report a lowering of soil pH in the brunizolics, but not podzols, of south-central Ontario after 18 years of pollutant deposition. Ulrich (1980b) and his colleagues (Ulrich et al. 1980) working in the more heavily polluted parts of central Germany report a long-term fluctuation of pH in the surface humus under beech and spruce. The pH values do not show a steady decline, but rather show cyclic variation between 4.2 and 3.8. This parallels deacidification and acidification phases alternating between cooler, moister summers and warmer, drier ones. From 1969 to 1980 under beech, and from 1973 to 1980 under spruce, there were substantial increases in the amounts of soil aluminum mobilized. These increases were associated with the continued entrapment and deposition of acid sulphate pollutant.

Various field and laboratory experiments of a simulation nature have also been set up to examine the effects of acidic deposition on soil acidity. Results indicate that artificial acidic deposition at pH<4 can lead to measurable decreases in soil pH (Abrahamsen et al. 1976; Bjor and Teigen 1980; Stuanes 1980). For example, simulated acidic deposition 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 a precise assessment. Natural soil acidification is an ongoing process in humid regions. Its impoverishing action is partially compensated for by weathering of primary minerals and by biological cycling of elements in vegetated areas. 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 in a Douglas fir ecosystem receiving precipitation three to four times more acid than normal (weighted average annual pH, 4.9), carbonic acid contributed approximately twice as much H^+ to the soil as did precipitation. However, a drop in pH to 4.0 (about 30 times more acid than normal) occurs in the most heavily impacted areas of eastern North America (Cogbill and Likens 1974) and results in H^+ inputs far in excess of that produced by carbonic acid. In the more acid soils having a pH of less than 5.5 (e.g., 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 in pH, but changes in the ionic make-up of the soil colloidal complex and ionic mobility may take place.

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. (1980b) 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%) compared to net internal flows. Ulrich (1980b), using essentially the same approach, stressed input-output balances to assess the long-term net acidification of soils caused by internal compensations of H^+ production and consumption and uptake and mineralization processes. He also pointed out important spatial considerations within the soil profile. For example, ammonium mineralization that consumes hydrogen ions might occur in litter layers while ammonium that produces hydrogen ions may occur 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 1980b). 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 and 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, the process of podzolization is hastened.

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

4.4.2 Impact on Mobile Anion Availability and Base Leaching

Acidification and soil impoverishment involves the displacement of basic cations (i.e., K, Ca, Mg, Na) from exchange surfaces, their replacement by H^+ and Al^{3+} ions, and the establishment of new exchange/solution equilibria (Wiklander 1973/74). Under natural conditions, two sets of processes seem to be involved: (1) there are exchange processes whereby H^+ ions displace base cations from the exchange surface, and (2) 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., cation exchange capacity or CEC and the relative degree of saturation of the CEC with bases or base saturation). In humid regions, the total permanent and pH dependant CEC of a productive soil under cultivation might range from 15 to 30 meq/100 g. In the surface horizons this might be higher and in the subsoil it may be lower. To illustrate this, in coniferous podzols the CEC of the humus layer may be high while beneath it values decrease abruptly with depth. It is presumed that the loss, particularly of those base cations of nutritive value (chiefly K, Ca, and Mg), could be accelerated under acidic deposition, with attendant adverse impacts on forest growth.

Various "simulated acidic deposition" 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 acidic deposition with a pH of 3.0 or lower (Abrahamsen 1980).

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 (Konova 1966). Soil pH and base saturation will thus decrease without a corresponding reduction in exchangeable base content (Ulrich 1980a). 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, causing 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% of the electrical charge balance of the leaching solution, while Al^{3+} and H^+ were the dominant cations in solution (Cronan 1980; Cronan et al. 1978; Cronan and 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). This generally implies that the effect of acidic deposition 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, (e.g., in the highly weathered soils of Tennessee), S accumulation could initially be beneficial in three ways: (1) prevent cation leaching by H_2SO_4 by immobilization of the SO_4^{2-} anion; (2) create new cation exchange sites; and (3) release OH^- from adsorption surfaces (Johnson et al. 1981). It follows, however, that once SO_4^{2-} exchange sites become fully occupied, cation leaching could commence. On Walker Branch Watershed, 48% of total S to input accumulates in the soil, whereas only 13% accumulates in vegetation (Johnson and Henderson 1979; Shriner and Henderson 1978). Along the same lines, one might expect the NO_3^- in acidic deposition 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 assimilated by plants during the growing season, thereby not contributing to cation leaching.

4.4.3 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 activities 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 acidic deposition. 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 on the effect of acidity on organic matter breakdown and soil respiration is not conclusive (Rippon 1980; Tamm et al. 1977). However, decomposition experiments suggest that acidic 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 acidic deposition inputs at pHs 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 partly dependent on soil type and severity of the simulated acidic deposition treatment.

In some soils, there are indications that acidic deposition 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 occur in moderate acidic leaching.

Besides carbon cycling, there is concern that acidic 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 acidic 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 nitrogen. Tamm (1976) predicted short-term increases in N availability and tree growth, due to net N losses from ecosystems. In Germany, Ulrich et al. (1980) resampled soils over a 13-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^+ ion production, immobilization of N, and mobilization of soluble Al^{3+}. Other studies, by Francis et al. (1980) and Alexander (1980) show ammonification and nitrification may decrease markedly in soils exposed to artificial rain at pHs 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. Norwegian studies show that both N availability and NO_3^- leaching were stimulated by H_2SO_4 inputs. This strongly suggests 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.

4.4.4 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. For perennial plants, including trees, P is assimilated through the intermediary mechanism of a mycorrhizal root association (Bowen 1973; Fogel 1980; Hayman 1980). 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 soils, $H_2PO_4^-$ ions may react with soluble Mn, Al and Fe compounds and be mostly precipitated as the insoluble and nonavailable metal hydroxyphosphate (Hsu and Jackson 1960). Also, under conditions of increasing acidity, $H_2PO_4^-$ tends to react with the insoluble oxides of Fe, Al and Mn, and in more weathered soils it may become fixed on silicate clays, through the process of anion exchange.

4.4.5 Effects on Trace Element and Heavy Metal Mobilization and Toxicity

A further effect of acidic deposition or increased soil acidification is an increased solubilization of heavy metals in the soil system. This can arise from the increased solubilization of metals that are already present in mostly insoluble or nontoxic forms or it may arise from metals being deposited along with an acidifying pollutant. Thus, at low concentrations naturally present Mn and Fe serve as essential nutrient elements for the growth of higher plants and except in alkaline or calcareous soils are usually present in adequate available amounts. However, at high concentrations these metals and Al can cause nutritional imbalance and growth impairment. Different plant species vary in their susceptibility to heavy metals, an example being Al. Barley, sugar beet, corn and alfalfa are very sensitive, whereas ericaceous shrubs and conifers appear much more tolerant. Soil characteristics also affect tolerance/susceptibility including soil pH, NH_4^+ compared with NO_3^- nutrition, Al-exclusion processes, Ca and P status, and organic-Al complexation (Foy et al. 1978). Striking examples of the effect of soil pH on the solubility of Mn and Al are given in Glass et al. (1980), concentrations rising very rapidly in each suite of soils when pH values moved from 5 to 4.

In acid forest soils that support highly productive forest in eastern Canada it is not unusual to have a pH gradient down the profile of from 3.0 to 4.6. Associated with such values are exchangeable Ca values falling from 2.0 to 0.15 meq/100g and exchangeable Al values falling from 7.0 to 0.40 meq/100g (Anonymous 1979). Of a very much wider Ca/Al ratio, however, is the Solling soil profile in Germany described by Ulrich et al. (1971), where exchangeable Ca and Al concentrations are respectively 0.2 and 4.7 meq/100g, and where Göttsche's beech studies in the acidification year of 1969 are plotted to reveal the remarkable correlation between the seasonal increase in soluble soil Al concentrations and the dramatic increase in fine-root mortality (Ulrich 1980b). Indeed, this correlation and other studies have encouraged Ulrich (1981) to advance his ecosystem hypothesis explaining the widespread "die-back" of fir in Europe. Fine roots are killed by high soil Al concentrations or high Al/Ca ratios with a subsequent invasion of the damaged tree tissues by rot fungi. There is evidence to indicate that increased amounts of aluminum can be mobilized in the soil and passed on to water bodies (Abrahamsen et al. 1976; Cronan and Schofield 1979). It is not clear whether the allegedly toxic concentrations present in the loess-derived forest soils of central Germany can also be expected to arise in the glacial till-derived soils of Scandinavia or northeastern North America (Tyler 1981).

Soil acidification in environments where there is also appreciable deposition of heavy metals is the second area of concern. Heavy metals arise from various industrial activities, including fuel combustion (Hansen and Fisher 1980; Watanabe et al. 1980). The scale of emissions and airborne transportation has caused increasing attention to be directed to the amounts of different elements being deposited in remote rural areas. Thus, at the Solling site in central Germany, for an open-site wet deposition of 23.8 kg of sulphur per hectare per year, there is an accompanying 10 kg of nitrogen, 10.4 kg of calcium, 1.9 kg of magnesium and 1.1 kg of aluminum (Ulrich 1980b). In south-central Ontario recent comparable figures are 10 kg for S, 6 kg for N, 5 kg for Ca, and 0.7 kg for Mg (Scheider et al. 1979). For the same locality figures for elements more commonly understood as "heavy" are 0.46 kg for aluminum, 0.54 kg for iron, 0.095 kg for zinc, 0.132 kg for lead, 0.033 kg for copper and 0.022 kg for nickel (Jeffries and Snyder 1981). These authors also point to the much higher deposition rates near smelters where cumulative levels of heavy metals in the soils have exercised pronounced toxic effects upon the vegetation (Hutchinson and Whitby 1974, 1976). However, there is danger in extrapolating from such heavily polluted local situations onto the more diffuse regional scale without taking into account the different parameters. Nevertheless, if the Solling site is taken as exemplifying the more diffuse rural situation, Heinrichs and Mayer (1977, 1980) found that the beech and spruce forests act as filters for atmospheric substances. Some elements (e.g., sulphur, lead, mercury, bismuth and thallium) are largely accumulated in the upper part of the soil profile but the complex biogeochemical picture that emerges suggests that far more needs to be known in other locations on the fate of deposited metals having potentially significant physiological and toxicological roles (Andersson et al. 1980a; Bradley et al. 1981; Smith and Siccama 1981). There is a rapidly expanding literature focusing on the soil behaviour of heavy metals derived from town wastes (Leeper 1978) and much of this related to pH-dependent considerations (Hatton and Pickering 1980; McBride and Blasiak 1979) and metal-organic compound complexes (Bloom et al. 1979; Marinsky et al. 1980; McBride 1980) should be applicable to the acidic deposition problem.

The dissolution and mobilization of many other trace metals in soils is also affected by acidic deposition and decreasing soil pH. Recent studies in the Adirondack Mountains of New York have determined from acidic leaching experiments on native bedrock that this process is an important contributor of Cu, Pb, and Hg in addition to Al (Fuhs et al. 1981). The trace metals Cu, Pb, Hg, Cd, and Zn were leached rapidly upon exposure to acid while Al and other major metals were leached more gradually. Leaching of soils and bedrock by long-term acidic deposition has resulted in soil impoverishment for metals such as Mn and Zn in New Zealand (Norton et al. 1981).

Other studies have demonstrated accumulations of trace metals in soils. Norton et al. (1980) found Pb and chemically similar metals accumulating in soils while Al and Mn were being leached. Leaching occurred in the upper soil horizons resulting in potential impoverishment for shallow rooted plants. Deeper rooted plants, on the other hand, are subjected to potentially toxic concentrations of dissolved metals. Tyler (1978) also showed that Pb is not readily leached from surface soils by acidic deposition 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. Mobility and transport within the soil horizons and direct atmospheric deposition is responsible for the accumulation of metals in the soil. For example, concentrations of Cu and Ni increased in soils with proximity to the Sudbury, Ontario smelter (Heale 1980). Studies of metal deposition in the Walker Branch Watershed in Tennessee, found that soils efficiently retained Pb, Cd, and Cu, and less readily accumulated Cr, Mn, Zn, and Hg (Andren et al. 1975). McColl (1980), however, found that the concentrations of Mn, Fe, Cu, and Zn were all greater in soil solutions than in acidic deposition falling in Berkeley, California.

In restricted areas, vegetation may be stunted or absent due to toxicity of metals such as Ni (Foy et al. 1978). In a well-known study on serpentine-derived soils in Czechoslovakia, Nevmec (1954) attributed the failure of pine plantations and various hardwood species to excessive levels of Ni, Cr, and Co. Plantation failure was considerably reduced by fertilization with lime and diabase dust. Around Sudbury, Canada, Ni and Cu added from atmospheric deposition from smelters are maintained in acidified soils in concentrations sufficiently high to be toxic to vegetation (Hutchinson and Whitby 1974, 1976). Thus, any possibility of mobilization of trace metals through decreasing soil pH by acidic deposition has implications for forest productivity. Accumulations of trace metals from atmospheric deposition can contribute to this problem.

4.5 SENSITIVITY ASSESSMENT

Several sets of sensitivity criteria have been proposed and used to define geographical regions most susceptible to acidic deposition effects (Johnson and Olson in press). Each set of criteria is based upon a different philosophy and is aimed at different target organisms or ecosystems (e.g., forests, fish, soil, bedrock, aquatic ecosystems). Those directed toward aquatic effects have emphasized bedrock geology (Hendrey et al. 1980; Norton 1980) or bedrock geology and soils in combination (Cowell et al. 1981; Glass et al. 1982; see Section 3.5). Those directed toward terrestrial effects have emphasized cation exchange capacity and base saturation (Klopatek et al. 1980; McFee 1980a,b; Wang and Coote 1981).

Terrestrial sensitivity has been defined in terms of forest productivity (Cowell et al. 1981; Table 4-11) and in terms of soil acidification (Wiklander 1973/74, 1980b; Table 4-12). In both cases effects in the soil body were emphasized. Cowell et al. (1981) regarded low pH soils as the most sensitive based on the assumption that these already had the smallest reserve of nutrient cations. Thus, any additional loss of forest nutrient cations, however small, would be significant to forest productivity in acid soil systems (even though these soils were less sensitive to acidification). This sensitivity assessment concentrated on the upper 25 cm of the soil profile where, at least in boreal ecosystems, nutrient cycling is most efficient. Acid soils are known to actively adsorb SO_4^{2-}, hence reduce cation mobilization, and are considered less sensitive than nonsulphate-adsorbing soils (Johnson and Cole 1977; Singh et al. 1980). This contrasts with the sensitivity concept suggested by Wiklander (1973/74, 1980b) whereby noncalcareous, moderately acid sandy soils (pH 5-6) with low cation exchange capacities are considered most sensitive. Wiklander (1973/74, 1980b) derived these criteria from laboratory studies in which he found that the cation displacing efficiency of H^+ was greatly diminished as base

TABLE 4-11. TERRESTRIAL FACTORS AND ASSOCIATED CRITERIA LIMITS TO ASSESS FOREST PRODUCTIVITY SENSITIVITY (Cowell et al. 1981)

TERRESTRIAL FACTORS	SENSITIVITY		
	LOW	MODERATE	HIGH
Soil Chemistry			
i) Exchangeable Bases	>15 meq/100g	6 to 15 meq/100g	<6 meq/100g
Surrogates:			
(a) Family Particle Size and pH in water	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
(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)
(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 content	———	low sulphate adsorption: high organic matter AND/OR low Al_2O_3 and/or Fe_2O_3 + Fe_3O_4 content
Soil Depth[a]	>25 cm	25 cm	<25 cm
Underlying Material			
i) Parent Material	carbonate bearing	noncarbonate bearing	noncarbonate bearing
ii) Bedrock Material	limestone, dolomite, and metamorphic equivalents, calcareous clastic rocks, carbonate rocks interbedded with noncarbonate rocks	volcanic rocks, shales, greywackes, sandstones, ultramafic rocks, gabbro, mudstone, metaequivalents	granite, granite gneiss, orthoquartzite, syenite

[a] If soil depth is less than 25 cm, Underlying Material is incorporated into the assessment

TABLE 4-12. THE SENSITIVITY OF VARIOUS SOIL CATEGORIES TO ACIDIC DEPOSITION CLASSIFIED ACCORDING TO: BUFFERING CAPACITY AGAINST pH - CHANGE, RETENTION of H^+ DEPOSITED OR PRODUCED BY NITRIFICATION OF HN_4^+, REPLACING EFFICIENCY OF H^+ FOR EXCHANGEABLE BASE CATIONS (Δ M/Δ H), AND ADVERSE EFFECTS ON SOILS (Wiklander 1973/74)

	Calcareous Soils	Noncalcareous clays, pH >6	Noncalcareous sandy soils, pH >6	Cultivated soils, pH >5	Acid Soils pH <5
Buffering against pH-change	Very high	High	Poor	High	High
H^+ retention	Maximal	Large	Large	Large	Slight
$\Delta M/\Delta H$	<1	≤ 1	≤ 1	≤ 1	<1
Adverse effects on soil	None	Moderate	Considerable	None - very slight	Very slight - slight

saturation and pH decreased. Thus, for a given H^+ input, very acid soils will yield fewer cations and are classed as less sensitive than moderately acid soils. Moderately acid soils with low cation exchange capacity (i.e., less buffering by exchange sites) will experience more rapid pH-change than very acid soils with the same exchange capacity. This concept of assessing soil acidification potential, in which the most sensitive soils are those experiencing the greatest change in their inherent properties, is specifically a soil sensitivity evaluation. No cause-effect relationships with vegetative or aquatic systems are specified.

4.5.1 Terrestrial Sensitivity Interpretations

Acidic deposition 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, acidic deposition in sufficient amounts may reduce productivity on sites with adequate N and S but deficient in cations. Other detrimental effects to forest productivity include changes in soil, microorganisms and Al toxicity. These effects are increased (Ulrich et al. 1980) with increased acidification. However, there is insufficient empirical evidence establishing cause-effect linkages between forest productivity and acidic deposition. It is not certain which ecosystem factors are most significant with respect to forest systems and thus it is not presently possible to map forest productivity sensitivity at any scale.

Sensitivity assessment for this section, therefore, will concentrate on soil characteristics and how pH, CEC and sulphate adsorption properties hypothetically relate to different effects. Terrestrial ecosystem effects to be considered are: loss of base cations, soil acidification and Al solubilization. Table 4-13 and Figures 4-5 and 4-6 depict hypothetical sensitivities (Johnson and Olson in press). For nonsulphate-adsorbing soils (Figure 4-5), it is assumed that each equivalent of incoming H^+ causes the leaching of an equivalent of some cation (including H^+ or Al^{3+}) through the forest soil.

Case 1. For soils with pH >6, H^+-base cation exchange is likely to be nearly 100% efficient (Wiklander 1973/74, 1980b), and thus soils are very "sensitive" to base cation loss (Figure 4-5a). If the soil with pH >6 has a high CEC (i.e., a large reserve of exchangeable cations and hence a large buffering capacity), it will take a very long time for a given acid input to acidify it. This is depicted by the width of the CEC box in Figure 4-5a. Thus, such a soil is thought to have low sensitivity to acidification and Al mobilization.

TABLE 4-13. THEORETICAL SENSITIVITIES OF TERRESTRIAL ECOSYSTEMS TO ACIDIC DEPOSITION EFFECTS GIVEN SOIL BASE CONTENT (eq/ha) AND SOIL SULPHATE ADSORPTION CAPACITY (eq/ha) (modified from Johnson and Olson in press)

SOIL PROPERTIES			TERRESTRIAL SENSITIVITY TO:		
	pH	CEC	Base Cation Loss	Soil Acidification	Al Solubilization
			I. Nonsulphate-adsorbing Soils		
1.	>6	High	High	Low	Low
2.	>6	Low	High	Low-moderate	Low-moderate
3.	5-6	High	High	Moderate	Moderate
4.	5-6	Low	High	High	Moderate
5.	<5	High	Moderate	Low	Moderate
6.	<5	Low	Moderate	Low	High
			II. Sulphate-adsorbing Soils		
7.	>6	High		Rare or nonexistent cases	
8.	>6	Low			
9.	5-6	High	Low	Moderate	Moderate
10.	5-6	Low	Low	High	Moderate-high
11.	<5	High	Low	Moderate	Moderate-high
12.	<5	Low	Low	High	High

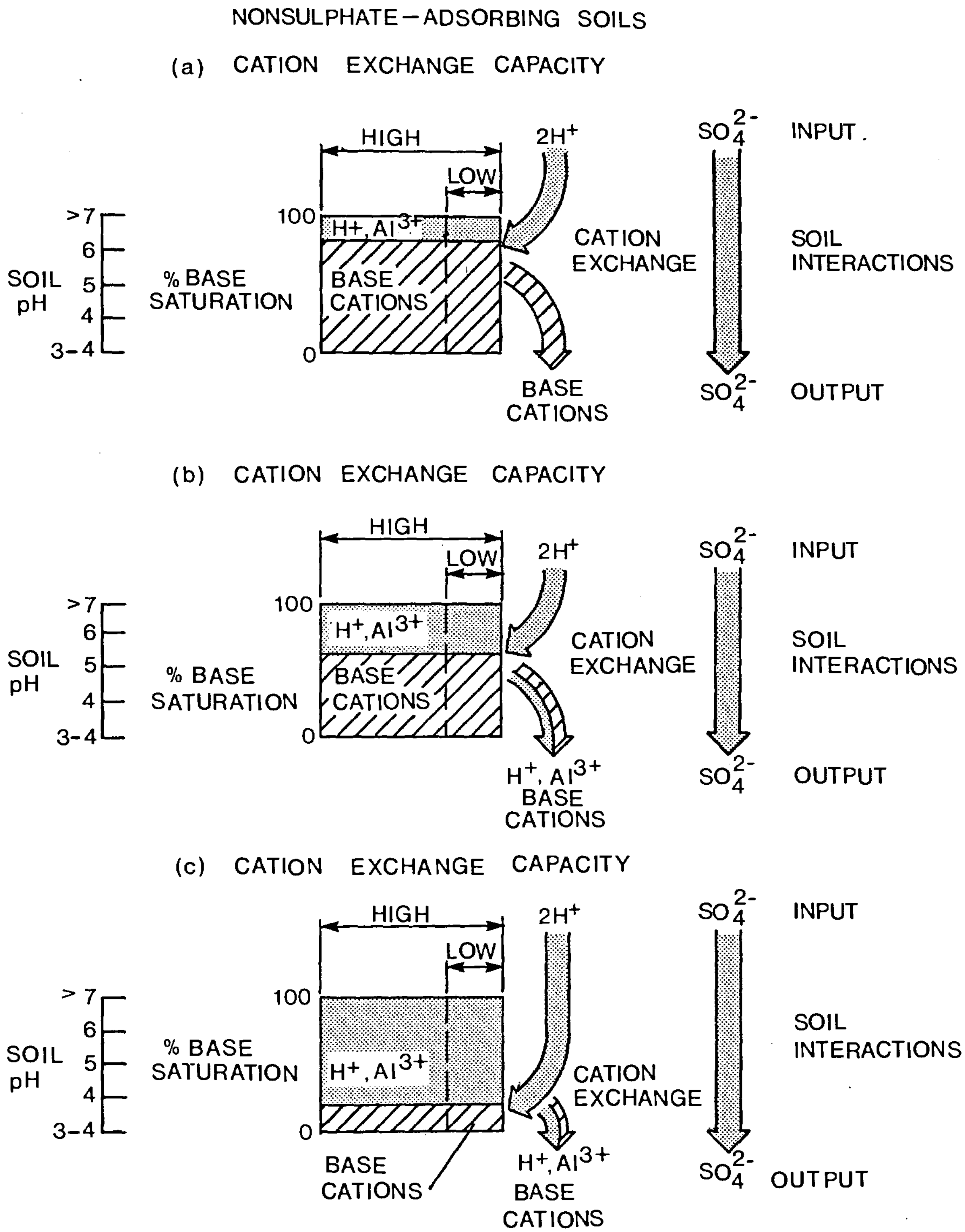


Figure 4-5. Effects on base cation loss, soil acidification and Al^{3+} solubilization for nonsulphate-adsorbing soils having (a) moderate to high pH (>6), (b) moderate pH (5-6) and (c) low pH (<5) (Johnson and Olson in press).

Case 2. If the soil with pH >6 has a low CEC (area depicted to the right of the dashed line in the CEC box in Figure 4-5a), it will take less time to deplete the exchangeable cation reserves and, therefore, a low-moderate rating is arbitrarily assigned to acidification and Al mobilization in soils to differentiate it from case 1. As in case 1, H^+-cation exchange is nearly 100% complete, so that soils are "sensitive" to base cation loss.

Case 3. If a soil has pH 5-6 (i.e., a moderate base saturation), H^+-cation exchange will be nearly as complete as in cases 1 and 2 while cation reserves (at a given CEC) will be lower (Figure 4-5b). For the high CEC case, a moderate rating is assigned to acidification and Al mobilization in terrestrial ecosystems. As in cases 1 and 2, soils are "sensitive" to base cation loss.

Case 4. In this case, the total reserves of base cations are low yet H^+-cation exchange is nearly 100% efficient (Figure 4-5b) and thus the soil is highly sensitive to base cation loss and acidification. Once base cations are depleted and the soil is acidified, Al may become mobilized; thus, a moderate rating is assigned to soil Al mobilization.

Case 5. In soils with pH <5 (i.e., low base saturation), H^+-base cation exchange is less efficient and therefore soils are only moderately sensitive to base cation loss but have a low sensitivity to further acidification (Figure 4-5c). Such a soil may be sensitive to Al mobilization given sufficiently high acid inputs, however. In the high CEC case, a moderate sensitivity is assigned to Al mobilization in soils.

Case 6. In this case, the soil is acid and has low CEC (Figure 4-5c), making it only moderately sensitive to base cation loss but highly sensitive to Al mobilization. These soils have only a low sensitivity to further acidification.

In sulphate-adsorbing soils, leaching of H^+, Al^{3+}, and base cations is inhibited for the reasons described previously. The degree of sulphate adsorption is dependent to some extent on pH (Harward and Reisenauer 1966) as well as on inherent soil properties such as organic matter and Fe- and Al-oxide content. Sulphate is more strongly adsorbed in most acid soils. Soils having a pH >6 would not be expected to exhibit high sulphate adsorption properties (cases 7 and 8; Table 4-13). High Fe- and Al-sesquioxide content required for sulphate adsorption would not be characteristic of these soils. Also, any soils having high CEC (cases 9 and 11; Table 4-13) would not be expected to adsorb sulphate if the exchange capacity was controlled primarily by organic matter. High organic matter content tends to block the adsorption potential of Fe and Al oxides (Johnson and Henderson 1979; Singh et al. 1980).

Cases 9 to 12 are analogous to cases 3 to 6, respectively, with regard to pH and CEC. Due to the sulphate adsorption capacity of soils in cases 9 to 12, however, base cation leaching is lower than in analogous soils in cases 3 to 6 (Figure 4-6). However, sulphate adsorption prevents H^+ transport as well as base cation leaching from soils in cases 9 to 12, and the displacing efficiency of H^+ for base cations is less of a factor in soil acidification. Soils in cases 9 to 12 are rated slightly more sensitive to Al solubilization than their counterparts 3 to 6.

The preceding discussion as well as Table 4-13 and Figures 4-5 and 4-6 by no means represent a rigid set of criteria for site sensitivity to acidic deposition. They merely represent a hypothetical construct based upon a combination of known and previously employed sensitivity criteria. These criteria have limitations and are by no means complete. For instance, while considering the sensitivity of terrestrial and aquatic ecosystems to acidic deposition effects, it is important to realize that acids are produced naturally within these systems (Rosenqvist 1978). The effects of atmospheric acid inputs must be viewed as an addition to natural, ongoing acidification and leaching processes within soils due to carbonic acid formation, organic acid formation, free cation uptake, and a variety of other processes (Andersson et al. 1980b; Sollins et al. 1980; Ulrich 1980a). Unfortunately, the data base for including natural acid formation criteria into regional sensitivity assessments is extremely limited. Thus, previous sensitivity rating schemes, by default, assume that atmospheric inputs add significantly to internal acid production, an assumption that is by no means universally accepted (Rosenqvist 1978).

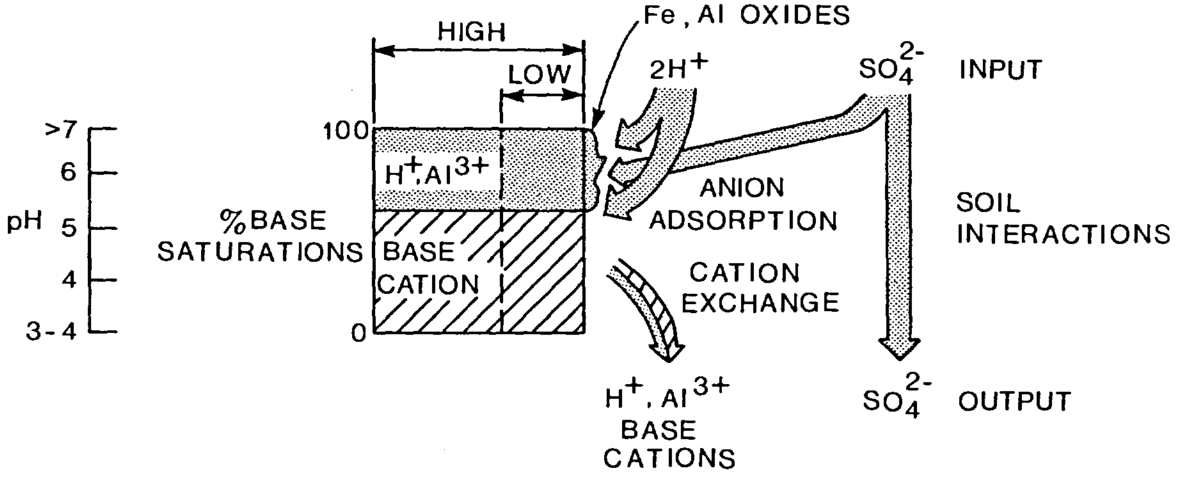
It is also important to distinguish between acidification and elemental leaching when considering the role of natural acid formation. Carbonic acid is a major leaching agent in some forest soils, yet it does not produce low pH (i.e., <5.0) solutions under normal conditions (Johnson et al. 1977). Organic acids may contribute substantially to elemental leaching in forest soils undergoing podzolization (Johnson et al. 1977), and they can produce low pH (i.e., <5.0) in unpolluted natural waters as well (Johnson 1981). Also, because leaching is only one of several processes that affect soil acidity (other major factors being humus build-up, plant cation uptake, and mineral weathering; Ulrich 1980a), the relative contribution of atmospheric acidic deposition to elemental leaching may be quite different from the relative contribution of atmospheric deposition to soil acidification.

4.5.2 Terrestrial Mapping for Eastern North America

The lack of empirical data identifying cause-effect linkages with respect to impacts of acidic deposition on forest and agricultural systems makes sensitivity mapping difficult. One must identify a target process (i.e., soil acidification, Al solubilization, cation loss, etc.) and then make specific assumptions regarding ecosystem interactions which result in a significant impact. The mapping

SULPHATE – ADSORBING SOILS

(a) CATION EXCHANGE CAPACITY



(b) CATION EXCHANGE CAPACITY

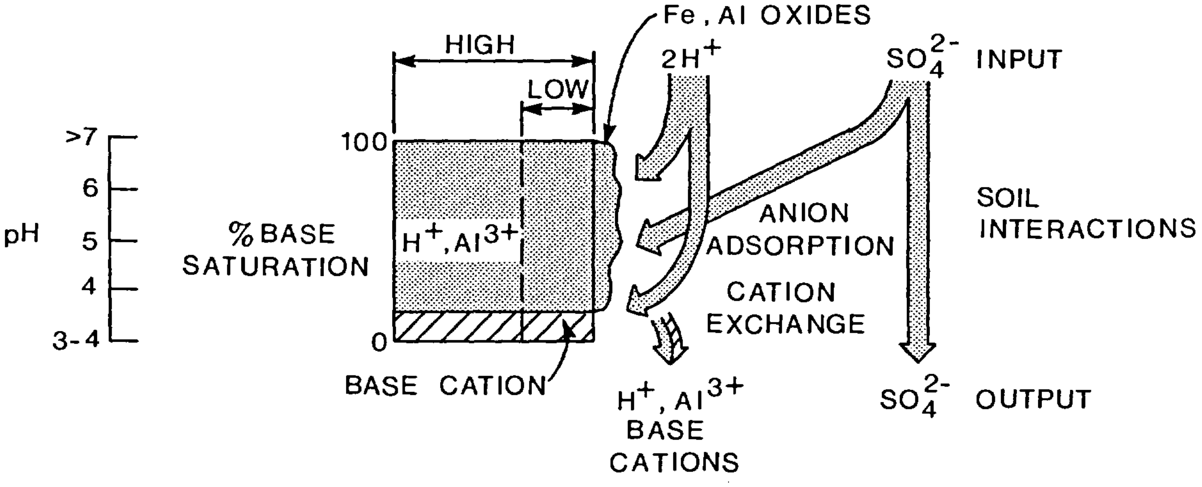


Figure 4-6. Effects on base cation loss, soil acidification and Al^{3+} solubilization for sulphate-adsorbing soils having (a) moderate pH (5-6) and (b) low pH (<5) (Johnson and Olson in press).

framework and thus the maps themselves could vary substantially depending on these assumptions and on which processes were targeted (Table 4-13). For this report mapping is concentrated on terrain characteristics, especially soil chemistry (or its surrogate), of eastern North America rather than sensitivity per se. It is hoped these maps will provide a useful basis for comparison and for eventual interpretations of terrestrial sensitivities once actual impacts are documented.

Figures 4-7 and 3-9 (in map folio) show terrain characteristics in the Eastern United States and Eastern Canada, respectively. Although an attempt was made to compile compatible and comparable maps, differences in mapping criteria and data quality exist between and within the two maps. Specific mapping factors and data sources are listed in Table 4-14. The data availability in some parts of eastern Canada necessitated map production at 1:1,000,000 to ensure adequate representation. The U.S. map, produced from the Geoecology Data Base (Olsen et al. 1980) is reproduced here at 1:5,000,000.

Terrain characteristics for the United States are mapped as soil chemical classes based on pH and CEC. These classes can be compared back to Table 4-13 to interpret relative sensitivities to acidic deposition for Al solubilization, cation loss and soil acidification. The discussion which follows deals primarily with potential for soil acidification based on the Wiklander (1973/74) concept of sensitivity. The limit of Wisconsin glaciation is shown on the map as a basis for comparison between younger soils of the north and northeast and the older, more deeply weathered soils characteristic of the south and southeast.

Bedrock geology has been included in terrain classes for the Canadian mapping because soils in Canada, especially throughout the Precambrian Shield, tend to be thin and discontinuous. In these areas the bedrock forms a major substrate for forest systems and represents the only "store" of nutrient cations. Because of a lack of soil chemical data for soils outside limited agricultural areas in Canada, soil texture and depth to carbonate data have been substituted (Table 4-14). These are the only surrogates available for soil chemistry at the scale of compilation (1:1,000,000). It is not possible, therefore, to relate the terrain classes on the Canadian map directly to the soil property classes shown in Table 4-13. However, some indirect comparisons can be made on the bases of soil order.

4.5.2.1 Eastern United States

The map showing various classes of soil characteristics covering the eastern 37 states (Figure 4-7) was produced at Oak Ridge National Laboratory (Olson et al. 1982). The analysis utilized various national resource inventories to map soil classes based on pH, CEC, Histosols and land use (Table 4-14). County-level data from the Geoecology Data Base (Olson et al. 1980) were used in the analysis to provide a regional perspective and understanding of soil characteristics which can be evaluated in terms of the potential for acidic deposition impacts on terrestrial ecosystems (Table 4-13). As more detailed data or new studies are completed, the resolution or interpretation of the map may need to be revised.

Initially counties that were predominantly (> 50%) urban or agricultural were excluded from the analysis. Management and land use practices (e.g., liming, fertilizing) in these areas would tend to determine current soil nutrient/pH conditions. The 1977 National Resource Inventory (USDA 1978) was used to define land in urban built-up areas and transportation corridors. The 1978 Census of Agriculture (USDC 1979) provided data on cropland. This resulted in 1,648 of the 2,660 counties in the east being included in the analysis as containing predominantly forest, range, or pasture.

Moderately acid soil (pH 5-6) and low CEC were used to identify soils which would be most sensitive to acidification (Wiklander 1973/74, 1980b). Very acid soils will yield fewer cations and thus, are classed as less sensitive than moderately acid soils (Wiklander 1973/74). Moderately acid soils with low CEC (i.e., less buffering by exchange sites) will experience more rapid pH change than very acid soils with the same CEC (Table 4-13). McFee (1980a,b) used CEC only as a first reasonable approximation to site sensitivity. He used a CEC value of 6.2 meq/100g to identify soils that would change most quickly under the influence of acidic deposition. This criterion was used to distinguish between "low CEC soils" and "high CEC soils" (Table 4-9). As noted earlier, however, the interpretation of soils sensitive to acidic deposition does not account for the relative significance of this deposition compared to internal acid generation. It is not presently possible to classify soils as to internal acid generation especially in a regional-level analysis.

Counties covered by 50% or more of soil types with a surface pH of greater than 5.5 and CEC less than 6.2 were classified as having a high potential to undergo acidification from acidic deposition. In addition, two other classes were defined which may undergo acidification but at a slower rate with similar levels of acidic deposition. Soils with a pH greater than 5.0 and CEC less than 6.2 constituted class 2. Class 3 included soils with pH greater than 5.0 and CEC less than 9.0.

Chemical and physical soil characteristics employed in the analysis represent average values for the A horizon (upper 20-25 cm) for the 82 great soil groups occurring in the eastern United States. These values were obtained from published literature (Klopatek et al. 1980). The great soil groups were combined to estimate values for the 195 soil mapping units that are mapped (USGS 1970) in the east. Although the exact proportions of great soil groups within map units are not readily available, the dominant great soil group was given a weighting factor of 0.66 to calculate average map unit values.

Proportions of soil mapping units within counties were estimated from the 1:7,500,000 scale soil map of the United States (USGS 1970).

Sulphate adsorption capacity was also considered in defining sensitive soils. Soils with sulphate adsorption capacity prevent the transport of cations by H_2SO_4 (Johnson and Cole 1977) and can increase soil exchange capacity (Wiklander 1980a) thus reducing the sensitivity of such soils to acidification. Because of the relative lack of empirical information on sulphate adsorption capacity, only Ultisols are considered as sulphate-adsorbing soils (Johnson et al. 1980). Even the data on sulphate adsorption capacity of Ultisols are limited in geographic extent. Ultisols have lower pH and higher CEC values than given above for defining soils sensitive to acidic deposition. Therefore, sulphate adsorption does not appear on Figure 4-7 as part of the classification. Soils other than Ultisols have varying capacities to adsorb sulphate and this factor may be important in mediating the acidification of a soil that would otherwise appear sensitive.

Counties were used both to integrate the various factors and to display the results. Although counties are generally uniform in size in the eastern United States, some of the larger counties occur along the U.S./Canada border in Maine and Minnesota. All the factors utilized a 50% criteria to classify counties. Therefore, significant areas can exist within counties that differ from the final designated classification. Thus Figure 4-7 displays the broad regional patterns but evaluation of an individual county requires more detailed analysis to determine the extent and coincidence of the various factors within that county.

Six classes were used to characterize soils (Table 4-15), with agricultural/urban areas shown as blank on the map (Figure 4-7). Classes 1 to 3 are specifically related to the increasing potential for soils to undergo acidification with acidic deposition. The other three classes were included to provide additional information on soils which could be used with alternate hypothesis of soil sensitivity or in better understanding acid inputs from soils to aquatic systems (Section 3.5). Class 4 includes low pH soils ($pH < 5.0$) and Class 5 includes high pH soils ($pH > 5.0$) that also have a high CEC ($CEC > 9.0$). Class 4 soils are those most likely to experience Al mobilization and have the potential to transfer both H^+ or Al^{3+} ions to aquatic systems, given sufficient inputs of acid. Section 3.5 with Figure 3-10 provides additional discussion on the potential transfer of acid to aquatic systems.

Class 6 includes areas dominated by Histosols (peat soils). Although these organic soils may not be sensitive to further acidification, it is important to recognize them in the overall assessment of acidic deposition impacts. Class 6 is most informative when compared to Figure 3-10 in Section 3.5 relative to acid inputs to aquatic systems. These and similar Canadian peatland areas naturally

TABLE 4-14. TERRESTRIAL FACTORS AND ASSOCIATED DATA BASES UTILIZED FOR TERRAIN CHARACTERISTICS MAPPING IN EASTERN CANADA AND THE EASTERN UNITED STATES

Terrestrial Factors/Surrogates	Data Sources[a]
EASTERN UNITED STATES	
1) Soil Chemistry	
i) Mean soil order pH (in distilled water)	Soil Map (USGS 1970)
ii) Mean soil order CEC	Soil Map (USGS 1970)
iii) Histisols (Organic soils)	Soil Map (USGS 1970)
2) Limit of Wisconsin Glaciation	USGS 1970
3) Land Use - urban areas	1977 National Resource Inventory (USDA 1978)
- cultivated (managed) soils	1978 Census of Agriculture (USDC 1979)
EASTERN CANADA	
1) Soil Chemistry	
Surrogates: i) Texture (sand, loam or clay) - Northern Ontario, Quebec, the Maritimes and Newfoundland/Labrador	Ecodistrict Data Base (Environment Canada 1981a,b,c)
ii) Depth to Carbonate (high, low or no lime) - Ontario	Ontario Land Inventory (OMNR 1977)
iii) Glacial Landforms - northwestern Ontario	Pala and Boissonneau 1979
iv) Organic Soils (≥50% of mapping unit)	Ecodistricts (Environment Canada 1981a,b,c)
2) Soil Depth - very shallow (approx. <25 cm), - shallow and deep (≥25 cm)	Ecodistricts (Environment Canada 1981a,b,c) and Ontario Land Inventory (OMNR 1977)
3) Bedrock Geology - lithology	Shilts et al. 1981
- % exposed	Ecodistricts (Environment Canada 1981a,b,c) and Ontario Land Inventory (OMNR 1977)

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[a] All U.S. data sources listed have been compiled within the Geoecology Data Base (Olson et al. 1980).

TABLE 4-15. SOIL CHEMICAL CLASSES AND AREAS DOMINATED BY HISTOSOLS IN THE EASTERN UNITED STATES AS MAPPED IN FIGURE 4-7

Class	Acidification Potential	No. of Counties	Characteristics
1	High	16	Moderate pH (>5.5), lowest CEC (<6.2)
2	Moderate	19	Moderate pH (>5.5), low CEC (<9.0)
3	Moderate-Low	45	Moderate pH (>5.0), low CEC (<9.0)
4	Low	849	Low pH (>5.0)
5	Low	700	Moderate pH (>5.0), high CEC (>9.0)
6	Low	13	Histosols

contribute acids of varying strength to lakes and streams due to high levels of organic acids.

4.5.2.2 Eastern Canada

The map of eastern Canada is the same as that used in Chapter 3 (Figure 3-9). The reader is referred to Section 3.5.1.1 for detail regarding map compilation.

This map shows 62 classes of terrain characteristics based on combinations of soil depth, soil texture (or depth to carbonate) and bedrock sensitivity. In the previous chapter it was used to define areas of varying potential to reduce the acidity of incoming precipitation prior to entering surface waters. In this section the 62 map classes are recombined in order to emphasize soil characteristics. The classes have been grouped according to five soil categories: (1) organic soils (I); (2) barren areas ($\geq$75% bedrock outcropping; II); (3) sandy soils (III); (4) loamy soils (IV); and (5) clayey soils (V; Table 4-16). These are correlated to soil orders of the Canadian System of Soil Classification. They are also subdivided on the basis of underlying bedrock sensitivities. It is possible to break down these divisions further, such as by soil depth (25 cm - 1 m and >1 m), or even to recombine classes if some other characteristic is preferred as a basis for discrimination. However, the grouping suggested in Table 4-16 provides a framework for summarizing soils of eastern Canada and discussing some aspects of terrestrial sensitivity.

Category I: Organic Soils (Histosols)

In Table 4-16, organic soils overlying carbonate bedrock are identified separately (IA) from those overlying other rock types (IB). Category IB map units occur over wide areas of Ontario, Quebec and Labrador and in small pockets throughout eastern Canada. Organic soils overlying carbonate strata is most common in the Hudson Bay Lowland of northern Ontario and northwestern Quebec.

The presence of limestones and dolomites beneath peat is significant because local hydrological conditions influence peat development and peatland chemistry. More minerotrophic types of peatland ecosystems occur where groundwater comes in contact with the substrate (Cowell et al. 1979; Sjörs 1963). Consequently large portions of IA organic soils have "fen" and "swamp" type ecosystems which may have a groundwater pH well in excess of 5. This could be a significant consideration with respect to the impact of acidic deposition on such terrain. This is also true for IB peatlands (and other wetlands) occurring on clay (northeastern Ontario and southern Ontario). Peatlands occurring on the Canadian Shield tend to be less minerotrophic but local soil/groundwater conditions need to be evaluated.

TABLE 4-16. TERRAIN CHARACTERISTICS OF EASTERN CANADA SUMMARIZED BY SOIL CATEGORY

Soil Category			Terrain Characteristics	Map Classes Represented on Figure 3-9	Map Area	
					km^2	% Eastern Canada
I	Organic Soils (predominately Organic and Gleysols[a])	IA	Organic soils covering ≥25% of map unit overlying rock Type 1[b].	O1a, O2a	205,782	6.57
		IB	Organic soils covering ≥25% of map unit overlying rock Types 2, 3 or 4.	O1b, O1c, O1d, O2c, O2d	236,159	7.54
II	Barren	IIA	Type 1 rocks exposed in ≥75% of map unit.	H1j, O3a	1,453	0.04
		IIB	Types 2 or 3 rocks exposed in ≥75% of map unit.	M1i, M1j, M1s, M1t, M1u, M1v, O3c	5,890	0.19
		IIC	Type 4 rocks exposed in ≥75% of map unit.	L1b, L1c, L1d, L1e, O3d	101,392	3.24
III	Sand or No Lime (predominately acid podzols)	IIIA	Soils ≥25 cm thick overlying Type 1 bedrock.	H1c, H1f, H1i	17,173	0.56
		IIIB	Soils ≥25 cm thick overlying Types 2 or 3 bedrock.	M1f, M1q, M1r, M4a, M4b, L4a, L4b	418,513	13.35
		IIIC	Soils ≥25 cm thick overlying Type 4 bedrock.	L2b, L2d, L3, L4c	1,362,454	43.42

TABLE 4-16. CONTINUED

Soil Category		Terrain Characteristics	Map Classes Represented on Figure 3-9	Map Area	
				km^2	% Eastern Canada
IV Loam or Low Lime	IVA	Soils ≥25 cm thick overlying Type 1 bedrock.	H1b, H1e, H1h	72,269	2.3
	IVB	Soils ≥25 cm thick overlying Types 2 or 3 bedrock.	M1c, M1d, M1o, M1p, M6a, M6b, M7a, M7b	214,884	6.85
	IVC	Soils ≥25 cm thick overlying Type 4 bedrock.	M3, M7c, L2a, L2c	184,557	5.89
V Clay or High Lime (predominately Luvisols and Gleysols)	VA	Soils ≥25 cm thick overlying Type 1 bedrock.	H1a, H1g	86,879	2.76
	VB	Soils ≥25 cm thick overlying Types 2 or 3 bedrock.	H2a, H2b, H3a, H3b, M1a, M1n	103,963	3.32
	VC	Soils ≥25 cm thick overlying Type 4 bedrock.	H3c, M2a, M2b, M5	116,260	3.71

[a] As defined in the Canadian System of Soil Classification.

[b] Bedrock sensitivity classes were defined by Shilts et al. (1981) on the basis of lithology. Specifically:

- Type 1 - Limestone, marble, dolomite
- Type 2 - Carbonate-rich siliceous sedimentary: shale, limestone; noncalcareous siliceous with carbonate interbeds: shale, siltstone, dolomite; quartzose sandstone with carbonates
- Type 3 - Ultramafic rocks, serpentine, noncalcareous siliceous sedimentary rocks: black shale, slate, chert; gabbro, anorthosite: gabbro, diorite; basaltic and associated sedimentary: mafic volcanic rocks
- Type 4 - Granite, gneiss, quartzose sandstone, syenitic and associated alkalic rocks.

Category II: Barren Areas

These are map units dominated ($\geq$ 75%) by exposed bedrock. Three classes of barren terrain have been mapped on the basis of bedrock lithology identified in Table 4-11 according to "sensitivity". Levels of sensitivity relate the potential or capacity of rock types to reduce acidity of atmospheric deposition as defined by Lucas and Cowell (1982). Most of these classes in eastern Canada lie above the treeline and southern limit of continuous permafrost.

Category III: Sand or No Lime Soils

According to the Soil Map of Canada (Clayton et al. 1977) these areas (IIIA to IIIC; Table 4-16) are primarily Humo-Ferric Podzols, "Rockland" ($\geq$60% exposed bedrock) and Dystric Brunisols. These soil types have acidic surface horizons (pH $<$5.5, dominantly $<$5) and correlate most closely with cases 5 and 6 in Table 4-13. They are thus considered to have a low sensitivity to acidification, a moderate sensitivity to base cation loss and a moderate to high sensitivity with respect to Al solubilization. Soils mapped as Mlq, Mlr, M4a and M4b (IIIB), and L2d and L3 (IIIC) in Figure 3-9 are probably the most sensitive because they are the shallowest. Category IIIA soils however overlie calcareous bedrock.

Boreal and northern temperate podzols are characterized by the accumulation of organic matter and Fe- and Al-sesquioxides (Stobbe 1968). Although high Fe and Al content are properties known to enhance sulphate adsorption (Johnson and Cole 1977), high organic matter tends to block the adsorption process (Johnson and Henderson 1979). Low pH, high CEC podzols in eastern Canada probably do not adsorb sulphate significantly (Case 11; Table 4-13) because their CEC is controlled primarily by organic matter. At this time however, there is very little empirical evidence regarding the sulphate adsorption capacity of Canadian soils.

Category IV: Loam or Low Lime Soils

Categories IVA to IVC are represented by loam/low lime soils of varying depth and overlie different bedrock types. It is not certain how these relate to the soil chemical classes identified in Table 4-13. They are mapped by Clayton et al. (1977) as primarily Podzolic and Brunisolic (and as Rockland). Based on the interpretation of texture and depth to carbonate as surrogates for soil chemistry, these classes are considered to exhibit the properties of Cases 3 and 4 in Table 4-13 (moderate pH).

Category V: Clay or High Lime Soils

These soils (VA to VC) are interpreted as having low to moderate sensitivity with respect to soil acidification and Al solubilization. However, sensitivity to base cation loss is high.

These soils are primarily Gray Luvisols and Gleysols (clay-rich and/or under periodic or seasonal flooding) according to the Soil Map of Canada (Clayton et al. 1977).

Map units in Figure 3-9, as noted earlier, are based on Ecodistrict and Ontario Land Inventory polygons. The best spatial resolution is in Ontario, south of 52°N latitude, where Ontario Land Inventory (OMNR 1977) units were used. Because soil and bedrock characteristics are identified on the basis of dominance, subdominant characteristics are not shown on the map. There remains a need for much improved soil chemistry data from nonagricultural areas in eastern Canada.

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

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

3. Improve 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 acidic deposition. Determine plant characteristics associated with susceptibility/tolerance to O_3 and acidic deposition.

5. Determine quantitative relationships between dose-response acidic deposition 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 acidic deposition.

8. Determine the 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 acidic deposition and ozone.

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

10. Identify beneficial as well as injurious effects of various components of acid pollution, with particular reference to rate relationships for principal terrestrial ecosystem types. Determine the 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. Based on actual field observations, quantify natural H^+ ion production and consumption rates for the principal terrestrial ecosystem types, and the clear distinction of anthropogenic and natural H^+ ion production. 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 acidic deposition effects on soil leaching of metal cations and transfer to aquatic ecosystems.)

12. Determine sensitivity of aquatic and terrestrial components of headwater pond and lake ecosystems to acid loadings.

13. Improve information, based on actual field observations on a representative range of soil types, on impact of acidic deposition on sensitive biochemical and/or chemical processes, and generally identify soil types sensitive to various pollutants and pollutant combinations.

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

15. Based on actual field observation on a representative range of mainly natural soils, improve information on impact of acidic deposition on soil biota, soil mineralogy and soil organic matter.

16. Improve understanding of relationships between forest productivity and acid sensitive properties of soils.

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

18. Improve system of mapping terrestrial sensitivity, hopefully incorporating existent data bases, to allow further identification of key sensitive areas.

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

20. Extended or "whole" ecosystem field studies of biological response to acidic deposition to understand the complex trophic interactions amongst the organisms and the resulting community changes, particularly those affecting wildlife and the top carnivores in the food chain.

21. Develop mitigative measures for correcting acidity impacts.

22. Determine the "threshold" or critical dosage of O_3 required to produce injury and/or suppression of growth and yield under a variety of field conditions.

23. Determine interactive response involving O_3 and chemical additives (i.e., insecticides, fungicides, nematocides, growth regulators). When responses occur, identify physical and chemical factors involved in the interactions.

24. Determine the diurnal pattern of O_3 occurrence in the major agricultural and forested regions as a guide for field fumigation studies and as a guide for calculation of realistic dosages.

4.7 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, soybeans and sweet corn. During the growth season frequent exposures to O_3 concentrations in excess of 0.1 ppm have produced up to 20% yield losses 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 acidic deposition 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 acidic deposition 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 adsorb SO_4^{2-} and resist nutrient cation leaching.

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

7. Multifactor 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 acidic deposition.

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SECTION 5

HEALTH AND VISIBILITY

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5.1 HEALTH

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 more completely, this report will focus on potentially indirect health effects associated with the transboundary deposition of acidifying substances, with only a brief summary of information on direct inhalation of the above mentioned pollutants.

Available information gives little cause for concern over direct health effects from acidic deposition. The pH of acidic deposition is generally well within the range normally tolerated by the skin and gastrointestinal tract. Although high levels of SO_2, NO_2, and acidic 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 (NAS 1977a; USEPA 1980), 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.

Evidence for the following potentially indirect health effects associated with acidic deposition is discussed below:
(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) prolonged direct contact with acidified water in recreation settings. In addition, a brief assessment is given on direct inhalation of common pollutant classes (i.e., photochemical oxidants, acidic aerosols and sulphur and nitrogen oxides) that can be associated with acidic deposition.

5.1.1 Contamination of Edible Fish

Some evidence suggests that acidic deposition may alter the biogeochemical cycle of metals, including mercury (Brosset and Svedung 1977; Jensen and Jernelöv 1972; Schindler 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. Scheider et al. (1979) 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 acidic 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 Jernelöv (1972), and several other investigators, have shown that inorganic mercury can be methylated in both aquatic and terrestrial ecosystems. One hypothesis that attempts 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 Jernelöv 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 higher pH regimes would thus be minimized. According to this hypothesis, 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, would then increase the bioaccumulation of methyl mercury in larger fish. Recent experiments, however, found a very poor correlation between mono- and dimethyl mercury versus pH, calling this hypothesized mechanism into question.

The processes leading to increased mercury burdens in fish are likely to be more complex, including considerations like the complexity of the food chain, redox conditions, inorganic and organic sequestering agents, watershed to lake area ratio (Suns et al. 1980), as well as the rate of atmospheric mercury input.

Although natural sources appear to contribute the major portion of atmospheric mercury (NRC 1978), emissions from coal combustion can be of significance on a regional scale. Lindberg (1980) collected air samples from a plume of a major coal-fired generating station and found that the mercury emitted was predominantly in the elemental vapour phase, with very little conversion to particles as the distance from the source increased. Due to the nature of the Hg, his findings support the theory that the majority of Hg emitted during coal combustion is deposited regionally rather than locally. Since the Hg is in the vapour phase, the major route of removal is thought to be via precipitation scavenging, which should theoretically increase in efficiency as the pH of the precipitation falls. Using calculations from Brosset and Svedung (1977), Tomlinson (1978), and Brouzes et al. (1977), it is 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 and Johnson 1980). These authors could detect no dimethyl mercury in air from measurements taken at several locations in Ontario. Although a clear association appears to exist between mercury in fish and acidity of lakes, the mechanism by which this phenomenon might be explained remains obscure. Although the extent to which acidic deposition may have contributed to mobilization or retention of mercury in fish is speculative, fish that are harvested from these lakes present a potential health hazard to humans.

Presently the mercury content of fish tested in the affected areas is usually less than the U.S. FDA recommended levels of 0.50 μg/g. If the situation is not changed, it would be prudent to assume that the mercury content of fish will continue to rise as lake pH drops (Figure 5-2).

Another important factor 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.

With respect to human health, elevated levels of mercury can lead to serious disorders. The severity of these ailments is usually related to the exposure level to mercury. This type of disorder has been reviewed in the past by many authors including Chang (1977). Generally the blood-Hg level for threshold effects lies somewhere between 100 and 200 ng/mL in a normal adult, but the maximum recommended blood Hg level for pregnant females is 20 ng/mL (NRCC 1979).

Epidemiological studies have been completed in Canada which investigated the health of populations, especially natives, that were exposed to increased concentrations of Hg in food and had as a result, elevated blood and hair Hg levels (Rudy 1980). For example, Rudy (1980) documented some mild neurological abnormalities in adult Cree men and an association between reflexes in young Cree boys and the concentration of methyl mercury in their mothers' hair during pregnancy. Due to the lack of accurate exposure modelling and many shortcomings, it would be premature to regard this work as an example of a long-range transport of air pollution associated problem.

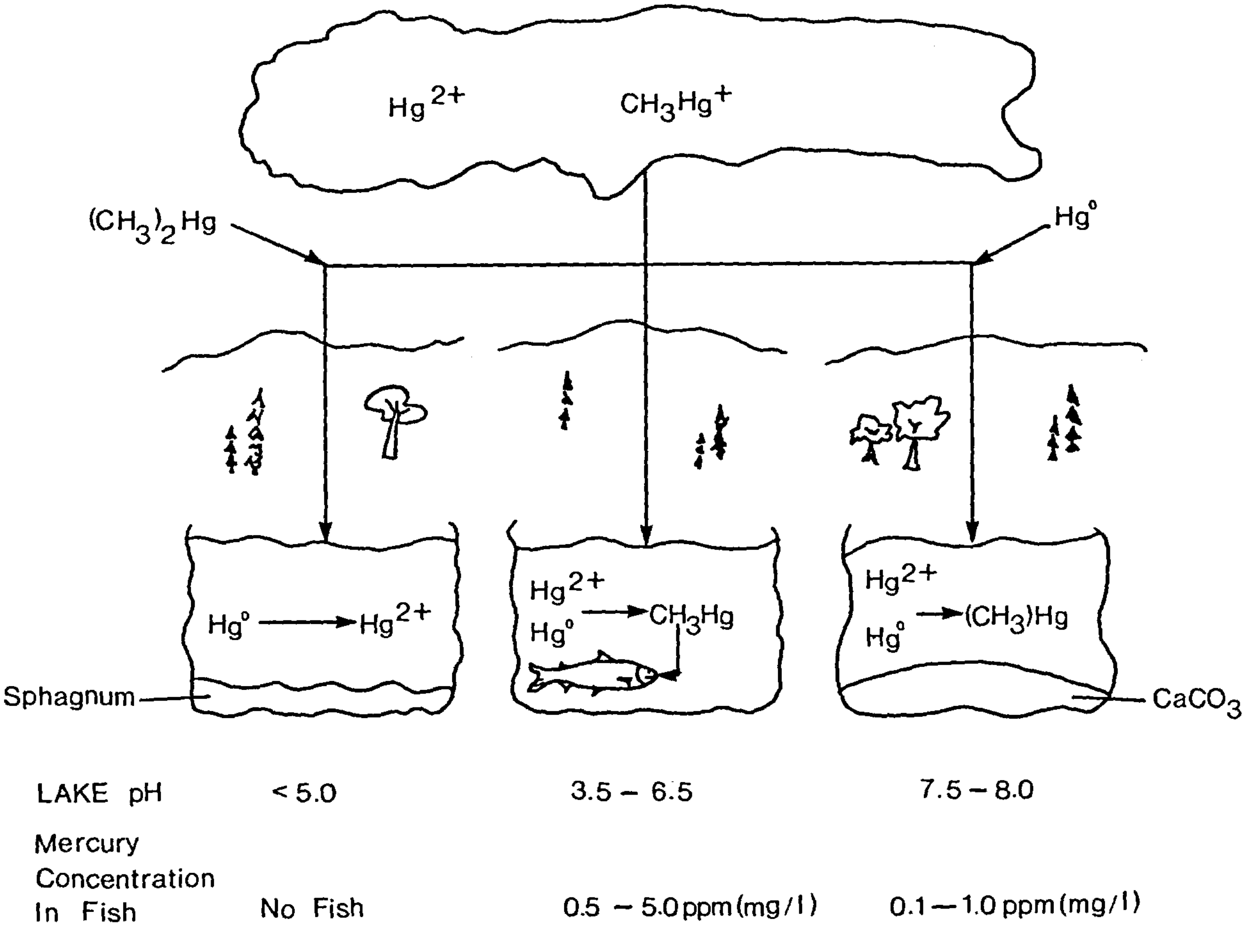

Figure 5-1. Varying effects of lake pH on the distribution of mercury in ecosystems (Tomlinson 1978).

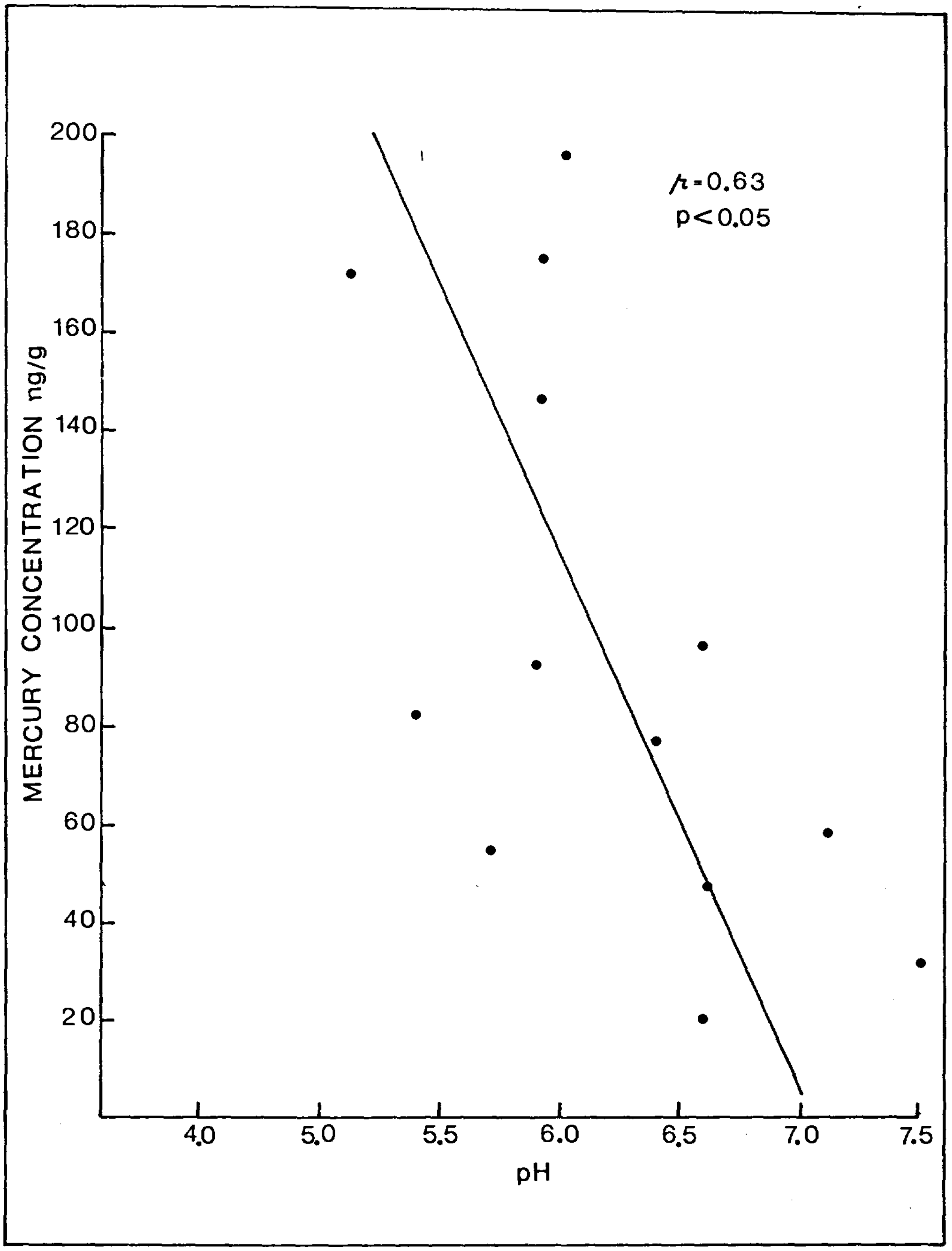

Figure 5-2. Mercury in yearling yellow perch and epilimnetic pH relationships (Suns et al. 1980).

However, an appreciation of the potential risk of long-term exposure to elevated levels of Hg in food should be maintained and careful monitoring of the situation should continue to avoid any further deterioration in health.

5.1.2 Contamination of Drinking Water

Acidic 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 acidic deposition are reported in the literature, but some potential problems are 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 tap exceed the maximum levels for human use (50 μg/L) recommended by the New York State Department of Health (Turk and Peters 1978).

Fuhs and Olsen (1979) investigated drinking water in the Adirondack region of New York State. They found high metal concentrationns at several test sites. At one home with a water pH of 5.71, copper and lead levels reached 6.6 and 0.10 mg/L respectively in a water line which had not been used overnight. In another home which had a water pH of 4.95, copper concentrations of 2.3 mg/L were recorded from a flushed line. Both of these homes obtained their water from shallow wells. The corrosive nature of the groundwater was estimated using the Langelier Saturation Index. The results indicate that a large portion of the water in the area is corrosive. From their study, Fuhs and Olsen (1979) concluded that high concentrations of metals are present in homes with metal piping especially if the lines are used intermittently.

Taylor (1982) has recently reported some of the data obtained from an examination of surface and groundwater drinking water supplies in New England. Utilizing the calcium saturation index and the aggressive index as indicators of water quality, he concluded that raw water supplies in the region were generally very corrosive. In addition, many of the watersheds tested had a very limited capacity to withstand further acid input without deteriorating further. An analysis of past water quality records for the area is proposed to determine what increment of the acidic conditions may be attributed to acidic deposition.

A recent study completed for the Department of National Health and Welfare (Meranger and Khan 1982), measured the leaching rates of metals from the plumbing systems of cottages in central Ontario on acid-sensitive lakes. In addition, samples of tap water taken from flushed and unflushed systems were analyzed for Cu, Pb, Zn and Cd.

Results from the leaching study indicate that the maximum rate of leaching occurs during the first 2 hours of water residence in the system, although levels do rise for up to 10 days. The maximum concentration of metals observed in the study resulted from 10-day static samples. Maximum values of 4.56 mg/L, 0.478 mg/L, 3.61 mg/L and 0.0012 mg/L were recorded for Cu, Pb, Zn and Cd respectively. The concentrations of all metals decreased after flushing but still remained above source levels. This indicates that the concentration of metals are related to the contact time in the distribution system.

The cottage survey consisted of obtaining tap water samples from standing and flushed supply systems for metal analysis. The median values recorded for static samples were 0.067 mg/L Cu, 0.014 mg/L Pb, 0.219 mg/L Zn and 0.0002 mg/L Cd. As anticipated, the metal concentrations in the water decreased by up to 80% following flushing. There was only one recorded instance where a sample slightly exceeded federal guidelines (0.053 mg/L Pb), and this value was obtained from a standing water supply.

Based on these preliminary data, no immediate threat to human health is perceived. Careful monitoring of the situation should continue to document any significant alterations in metal levels that may occur in the future.

Consumption of drinking water with a low pH from municipal sources is not a major issue. The raw water utilized by the treatment plant is adjusted to drinking water standards by the addition of appropriate substances. The only health concern related to this matter is to ensure that no excessive accumulation of cations (e.g., Ca^{2+}) develops as a result of the neutralization process.

Groundwater may also become acidified in poorly buffered areas (Cronan and Schofield 1979). For example, in Sweden some well water became so acidified that substantial corrosion of household plumbing occurred (Hultberg 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.

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 85 groundwater samples were field-tested, and 28 samples were analyzed in the laboratory for major ions and some trace metals. Groundwater was sampled in July from shallow springs and wells from both bedrock and overburden formations. Eleven of the 85 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.

5.1.3 Drinking Water From Cisterns

Sharpe et al. (1980) provide significant information on the effects of deposition of lead and cadmium as well as acidic 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% 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 soldered joints in the cistern and plumbing. Thus, cistern water users are at special risk in areas of high acidic 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 1977c), although the actual standard for drinking water lead levels in the United States and Canada is 50 µg/L.

5.1.4 Recreational Activities in Acidified Water

Due to the increased atmospheric fallout of acids, poorly buffered bodies of water have shown a decline in pH. Some of these lakes and rivers have attained acidity levels in excess of the federal guidelines for drinking water of pH 6.5 (NHW 1980). As a result of this situation, attention has been focused on the safety of these affected waters. There is concern that recreational activities in these waters (e.g., swimming) may prove to be detrimental to human health.

However, the rationale for the federal pH standard, which was accepted by most provinces in Canada, is based on corrosion and incrustation effects, not on health considerations. Generally metal corrosion may become a problem when the water pH falls below 6.5 and scale build-up on supply systems is usually encountered above pH 8.5. If an organ system was susceptible to the effects of acidified water, then it is felt that the eye would be the most likely candidate. This possibility is rather remote at best.

TABLE 5-1. CANADIAN AND UNITED STATES DRINKING WATER GUIDELINES FOR TOXIC METALS (μg/L)

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

Doull et al. (1980) states that acid-induced eye damage is a function of pH and the capacity of the anion in question to combine with protein. Therefore the clinical findings may vary depending on the concentration and type of acid under consideration. Exposures to mixtures of acids would be even more complicated to assess. With hydrochloric acid virtually no clinically significant effects are present above pH 3 while some discomfort was evident between pH 4.5 and 3.5. Doull et al. (1980) and Grant (1974) reported that in normal rabbit eyes, only acid solutions below pH 2.5 produced any significant eye injury and in humans brief contact of solutions from pH 7 to as low as pH 2 caused no damage. However, the subjects did complain of "an increasingly strong stinging sensation" as the acid level increased.

Due to the lack of scientific data on this issue, the Department of National Health and Welfare (Canada) is funding research into investigating the effects of acidified water on the eye. The water used in this work will be obtained from some of the most severely affected lakes in central Ontario to simulate the worst possible conditions a person may be subjected to. Results from this study are anticipated in mid-1982. A preliminary study by Basu (1981) has indicated that there are no ocular clinical effects produced by short-term exposures to lake water with pH values as low as 4.6. Based on all of the above information it would seem unlikely that any ocular exposure to the mildly acidic waters in affected regions would produce any harmful health effects. However, a final conclusive statement on this matter should be reserved until the results of the Health and Welfare study are complete.

5.1.5 Direct Effects: Inhalation of Key Substances Related to Long Range Transport of Air Pollutants

Although no direct health effects were associated with acidic deposition *per se*, deleterious effects have long been attributed to inhalation of high concentrations of several important pollutant classes that were implicated as precursors to acidic deposition. These include ozone and other photochemical oxidants, acidic aerosols and other particulate matter, and oxides of sulphur and nitrogen. The effects associated with these pollutants led to the establishment of minimum air quality standards for each pollutant in both the U.S. and Canada (Table 5-2). Extensive reviews of the health effects literature were recently conducted for these pollutants (e.g., NAS 1977a,b, 1978; USEPA 1978, 1980, 1981, 1982; WHO 1979). These reviews generally support the notion that attainment of the respective air quality standards will protect public health. The reader is referred to these documents for a comprehensive assessment of the effects literature. The discussion below is intended only as a brief summary of some aspects of interest.

TABLE 5-2. CURRENT HEALTH-RELATED AMBIENT AIR QUALITY STANDARDS

	UNITED STATES		CANADA (Maximum Acceptable Level)	
POLLUTANT	LEVEL	TIME	LEVEL	TIME
Ozone (O_3)	0.12 ppm (235 μg/m^3)[a]	1 - hr	0.08 ppm 0.025 ppm 0.015 ppm	1 - hr 24 - hr Annual [c]
Nitrogen Oxides (NO_2)	0.05 ppm (100 μg/m^3)	Annual[c]	0.21 ppm 0.11 ppm 0.05 ppm	1 - hr 24 - hr Annual[c]
Sulphur Oxides (SO_2)	0.14 ppm (365 μg/m^3)	24 - hr[b]	0.34 ppm 0.11 ppm 0.02 ppm	1 - hr 24 - hr Annual[c]
	0.03 ppm (80 μg/m^3)	Annual[c]		
Suspended Particulate Matter	260 μg/m^3[e]	24 - hr[b]	120 μg/m^3	24 - hr
	75 μg/m^3[e]	Annual[d]	70 μg/m^3	Annual[d]

[a] The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 235 μg/m^3 is equal to or less than 1.

[b] Not to be exceeded more than once per year.

[c] Annual arithmetic mean.

[d] Annual geometric mean.

[e] Currently under review and possible revision.

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. Morphological and biochemical changes in the lung are also observed following exposures to low levels of O_3. In addition, extrapulmonary effects were documented. Changes in the circulating red cells of animals exposed to ozone were reported. Since O_3 is unlikely to penetrate the pulmonary mucosa, the alterations are suggested to arise as a result of a chain reaction when various free radicals are formed (Goldstein 1980).

The effects of ozone are influenced by factors other than concentrations and length of exposure and young animals are more susceptible. Elevated temperatures, increased relative humidity and exercise all increase the toxicity of O_3 (Doull et al. 1980). As with other toxicants, the individual health of a person has an effect on the results. People with respiratory disease (e.g., asthma, emphysema or bronchitis) are believed to be particulary sensitive to low-level exposures.

Ozone produces eye, nose and throat irritation in the 0.1 - 0.15 ppm range (Ferris 1978), and the Americn 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-hour 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).

There is some controversy surrounding the possible synergistic properties of O_3 in combination with other pollutants. Although evidence was developed that suggested ozone has an enhanced toxicity when combined with SO_2 (Hazucha and Bates 1975; NRC 1975), recent studies have found no clear support for such synergism (Bedi et al. 1979; Kleinman et al. 1981).

One theory gaining some acceptance deals with exposures to low concentrations of ozone over several days. Ozone is thought to have a short-term cumulative effect above a threshold value (Folinsbee et al. 1980). In consecutive exposure studies a decrease in pulmonary function is maximized during day 2-3. Additional exposures result in a return to pre-exposure values or an improvement in pulmonary response on day 4-5 (Farrell et al. 1979; Hackney et al. 1977). These results also support the notion that some form of adaptation or tolerance is developed following repeated exposures. This tolerance, however, may be of limited duration and dependent on peak concentration. All of these experiments have dealt only with short-term responses, and the consequences of biological changes resulting in tolerance are not known. Specifically, more data is required on chronic or long-term exposures in view of animal studies suggesting increased susceptibility to infection, morphological abnormalities and extrapulmonary effects (USEPA 1978).

In summary, brief exposures to ozone can be linked to alterations in pulmonary function. At low levels, O_3 produces eye, nose and throat irritation. Based on the available quantitative evidence, the established air quality standards appear to be protective of public health. Ozone levels achieve maximum readings from April to July and the annual mean concentration exceeds maximum acceptable levels at several locations, predominantly in eastern Canada (see Tables 4-6, 4-7). The ozone air quality standards are also exceeded in a number of northern U.S. cities (Table 4-5).

Nitrogen oxides, among the photochemical irritants, are primarily derived from internal combustion engines, and NO is rapidly converted to NO_2 in the atmosphere. A recent national air pollution survey (Environment Canada 1979) indicates that NO_2 concentrations are highest from January to July, but concentrations do not exceed existing Canadian guidelines. 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. There is some evidence that elevated levels of NO_2 will produce an increase in respiratory disease (Florey et al. 1979; Guidotti 1978; Speizer et al. 1980), but presently it is not clear whether transient peaks of NO_2 or long-term exposure to low levels are primarily responsible for these observations. The levels of NO_2 in Canada are relatively low and unless further information becomes available, current standards seem adequate to protect human health.

Sulphur oxides (SO_2) and related particulates are also respiratory irritants. An important feature of sulphur oxides are their ability to interact with other pollutants to form substances that vary in their respiratory instancy potential. The most prominent response to inhaled SO_2 is bronchial constriction leading to increases in flow resistance. Healthy individuals begin to respond to SO_2 peaks of about 5 ppm while sensitive individuals may respond to short-term exposures of less than 1 ppm (USEPA 1981).

Various sulphate forms have also been associated with increases in pulmonary disease and some concern has been raised over statements linking airborne sulphates to human morbidity/mortality (Lave and Seskin 1973). This and other investigations were reviewed by the subjects and from ill-defined groups that may have confounding factors (e.g., smoking habits and health problems) and may lack good exposure estimates and contain uncertainties with respect to statistical models. This limits the use of these studies for assessing health effects of specific pollutants. At best, they provide qualitative support for the association of sulphur-particulate pollution with health effects (USEPA 1981).

As with nitrogen oxides, the levels of SO_2 asssociated with transboundary transport between the U.S. and Canada are relatively low, and current standards seem adequate to protect human health. However, some concern has been expressed about regional transport of sulphur containing fine particles including sulphuric acid, sulphates and associated substances. The effects of general particulate matter and sulphur oxides were reviewed recently by Ware et al. (1981) and Holland et al. (1979) and are the subject of a revised EPA criteria document (USEPA 1981) and staff paper (USEPA 1982). 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. 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.

In summary, to the extent that transboundary transport contributes significantly to violations of the air quality standards listed in Table 5-2 (an issue for Work Group III to resolve), the matter should be the subject of the bilateral discussions.

5.1.6 Sensitive Areas and Populations at Risk - Health

Certain areas are sensitive to acidic deposition resulting in contamination of fish and drinking water supplies. These include areas with poorly buffered lakes and streams (with a viable fish population), watersheds with unusual accumulations of metals in sediments or soils, areas which lack drinking water treatment facilities, and areas with substantial lead plumbing.

Some populations are more susceptible to environmental insults than others. These populations include those dependent on fish from acidified waters as a major dietary staple, those with elevated mercury or lead blood levels from other exposures, those dependent on cisterns as a primary source of drinking water, and women of childbearing age as well as children.

5.1.7 Research Needs

Due to the common areas of interest between the health effects and aquatic sections, there are also similar gaps in data bases and research requirements. For example, work is required in the following areas:

1. Acidic deposition appears to increase the mobilization of metals from soils and the leaching rates in water distribution systems. Therefore, data is needed to further clarify the

levels, species, and temporal variations of these metals and their effects on biological systems.

2. A data base needs to be developed that will enable researchers to identify sensitive areas and receptors in order to predict which regions have a greater risk of developing health related problems.

3. There is an apparent relationship between declining water pH and increasing Hg levels in the food chain. Therefore, more data related to their exposure levels and Hg content in various species is needed.

4. More research is needed to differentiate the health effects resulting from short-term exposures and long-term exposures to pollutants subjected to long range transport.

5. Carefully designed and controlled epidemiological studies are necessary in order to relate exposure to various air pollutants to the health of susceptible individuals as well as the general population.

6. The relative contributions of transported air pollutants that contribute to acidic deposition should be determined. The levels of these pollutants should be compared to the National Ambient Air Quality Standards.

5.2 VISIBILITY

This discussion is largely adapted from a recent EPA staff assessment (USEPA 1982). The effect of transboundary pollution on visibility is directly related to air quality, rather than deposition. The particulate phase precursors to acidic deposition (mostly sulphuric acid aerosol and various ammonium sulphate aerosols) as well as other fine particles 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. For some isolated point sources, however, NO_2 may produce visible brown plumes at distances of 100 km from the source (Menlo 1980).

5.2.1 Categories and Extent of Perceived Effects

Impairment of visibility is perhaps the most noticeable and best documented effect of particles in current North American atmospheres. It is often equated with "visual range" as measured by airport weather observers. However, visibility in a broader context relates to visual perception of the environment and involves colour and contrast of viewed objects and sky, atmospheric clarity, and the psychophysics of the eye-brain system (USEPA 1979).

For present purposes, it is useful to classify pollution-derived effects on visibility into two categories: (1) regional haze, and (2) visible plumes. The nature and extent of these effects are determined largely by the distribution and characteristics of anthropogenic and natural particles and, to a lesser extent, by NO_2. Salient features of both categories are outlined below.

Regional haze is relatively homogeneous, reduces visibility in every direction from the observer, and can occur on a geographic scale ranging from an urban area to multistate regions. Increased haze reduces contrast causing more distant objects to disappear. Nearby objects can appear "flattened" and discoloured, the horizon sky is whitened, and scattered light is perceived as a gray or brown haze (Charlson et al. 1978). When urban light and haze combine at night, the contrast between the night sky and the stars is reduced, markedly limiting the number of stars visible in the night sky (Leonard et al. 1977).

The best available indication of the extent and intensity of regional haze with time is visibility (visual range) data routinely measured at airports and some other locations. Some uncertainties arise from the use of such data to characterize regional visibility; among them are differences in target quality and observers between sites and at the same site, representatives of the airport location, and potential biases in measurement techniques. Analyses of airport visibility trends from 1948 to 1974 suggest that visibility in the eastern U.S. declined over that period, particularly during the summer months (Husar et al. 1980; Trijonis et al. 1978b). The analysis of visibility trends has recently been extended for this report by Husar and co-workers (Husar pers. comm.) to include Canadian and U.S. data through 1980. Figure 5-3 presents the results of the preliminary analysis. This figure represents extinction weighted airport visibilities for about 300 U.S. sites and 177 Canadian sites (94 in eastern Canada). Sites were selected on the basis of a reasonably continuous record. The airport data reflect 5-year quarterly means of noon extinction, (3.9/visibility) from 1950 to 1980 exclusive of readings with fog, precipitation or blowing material. Because the figure represents average extinction, the estimated visibility as derived from the indicated scale is weighted to lower than actual average visibility on fog/precipitation free days. These data are quite preliminary and subject to the usual caveats regarding airport visibility trends. The U.S. results appear consistent with other published data. The lower density and variability of Canadian sites make regional representations presented considerably less reliable. Differences exist between some features in the figure and other examinations of specific sites in Canada; these may be related to site or to different treatment. Until further examination of the Canadian data is completed, the results should be treated with caution (Christe pers. comm.).

The figures show eastern visibility is substantially less than that in the west. The unusual area of persistent low visibility in

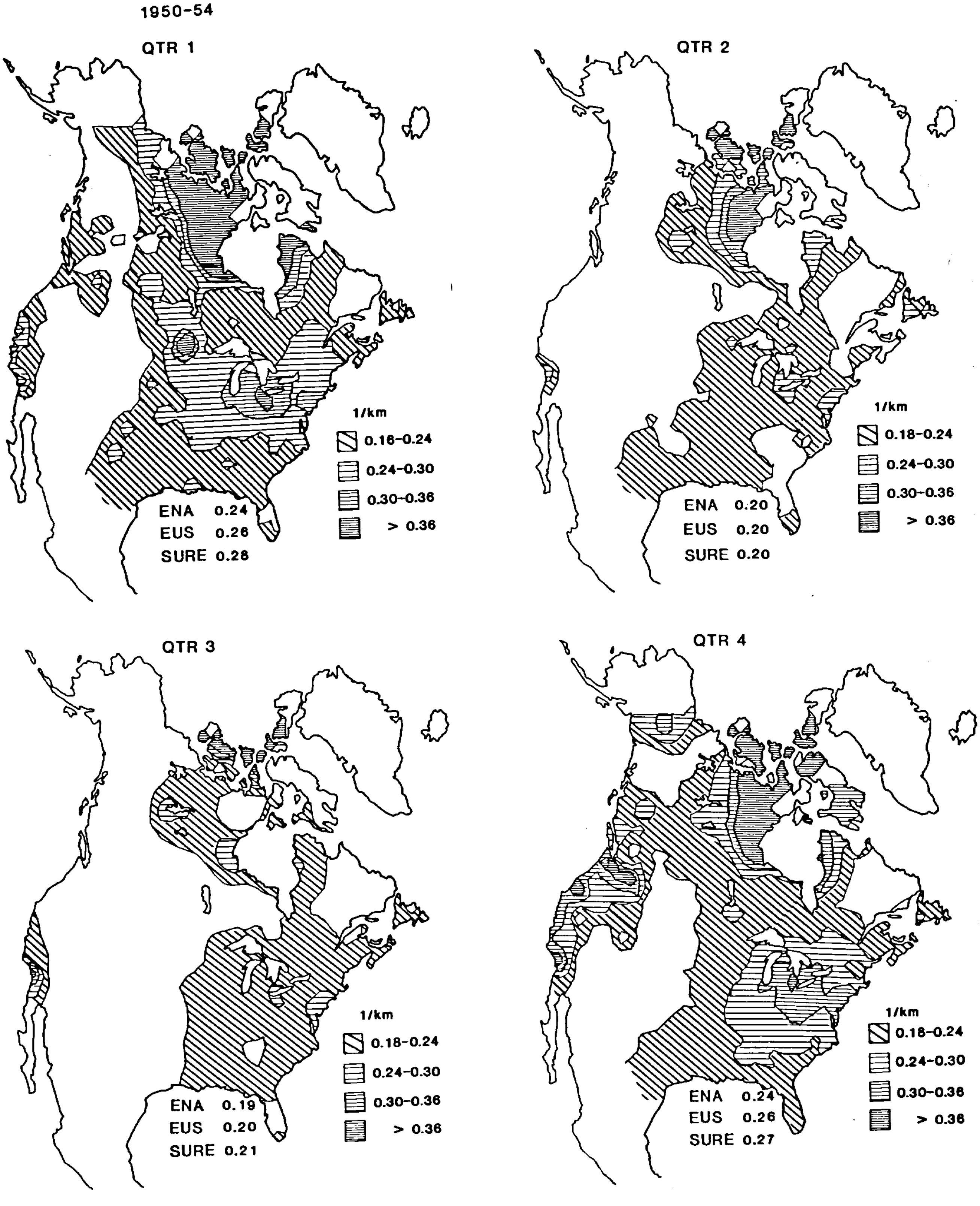

Figure 5-3a. Seasonal and spatial distribution of long-term trends in extinction - weighted airport visibilities for North America, 1950-54 (after Husar pers. comm.).

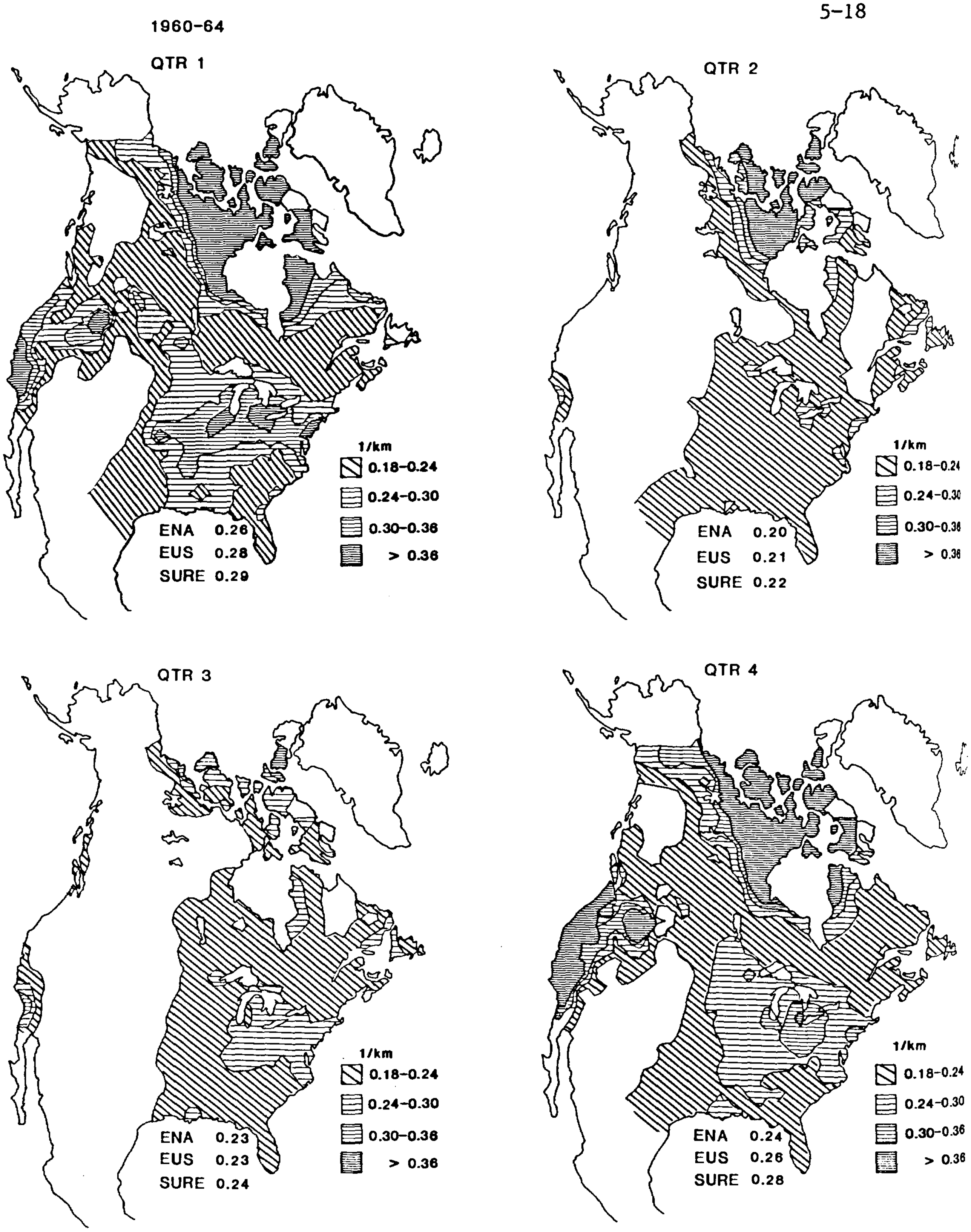

Figure 5-3b. Seasonal and spatial distribution of long-term trends in extinction - weighted airport visibilities for North America, 1960-64 (after Husar pers. comm.).

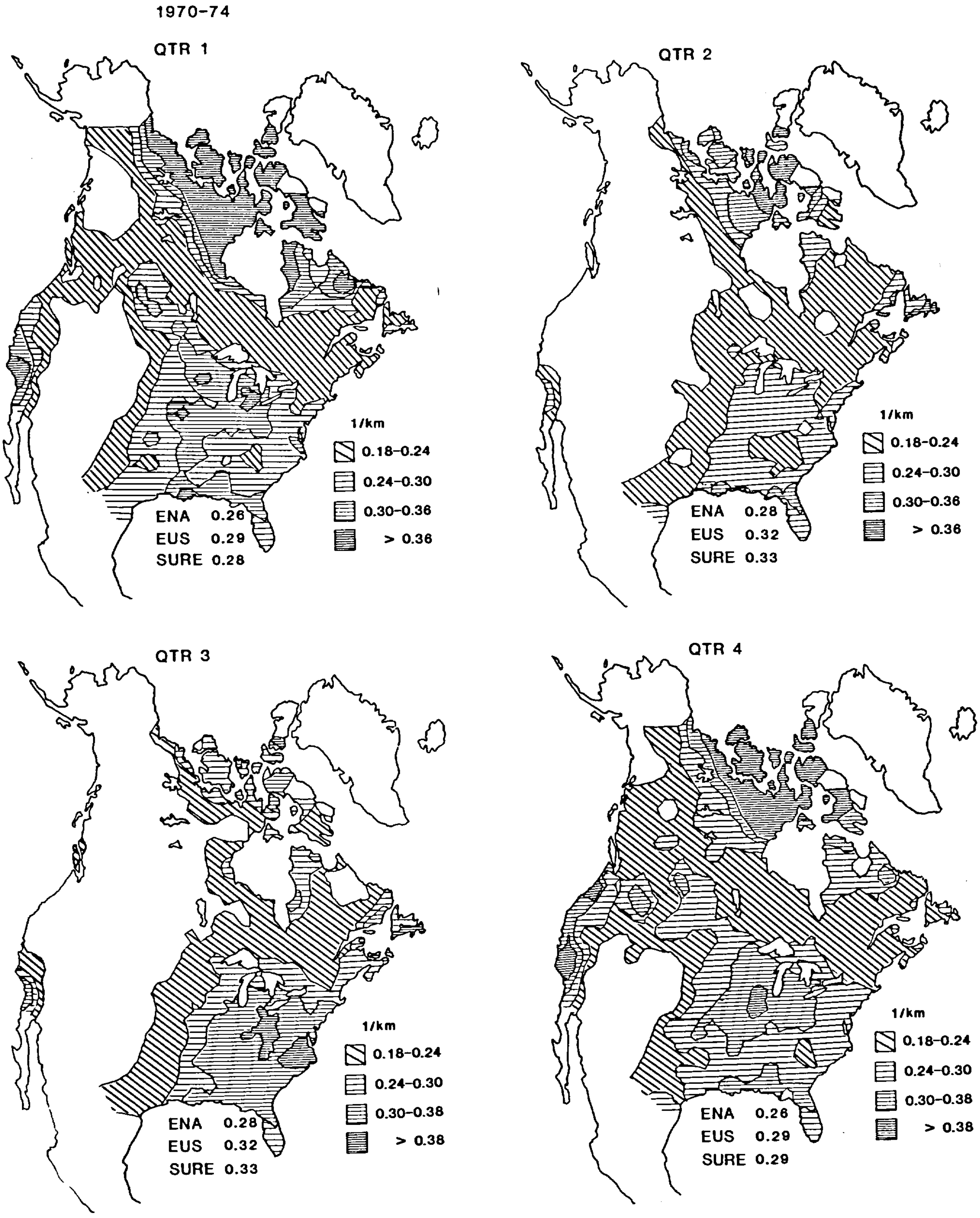

Figure 5-3c. Seasonal and spatial distribution of long-term trends in extinction - weighted airport visibilities for North America, 1970-74 (after Husar pers. comm.).

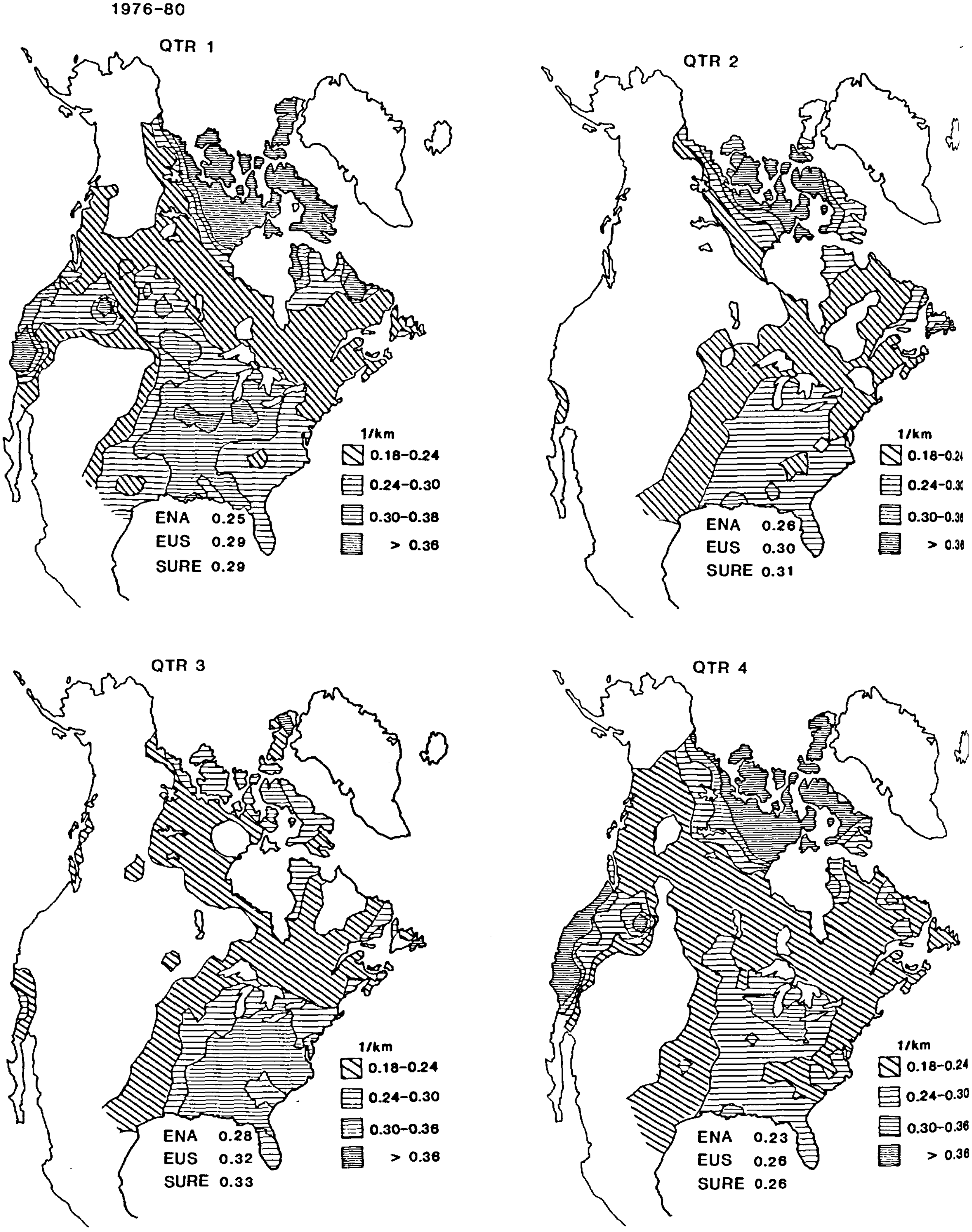

Figure 5-3d. Seasonal and spatial distribution of long-term trends in extinction - weighted airport visibilities for North America, 1976-80 (after Husar pers. comm.).

northern most Canada has not been explained, but may be related to very high humidity and the presence of ice crystals and, in wintertime, reduced daylight. It is unlikely to be related in any substantial way to anthropogenic sources. Moreover, the number of sites in this large region is quite limited, and may not be truely representative of precipitation/fog free days.

Consistent with earlier U.S. work, Figures 5-3a,b and c shows that while visibility in some urban areas improved or stayed the same from 1950-74, the occurrence of episodic regional haze appears to have increased in the eastern U.S. and portions of southern and eastern Canada. Summertime (Quarter 3) trends are most pronounced in these areas. Since 1972, regional visibility in eastern Canada (Figure 5-3d) and in both the east and west of the U.S. apparently has improved slightly but not to pre-1960 levels (Marians and Trijonis 1979; Sloane 1980). Whether this recent improvement is related to more favourable meteorology or reduced regional particle and sulphur oxide emissions is not known with certainty, but such reductions are reflected in emissions inventories in both east and west.

Regional differences in average U.S. visibility are illustrated in Figures 5-4 a and b. As indicated by suburban and nonurban airport data, visibilities in the east are substantially lower than in most of the west. Some of the differences between east and west may be related to the lower regional humidity in the west, but a more important difference is the generally higher regional particle loading in the east. Based on: (1) long-term historical data in the northeast from 1889 to 1950 (Husar and Holloway 1981); (2) examination of airport visibility trends after deleting data possibly influenced by obvious natural sources (i.e., fog, precipitation and blowing dust) (Figure 5-3); and (3) current assessments of natural sulphur sources and regional fine particles levels (Ferman et at. 1981; Galloway and Whelpdale 1980; Pierson et al. 1980; Stevens et al. 1980), anthropogenic particulate pollution would appear to dominate eastern regional haze. Relying on the analysis of Ferman et al. (1981), it has been estimated that in the absence of anthropogenic sources summertime visibility in the Shenandoah Valley would range between 60 and 80 km (36-50 miles) (USEPA 1981). The median daytime visual range actually observed during the 1-month study at this site was four to five times lower (9 miles).

Visible plumes of smoke, dust, or coloured gas obscure the sky or horizon relatively near their source of emission (USEPA 1979). Black, gray, or bluish plumes are caused by particles. Brownish plumes may be caused by NO_2 or particles. Perception of plumes (and regional haze) is strongly influenced by factors such as viewing angle, sun angle, and background objects (USEPA 1981). Because visible particle plumes often are subject to opacity regulations and because they are usually quite localized in character, the focus here will be on urban and larger scale regional haze.

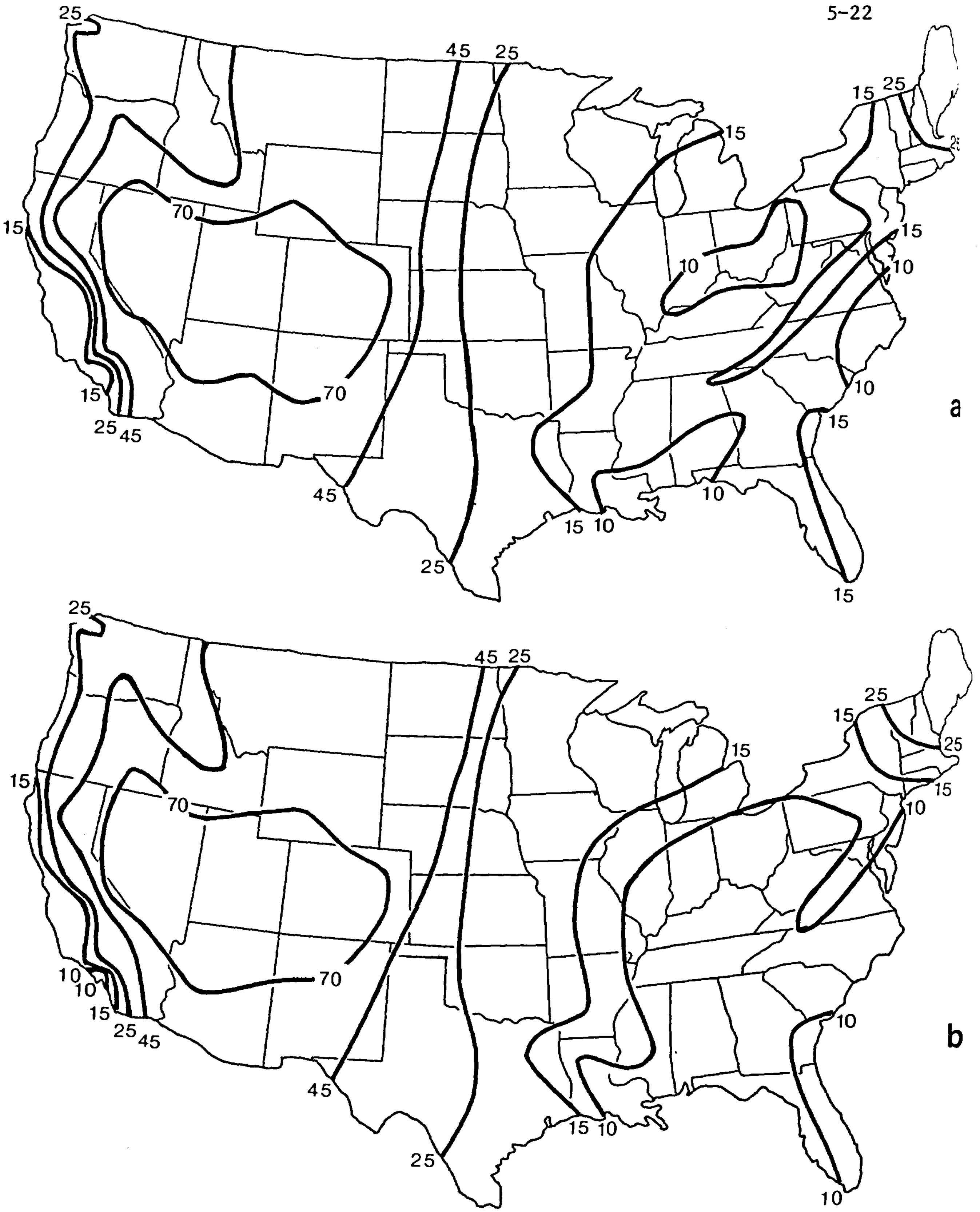

Figure 5-4. Median 1974-76 visibilities (miles) and visibility isopleths for suburban/nonurban airports: (a) yearly, and (b) summertime (Trijonis and Shapland 1979). Data are subject to uncertainties associated with suburban airport observations, but show general regional patterns. The clear differences between east and west are parallelled by regional humidity and nonurban fine particle levels. Summertime fine mass averaged from 22 to 25 $\mu g/m^3$ at 12 eastern nonurban sites (Watson et al. 1981) and about 4 $\mu g/m^3$ for 40 Rocky Mountain and southwest background sites (Snelling 1981).

5.2.2 Evaluation of Visibility

Visibility impairment may adversely affect public welfare in essentially two areas: (1) the subjective enjoyment of the environment (aesthetics, personal comfort and well-being), and (2) transportation operations. The aesthetic aspects of visibility values can be categorized according to: (1) social/political criteria, community opinions and attitudes held in common about visibility; (2) economic criteria, the dollar cost/benefit associated with visibility; and (3) psychological criteria, the individual needs and benefits resulting from visibility. These categories are not exclusive, but relate to different approaches for measuring somewhat intangible values. Evidence on visibility effects is drawn from studies of social perception and awareness of air pollution, economic studies, and visibility/air transportation requirements. These studies are summarized in Table 5-3 and evaluated briefly below.

5.2.2.1 Aesthetic Effects

Assessment of the social, economic and psychological value of various levels of visibility is difficult. The criteria document, an EPA report to Congress (USEPA 1979), Rowe and Chestnut (1981), and Fox et al. (1979), discusses and evaluates several approaches that have been used or proposed towards this end. In particular, preliminary studies of social awareness/perception and the economic value of visibility in urban and nonurban areas support the notion that visibility is an important value in both settings.

Early social awareness studies (DHEW 1969; Schusky 1966; Wall 1973) conducted in polluted urban areas have generally shown that at higher pollution levels an increasing portion of the population is aware of air pollution and considers it a nuisance. In St. Louis, a linear relationship was observed between annual particle levels (50-200 $\mu g/m^3$ TSP) and public awareness and concern. At 80 $\mu g/m^3$ annual geometric mean TSP, about 10% of those surveyed reported air pollution as a nuisance (Schusky 1966). Although it is reasonable to attribute more of these and other perception results to particulate matter than to gaseous pollutants (Barker 1976; Wall 1973), the relative importance of visibility degradation by plumes and haze as compared to dustfall was not clearly addressed in these studies. A more recent study of perception of air pollution in Los Angeles (Flachsbart and Phillips 1980) represents the most comprehensive evaluation of major pollutant indicators and perception to date. Five gaseous pollutants (O_3, CO, NO_2, NO, SO_2), four particle related indices (TSP, dustfall, CoH, visibility) and six averaging times were compared with perceived air quality as reported by 475 respondents living in 22 residential areas in Los Angeles County. Only two indices, visibility and ozone, were consistently significantly related ($\alpha = 0.001$) to perceived air quality for all averaging times. The highest correlation coefficient (Kendall's τ) occurred for yearly visibility ($\tau = -0.29$) and for number of days

TABLE 5-3. SUMMARY OF QUALITATIVE EVIDENCE FOR VISIBILITY RELATED VALUES

	Effect of Increased Visibility	Affected Groups	Averaging Times[a]	Supporting Observation
Transportation	More efficient, lower risk operations, visual approach permitted	Airport users, operators civilian and military	1 - 3 hr readings	Visual approach permitted when visibility 3-5 miles; airport specific (FAA 1980b)
	Increased opportunity to operate aircraft	General aviation aircraft (no-instrument capable pilots, aircraft)	1 - 3 hr readings	VFR permitted when visibility 3 miles (FAA 1980a)
Aesthetic:				
1) Social Criteria	Decreased perception of air pollution	Substantial percentage of general population; urban areas	Daily to annual	Perception of air pollution in Los Angeles significantly related to visibility for all averaging times (Flachbert and Phillips 1980). Perception, annoyance significantly related to particulate matter (Schusky 1966)
	Options values; maintaining or increasing opportunity to visit less impaired natural and urban settings	Outdoor recreationists, campers, tourists	Daily, peak visitation in summer months	Aggregate of activity values in iterative bidding studies suggests importance of options values (Rowe and Chestnut 1981)
	Improved view of night sky	Amateur astronomers, other star watchers	Nightly	Decrease in star brightness by by fine particles (Leonard et al. 1977)
2) Economic Criteria	Increased property values	Home owners	Long-term	Property values related to perception of air pollution, hence visibility (Brookshire et al. 1979; Rowe and Chestnut 1981)
	Enhanced enjoyment (user or activity values) of environment in:			
	a) Urban settings	Urban dwellers	Long-term	Willingness to pay for increased visibility in urban (Brookshire et al. 1979) and nonurban settings (Rowe et al. 1980)
	b) Natural settings	Outdoor recreationists, campers, residents of non-urban areas	Daily, peak visitation in summer months	
3) Psychological Criteria	Existence values; maintaining pristine environments	General population	Long-term	Existence values may far outweigh activity or user values (Rowe and Chestnut 1981)
	Less concern over perceived health effects	General population urban areas	Daily to long-term	About 2/3 of bid for improved visibility in Los Angeles was related to concern over potential health effects (Brookshire et al. 1979)

[a] Represents staff judgement of most important averaging time based on supporting observation. Because averaging times are related it is difficult to specify single (long or short) averaging time as most significant. Perception of visibility is essentially instantaneous.

visibility was less than 3 miles (T = 0.32).[a] Of the other particle indices, only monthly average dustfall was significantly correlated (T = 0.12) with perception. Consistent with other studies, the survey also found that air quality is valued less by minority groups and long-time urban residents than by whites (all income classes) and those with some history of rural residence.

The two major approaches to economic valuation of visibility include: (1) survey (e.g., iterative bidding), and (2) property value studies. The major published iterative bidding studies of visibility, conducted in the rural southwest and in the Los Angeles area (South Coast Air Basin), are summarized and evaluated in Table 5-4. The Four Corners and Lake Powell studies deal only with single sources and visible plumes, while the Farmington and Los Angeles studies address haze. The preliminary nature of these studies makes them useful primarily as qualitative indicators of the economic value of visibility. Among the more important limitations of the published results are the following:

1. None of these studies has measured existence values (benefit of just knowing pristine areas exist, regardless of intent to use them) or options values (wish to preserve the opportunity to view an unimpaired vista). Rowe and Chestnut (1981) suggest that existence values of good visibility in natural settings may be significantly greater than measured activity values.

2. The studies may be subject in varying degrees to methodological problems. The Farmington study, in particular, discovered a number of biases probably related to the credibility of the contingent market. These biases were not always large but show the difficulty of valuing visibility through iterative bidding.

3. Even if the available results could be taken at face value, so few studies have been conducted that results cannot be directly transferred to other areas of the country. For example, it might be expected that willingness to pay for improved visibility in Los Angeles might be greater than that for areas in flat terrain without background hills or mountains.

Despite their limitations, the iterative bidding studies suggest that visibility is of substantial economic value in both urban and natural settings. Although the value of visibility in other areas may vary significantly from that suggested by studies in the rural southwest and Los Angeles, no a priori reason exists to suggest that visibility is of little value in heavily populated eastern urban and rural areas. With respect to recreational settings, of the 23 most heavily used national parks and monuments, 11 were in the East (NPS 1981). In 1979 over 90 million visits were recorded in all eastern National Park Service managed facilities.

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[a] Kendall's T is a nonparametric statistic. The negative correlation between the number of people perceiving poorer air quality and visibility and the positive correlation with the number of days visibility is less than 3 miles are consistent with expectations.

TABLE 5-4. SUMMARY RESULTS OF ITERATIVE BIDDING VISIBILITY STUDIES (after Rowe and Chestnut 1982)

Design Elements/Study (Year)	Four Corners NM (1972)[b]	Lake Powell UT/AZ (1975)[c]	Farmington NM (1977)[d]	South Coast Air Basin CA (1978)[e]
Total Interviews Conducted (Percents Usable)	1,099 (69%)	104 (79%)	130 (92%)	345 (NR)
Scenarios	Emissions, strip minings, transmission lines, single power plant	Air Quality and Power Plant	Air Quality and Power Plant	Air Quality and Health
	A-worst	A-No plant	A-Visibility 120 km	A-Poor Visibility-2 miles
	B-middle	B-Plant, no plume	B-Visibility 80 km	B-Fair Visibility-12 miles
	C-best	C-Plant with plume	C-Visibility 44 km	C-Good Visibility-28 miles
Payment Vehicle	User fees/ Electricity Bill	User Fees	Utility Bill/ Payroll Reduction User Fee	Utility Bill/ Monthly Payments to Conservation Fund
Willingness to Pay Bid Comparisons				
a) Yearly bids for individual residents households	A-C[a] $85 B-C $50 A-B -	--	A-D[a] $82 A-B $57 B-D $43	A-C[a] $245 B-C $243 A-B $174
b) Daily bid for individual recreationists min. $1.00	--	A-C $2.95	A-D $2.44	--
c) Aggregate Yearly Value	A-B $15.54 M A-C $24.57 M	A-B $.414 M A-C $.727 M	A-B $1.47 M A-C $1.99 M A-D $2.14 M B-C $1.1 M	30% improvement $.58 - $.65 B
Tested for bias/found biases	No/No	No/No	Yes/Yes	Yes/Yes
Comment on Total Values	Values for total affected four corners region; attributed mostly to particulate air pollution reduction at single source, but difficult to separate from other visible factors due to unstandardized scenarios. Measured activity values only.	Examined one of fifteen potentially affected parks; pictoral representations not consistent across A-C. Measured activity values only.	Value for San Juan County, New Mexico and Mavajo recreation area only. Affected area up to 10 times larger strategic bias not found, but other bias problems with contingent market found. Measured activity values only.	About one-third of benefits are related to aesthetics, two-thirds to health. Results reasonably consistent with companion property value study. Measured user values. Some questionnaire design biases related to aesthetics.

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[a] Capital letters refer to scenarios listed above. Thus "A-C" in the Four Corners case refers to the bids for going from scenario A (worst) to scenario C (best).

[b] Randall et al. 1974

[c] Brookshire et at. 1976

[d] Rowe et al. 1980

[e] Brookshire et al. 1979

A large number of property value studies related to air quality have been conducted. These have been reviewed by Freeman (1979a,b) and Rowe and Chestnut (1981). Although a variety of air quality indicators have been used, the results of awareness/perception studies strongly suggest visibility plays an important role in air quality related impacts on property values (Rowe and Chestnut 1981). This contention is best documented in the case of the South Coast Air Basin property value survey (Brookshire et al. 1979). There, the estimated annual benefit of a 25-30% improvement in air quality based on property values was about $500 U.S. per household. These results are qualitatively similar to the companion iterative bidding study (about $300 U.S./household). The bidding study suggests that 22-55% of the bids to improve visibility were related to aesthetic effects. Both the bidding results and the perception study (Flachsbart and Phillips 1980) conducted in the same area support the possibility of substantial impacts of visibility on Los Angeles area property values.

None of the other published property value studies are accompanied by companion studies that suggest what portion willingness to pay for improved air quality may be due to visibility. Moreover, theoretical problems remain in relating willingness to pay functions from property value differentials (Rowe and Chestnut 1981). No single study has examined all of the variables that might be important in influencing property values. Because air pollution tends to be a small influence compared to other variables, earlier studies that examined a limited number of variables are particularly suspect. In essence, the available literature suggests that perceived air pollution, and hence visibility, may have tangible effects on property values in urban areas such as Washington, Boston, Los Angeles, and Denver (Rowe and Chestnut 1981); nevertheless, additional theoretical and empirical work is needed before reliable and transferable quantitative relationships for visibility evaluation can be established.

5.2.2.2 Transportation Effects

Although all forms of transport may be affected by poor visibility (e.g., slowing of highway traffic by anthropogenically induced fog), at current ambient levels, aircraft operations appear to be most sensitive. When visibility drops below 3 miles, both U.S. FAA and Canadian safety regulations restrict flight in controlled air spaces to those aircraft and pilots that are certified for operation under Instrument Flight Rules (IFR) (FAA 1980a). The most severe impact in such cases is usually on non-IFR general aviation aircraft which are, in effect, grounded or forced to search for alternate landing sites. In 1979, there were about 210,000 active general aviation aircraft which accounted for about 84% of total airport operations in the U.S. Over 23% of all general aviation aircraft had no IFR capability (Schwenk 1981). Estimates of the percentage of pilots certified for IFR in the U.S. and Canada are not available. Commercial, military, and other IFR aircraft operation also may be affected by reduced visibility. Under IFR conditions, the number of arrivals and departures per hour can be significantly decreased as compared to Visual Flight Rules (VFR) conditions. The effect varies with airport, and in some cases, the visual range cutoff for the most efficient visual approaches (VAPs) may be 5 miles (FAA 1980b). For example, the performance standard for one configuration at Boston Logan International Airport is 109 operations per hour for VAPs (5 miles), 79 operations per hour for "basic" VFR (3-5 miles), 79 operations per hour for "controllers" visual approach IFR (2-3 miles), and 60 operations per hour for "category I" IFR (2 miles). Thus, depending on airport configuration, schedules, and the extent and duration of haze induced visibility reduction, delays in commercial and other aircraft operations can occur. In large segments of the eastern U.S., midday visibilities less than 3 miles with no obvious natural causes occur 2-12% of the days in the summer and 1-5% of the time during other seasons (USEPA 1981). Visibilities less than 5 miles would, of course, be more frequent. Based on typical eastern summertime diurnal cycles in humidity and light scattering (e.g., Ferman et al. 1981), the occurrence of morning visibilities (6-8 a.m.) less than 3-5 miles would be somewhat greater than for midday visibility, even discounting naturally occurring fog.

Compared with other modes of transport, air travel is generally considered to be safe. It is not, however, riskfree; based on reasonable expectations and the available record, air pollution visibility impairment would tend to increase risks of aircraft operation (U.S. Senate 1963). Failure to see and avoid objects and obstructions during flight is one of the ten most frequent cause factors for general aviation accidents (FAA 1978). Another important cause factor is continued VFR flying into adverse weather. Although such action is normally attributed to errors in judgment (FAA 1978), in some cases, pilots who by choice or necessity fly in the mixing layer, could fail to distinguish storm fronts or thunderclouds from the prevailing haze until they are upon the adverse weather. The available data in the criteria document do not, however, permit any quantitative assessment of the risks to commercial and general aviation aircraft operation associated with reduced visibility.

The available information of the effects of visibility on transportation suggests that episodic eastern regional haze tends to curtail substantial segments of general aviation aircraft and slow commercial, military, and other IFR operations on the order of 2-12% of the time during the summer. The extent of any delays varies with airport. Reduced visibility may also tend to increase risks associated with aircraft operations in the mixing layer, but quantitative assessments are not available.

5.2.3 Mechanisms and Quantitative Relationships

The mechanisms by which atmospheric pollutants degrade perceived visibility are reasonably well understood (Friedlander 1977;

Middleton 1952). Visibility impairment is the result of light scattering and absorption by the atmospheric aerosol (particles and gases). The "extinction" or attenuation coefficient (σ_{ext}) is a measure of aerosol optical properties and is the sum of blue sky of Rayleigh scattering by air molecules (σ_{Rg}), absorption by pollutant gases (σ_{ag}), and particle scattering (σ_{sp}) and absorption (σ_{ap}). Visibility is inversely related to total extinction from these sources. Blue sky scattering is relatively constant and is significant only under relatively pristine conditions. Absorption by pollutant gases, notably NO_2, usually contributes only a small amount to total extinction (USEPA 1981). Even brown hazes in Denver and Los Angeles formerly attributed solely to NO_2, are often dominated by particles (Groblicki et al. 1980; Husar and White 1976). Thus atmospheric extinction and visibility impairment are normally controlled by particulate matter. Important causes include natural sources (e.g., fog, dust, forest fires, sea spray and biologic sources) and anthropogenic sources of sulphur oxide, soot and other particles, nitrogen oxides, and volatile organics (USEPA 1979).

Reduction of visual range by particle extinction is normally dominated by fine particles.[a] The only important exceptions are some naturally occurring phenomena including precipitation, fog, and dust storms, where larger particles control visibility. Theoretical calculations show that extinction/unit mass efficiencies are substantially greater for fine particles in the 0.1 to 2.0 size range than for larger particles (Faxvog and Roessler 1978). For most commonly observed size distributions of particulate matter, the increased extinction efficiency of fine particles results in fine particles accounting for most of total extinction even though they are only a third or so of the total mass of particles (Latimer et al. 1978). This theoretical expectation is borne out by the unique experiment of Patterson and Wagman (1977) where independent measurement of light scattering and particle size distributions verified the importance of fine articles in controlling scattering in New York City. In addition, a number of experiments have found consistently high correlation (0.8 to 0.98) between light scattering and fine mass (USEPA 1981).

The relative importance of scattering and absorption as well as the extinction efficiency per unit equilibrated mass (γ) of fine particles varies with location. On large regional scales, about 80-95% of particle extinction is due to light scattering (Waggoner et al. 1980; Wolff et al. 1980), with the remainder due to absorption. In urban areas absorption may account for up to 50% of particle extinction (Waggoner et al. 1980; Weiss et al. 1978). The particle scattering efficiency/unit mass varies from about 3-5 m^2/g at various sites, with higher values tending to occur in eastern locations (USEPA 1981).

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[a] For purposes of this document, fine particles include those smaller than 2.5 μm AED.

The variations in fine particle extinction noted above are due largely to variations in size, chemical composition and to some extent, relative humidity. Based on theoretical (Faxvog and Roessler 1978) and empirical (e.g., Groblicki et al. 1980; Stevens et al. 1980; Trijonis et al. 1978 a,b) results, two components, hygroscopic sulphates and elemental carbon, generally tend to be most significant. Sulphate, with associated ammonium, and hydrogen ions and water, often dominates regional fine mass and extinction, particularly in the East, while elemental carbon accounts for most of the particle absorption observed in urban areas. The relative importance of sulphates to extinction depends on relative humidity, both at the site in question and perhaps along the transport path where secondary formation occurs. Project VISTTA found that sulphates formed in dry desert air were of relatively low light scattering efficiency, compared to sulphates apparently formed in more humid conditions in southern California and transported to the desert (Macias et al. 1980). Our understanding of the role of fine organics and nitrates in light scattering is hindered by the lack of reliable data. In the eastern regional haze these components are likely to amount to less than half of the sulphate component, but may dominate scattering in western urban areas such as Denver and Portland (Cooper and Watson 1979; Groblicki et al. 1980). The remainder of fine mass (soil-related elements, lead and trace species) contributes only a minor amount to extinction in most U.S. atmospheres (Stevens et al. 1978).

Humidity is important to visibility because of the presence of fine hygroscopic aerosols (e.g., sulphates) which tend to absorb atmospheric water and thus increase light scattering. Measurements in several areas suggest that the extinction due to fine particle scattering will increase by a factor of about two as relative humidity is increased from 70% to 90% (Covert et al. 1980). Based on laboratory studies, reduction in humidity from 90% to 70% might not produce corresponding decreases in scattering because of hysteresis (Tang 1980). In essence, the hysteresis effect means that the aerosol may tend to retain water absorbed at higher humidities even at lower relative humidities. This effect has not yet been demonstrated to occur in the ambient air.

Through the Koschmieder equation, the extinction coefficient, measured or estimated from fine particle levels, may be used to estimate visual range (USEPA 1979). The relationship has the general form:

$$V = \frac{K}{\sigma_{ext}} \qquad (1)$$

Where: V = the visual range, the distance at which a large black object is just visible against the sky.

σ_{ext} = total extinction, the sum of light scattering and absorption by air molecules, fine particles, and NO_2.

K = a function of the intrinsic target brightness and observer threshold contrast (E). E is a function of the observer and of target size.

Although a number of factors may limit the applicability of this relationship, for homogeneous pollution, reliable extinction measurements, uniform illumination, large dark targets, and moderate visual ranges, agreement between experiment and theory is rather good. The correlation between visual range and the scattering portion of extinction is typically on the order of 0.9 where comparisons have been made (USEPA 1981).

This relationship depends, in part, on human perception of contrast as well as target size and brightness. For a typical observer with a reasonable time for observation and large black targets, a "threshold" of 0.02 is commonly assumed with K = 3.9 (USEPA 1979, 1981). Empirical determinations of K have yielded somewhat lower values, ranging from 1.7 to 3.6 for studies discussed in the EPA criteria document (USEPA 1981). The most complete analysis (Ferman et al. 1981) reported a value of 3.5 for well mixed periods. The lower values likely arise from higher threshold contrasts, nonideal targets, (too bright and/or too small), and the exclusion of absorption estimates. The available data also suggest that reported airport visibilities may significantly underestimate standard visual range. Thus lower values of K may be more appropriate for matching airport data with higher values for observations in natural setting.

The relationship between extinction due to dry particle scattering and fine mass is sufficiently stable over a wide range of areas that reasonably quantitative estimates of fine/particle visibility relationships can be made where long-term relative humidity is low (<70%) and particle absorption is small or otherwise known. For such purposes, the Koschmieder relationship can be written as:

$$V = \frac{K}{\sigma_{ag} + \sigma_{Rg} + \text{FMC}} \qquad (2)$$

Where FMC = fine mass concentration, and

$\gamma = (\sigma_{ap} + \sigma_{sp})/FMC$

σ_{ap} = particle absorption coefficient (in units of inverse distance; e.g., km^{-1})

σ_{sp} = particle scattering coefficient

σ_{Rg} = Rayleigh or "blue sky scattering" ($Rg \simeq 0.12\ km^{-1}$)

σ_{ag} = absorption by gases (usually small in nonurban areas)

Thus, with appropriate K and γ derived from available studies, visual range can be estimated from fine mass. Although less certain, the measurements of Covert et al. (1980) and regression relationships developed by a number of investigators can be used to estimate fine particle/visibility relationships for higher humidities and hygroscopic aerosols. The criteria document indicates that to correct for the humidity effect (as determined by heated nepholometers and equilibrated filters), the amount should be increased by a factor of about 1.5 at 80% RH, and about 2 at 90% RH. The Koschmieder relationship strictly applies for short-term observations. In estimating long-term (e.g., annual) average visibility from long-term fine mass data, the temporal distribution of fine particle concentrations (e.g., lognormal) must be specified, or median values used.

Figure 5-5 presents fine particle/visual range relationships for three cases selected as representative of the range of normal situations encountered in the eastern North American regional haze and in western urban areas:

1. $\gamma = 3\ m^2/g$; representative of a dry aerosol, (USEPA 1981) at $\leq 50\%_2$RH. Absorption may be 10% of extinction where σ_{sp}/unit mass = $2.7\ m^2/g$. This is close to typical measurements in western areas but below most eastern data (USEPA 1981).

2. $\gamma = 6\ m^2/g$; representative of the same aerosol as in 1) at 90% humidity, σ_{sp} increased by a factor of 2.

3. $\gamma = 10\ m^2/g$; representative of the similar aerosol, but with absorption accounting for 40% of extinction. Such high absorption (predominantly associated with carbon) is likely only in urban areas.

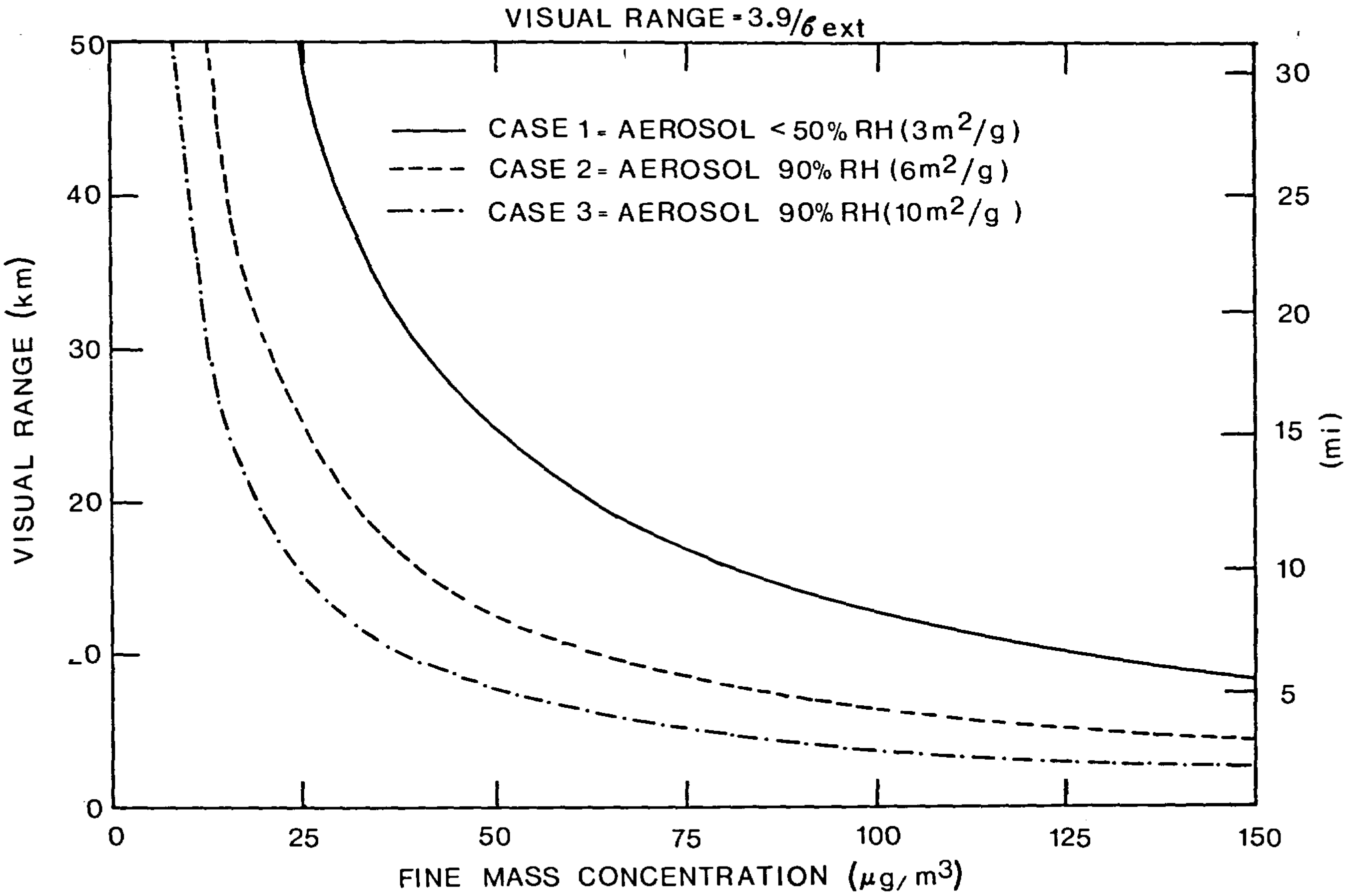


Figure 5-5. Visual range as a function of fine mass concentration (determined from equilibrated filter) and γ, assuming the "standard" K = 3.9. Because K is commonly lower in nonideal application, results from this relationship should not be compared directly to airport visibility data.

Each case may actually be representative of a variety of aerosols. For example, case 2 closely approximates the aerosol observed by Ferman et al. (1981) during their month long study in the Blue Ridge Mountains, even though typical daytime humidities were less than 70%. In this study corrected $\gamma = 5.5\ m^2/g$ as measured by heated nephelometer and when the measured effect of condensed water is added, γ increases. Thus, even though 90% RH is comparatively rare during the daylight hours, case 2 is likely to be closer to typical summertime eastern conditions than is case 1.

Figure 5-5 shows the powerful effect of humidity and carbon absorption on visual range for a given particle level. The curves also indicate that visibility becomes more sensitive to changes to fine particle levels below about $100\text{-}200\,\mu g/m^3$. Results from this figure should not be compared directly with airport visibility data. Due to non-ideal targets and observation conditions, airport visibilities will tend to be lower than predicted by the Koschmieder relationship with $K = 3.9$.

When background fine particle concentrations are understood, the Koschmieder equation can be used to relate predicted sulphate levels to resulting visual range. Available nonurban summertime fine particle data are summarized in Figure 5-6. Actual impacts must be derived from the results of regional modelling runs provided by Workgroup II. If the results of the model are to be "tuned" to airport visibility data, K in the Koschmieder equation should be 2.9 - 3.5 and γ for eastern conditions should be $6\text{-}8\ m^2/g$.

5.2.4 Sensitive Areas and Populations

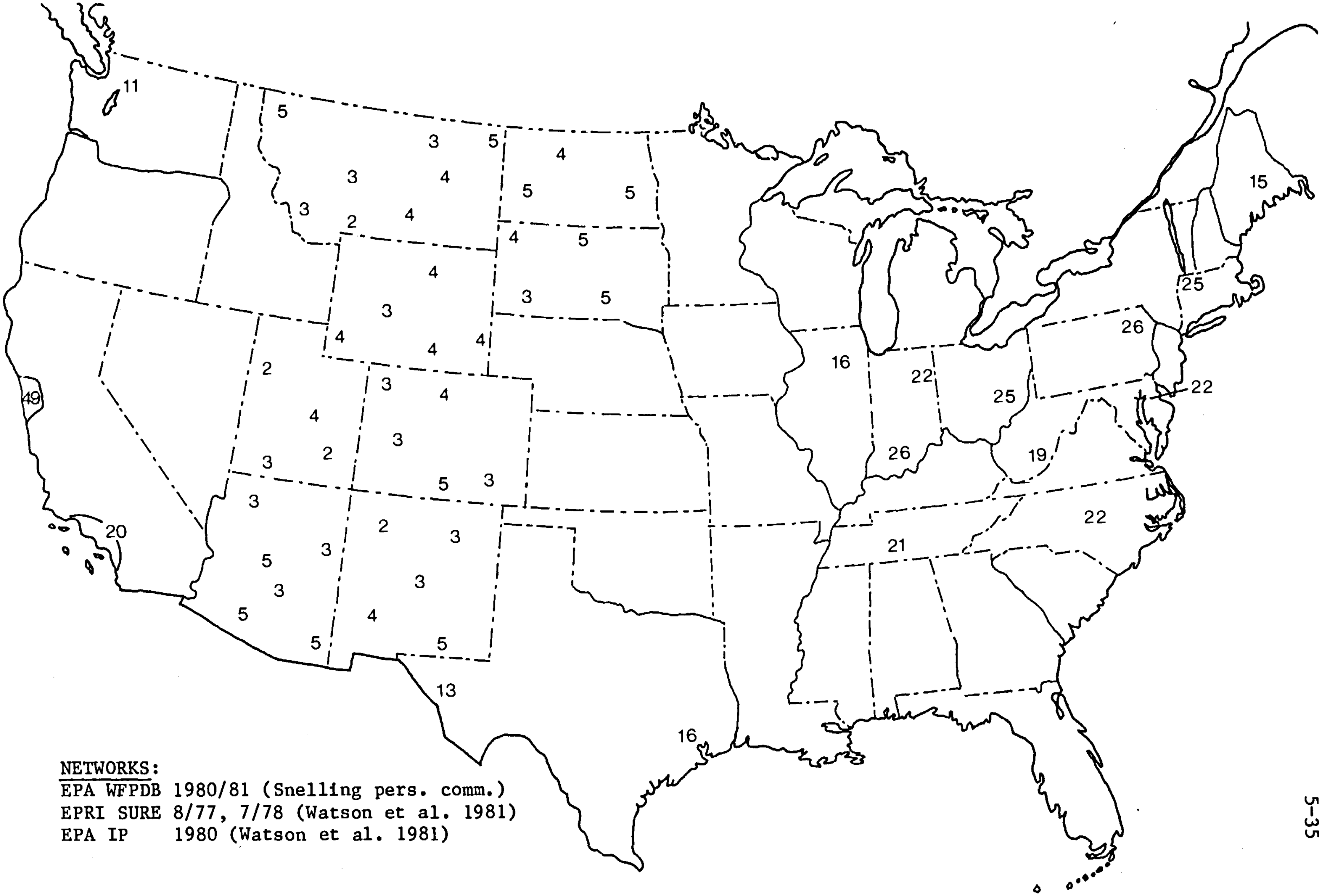
Clean areas such as found in western North America, are the most sensitive to visibility degradation. In the U.S., the Clean Air Act affords special protection to visibility in 156 'Class I' areas, including national parks and wilderness areas. Many of these Class I areas are located near the U.S./Canada 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.

5.2.5 Data needs/Research Requirements

The following instruments are required to complete work related to the effects of atmospheric deposition on visibility:

1. Analyses of the contribution of transported air pollution to visibility impairment by the modeling work groups.

2. Further work on the value of visibility in the Eastern North American context.



NETWORKS:
EPA WFPDB 1980/81 (Snelling pers. comm.)
EPRI SURE 8/77, 7/78 (Watson et al. 1981)
EPA IP 1980 (Watson et al. 1981)

Figure 5-6. Summertime fine particle levels ($\mu g/m^3$) for nonurban sites.

3. Continued analysis of regional North American visibility data to further elucidate reliability of data and implications for anthropogenic contribution.

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SECTION 6

EFFECTS ON MAN MADE STRUCTURES

SECTION 6

EFFECTS ON MAN-MADE STRUCTURES

6.1 INTRODUCTION

Previous sections of this report have focused primarily upon the effects of pollutants on sensitive receptors in remote wilderness areas. In this section, the receptors (i.e., man-made structures) are usually co-located with the pollution sources. The distinction between the effects of pollutants from near or intermediate sources (i.e., 10's to perhaps 100 km away) and from distant sources (i.e., 100's to perhaps 1000's of kilometres away) is difficult if not impossible to make. This is particularly the case when local primary species, SO_2 for example, oxidize to secondary products (SO_4^{2-}) at a nearby site which is also receiving SO_4^{2-} from distant sources of primary SO_2 which has oxidized during its atmospheric residence time. In most cases, the atmospheric load from local sources tends to dominate the low concentrations arriving from remote sources upwind.

In the context of material deterioration, the distinction between local and distant sources may be academic since damage in general would be reduced through a reduction in concentration of the major agents, regardless of the distance these pollutants traveled to the deposition site.

Consideration of damage will be limited to exterior surfaces, not only because the wet deposition of pollutants and surface wetting is primarily limited to exterior surfaces, but also because the concentrations of corrosive species are usually much higher outside than inside buildings. Textiles and fabrics are usually associated with confined environments and are beyond the scope of this section.

Although the economic consequences of material deterioration due to air pollution are discussed elsewhere in this report (see Section 8.5), this section contains a brief description of some of the attempts which have been made to quantify damage in economic terms and the inadequacies of these assessments. For sulphur dioxide, perhaps the most important corrosive agent, direct costs of duplication, replacement or protection of certain materials can be approximated. Before the economic implications can be adequately addressed, a better understanding is needed of the dose-response relationships of materials to different pollutants, of the distribution of materials, and of the replacement and maintenance factors.

In this section, there is discussion of the effects of four types of pollutants; SO_2, NO_2 and O_3, NH_3, and particulates on four classes of materials; metals and alloys, coatings, masonry, and elastomers.

There are several quantitative examples of calculated erosion and corrosion of materials over time.

6.2 OVERVIEW

All building materials degrade to some extent with time, even in the absence of air pollution. Hence, it is important to differentiate between expected weathering, and accelerated deterioration attributable to air pollutants. There are reviews available of the weather factors affecting the corrosion of metals (Ashton and Sereda 1981; Sereda 1974) and the durability of stone (Julien 1884), concrete (Maslow 1974), and polymers (Eurin 1981). In northern climates, deterioration effects due to atmospheric pollution may be masked in winter by the impact of road deicing salts ($CaCl_2$ and/or NaCl), which damage porous masonry and are particularly corrosive to metals. As noted above, the assessment of deterioration, due to pollutants transported over long distances, is confounded by the impact of pollution produced locally.

The apparent chemical/physical degradation processes resulting from interactions of materials with pollutants and naturally occurring atmospheric constituents have been reviewed in the literature (Benarie 1980; USEPA 1978, 1981a,b; Yocom et al. 1982). A number of field studies estimate the relationship between deterioration and atmospheric deposition without full environmental characterization of the test sites, including measurement of meteorological and air quality variables. Laboratory tests have also been used to quantify materials damage from pollutants. However, quantitative relationships derived from chamber tests cannot be used directly to predict damage to exposed materials.

At the outset it must be acknowledged that the objective assessment of the response of materials to corrosive agents cannot provide adequate estimates of "loss" resulting from deterioration of historic materials. Monuments must be distinguished from other structures because here the net loss by deterioration embraces aesthetic and historical contributions where monetary scales may not apply. Trade-offs made in mitigating the impact of air pollutants should address the preservation of the qualities that constitute the significance of the monument.

The architectural and sculptural expressions of our two heritages are a precious nonrenewable resource. 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, there is similar legislation. For example, the Archeological Sites Protection Act was enacted in 1953, the same year the Historic Sites and Monuments Act was adopted.

Studies of the economics of damage due to air pollution are contained in papers by Haynie (1980a), Yocom and Upham (1977), Spence and Haynie (1972), Waddell (1974), Liu and Yu (1976), Yocom et al. (1981), and Yocom et al. (1982) among others. In these instances, dose-response relationships were obtained by relating the concentrations present in the atmosphere to the degree of damage observed or measured. As an example, a report released by the Organization for Economic Cooperation and Development (OECD 1981), indicates that for the eleven European countries studied, based on an expected production of 24.4 million metric tons of SO_2 in 1985, the resulting benefit of a 50% reduction in SO_2 emissions would be of the order of $1.16 billion per year in terms of reduced damage. In this case, the benefit is based on corrosion of a limited number of metals and excludes masonry and coatings since no exact dose-response relationships are available between deposition of sulphur compounds on these materials and deterioration rates. The loss due to the impoverishment of cultural heritage is not assessed. As noted earlier, the more difficult task of relating this damage to human response (i.e., replacement, substitution or protection) has not yet been completed and will be more fully discussed in subsection 6.8.

6.3 MECHANISMS AND ASSESSMENT OF EFFECTS

The quantitative expression of a relationship between exposure to a particular pollutant, and the type and extent of the associated damage to a specific material is known as a dose-response relationship or a damage function (Hershaft 1976). The damage function should express a quantitative cause-to-effect link (Benarie 1980). A significant mathematical correlation between a measured damage and an ambient pollutant concentration is not sufficient proof of a causal relationship. Because a particular kind of damage may also occur in the absence of the pollutant(s), the damage function should explicitly describe the incremental effect attributable to the pollutant(s). Moreover, in some cases for metals, a certain minimum dose or threshold value is required before an effect is observable and at high doses a saturation level may also be observed.

6.3.1 Factors Influencing Deposition

The relation between concentration of pollutants in ambient air and in precipitation and the amount of pollutant delivered to a material surface is known as the deposition velocity. Deposition is a two-step phenomenon beginning with delivery of the pollutant to the surface controlled by aerodynamics and followed by pollutant - material interaction. Gaseous deposition velocities can be as rapid as 0.021 - 0.6 m/min (Judeikis 1979). However, large variations are found in measured deposition velocities (McMahon and Denison 1979). This scatter is in part due to intrinsic properties of materials and in part due to extrinsic factors (e.g., surface moisture, wind speed and temperature).

Acidic deposition can occur on materials under both wet and dry conditions. Under wet conditions, the aqueous form of the pollutant, (e.g., sulphuric acid) reacts with the material in question to form reaction products. These products may be either more or less soluble than the original material. The detailed kinetics of these reactions are not well known and variations in reactions may occur due to the surface conditions of the material and the presence of additional chemical species.

Deposition may also occur under dry conditions. In theory, a gaseous pollutant such as SO_2 or NO_x can react directly with metals and masonry without going through an aqueous phase (Torraca 1981a; Van Houte et al. 1981). As a practical matter, the reactions in the environment always involve the presence of humidity. Consequently, reaction rates have not been studied under completely dry conditions (Haynie and Upham 1974; Judeikis and Stewart 1976; Spedding 1969). It is assumed that dry deposition reactions do in fact involve an intermediate stage where the gaseous pollutants are oxidized in the presence of available surface moisture and proceed to attack the materials in aqueous form. The major distinction between this kind of deposition and what is termed wet deposition is that in the latter the moisture involved comes only from precipitation. Dry deposition involves all sources of moisture other than precipitation.

These other sources of moisture include surface condensation, which occurs under certain conditions of relative humidity, dew point, and surface temperature. There may also be internal condensation arising when warm, humidified indoor air attains the dew point within a cooler masonry wall (ICOMOS 1967; Torraca 1981a; Winkler 1975). Groundwater wicked up through masonry walls by capillary action is another source for moisture in masonry walls (Melville and Gordon 1973). Porous materials (e.g., stone, brick and concrete) may retain significant amounts of moisture in the pores even during prolonged spells of dry weather.

Surface moisture has a strong influence on deposition velocities. It has also been suggested that the rate-limiting step for deposition of pollutants may be the atmospheric transport processes that controls the delivery of gases through the quasi-laminar boundary at the surface (Hicks 1981). These transport processes would increase with increased local wind speed (Lawrence 1962).

Particulate matter on the surface can also affect the deposition velocity. Hygroscopic particulates like marine salt tend to increase the time the surface is wet (Fassina 1978). Elements commonly found in particulates (e.g., iron, manganese, and copper) have been identified as serving as catalysts in the oxidation of SO_2 to SO_4^{2-} (Hegg and Hobbs 1978).

The condition of the surface itself will also influence the deposition velocity. A material that has been exposed for a significant amount of time may show a deposition velocity different from the initial one (Judeikis 1979). In the case of most metals, iron being the notable exception, a tight layer of reaction products (e.g., oxides, carbonates and chlorides) will form on the surface giving some degree of protection. In stone, however, the coating of reaction products remains porous and the rate of attack does not decrease (Van Houte et al. 1981). In fact, it may increase as the effective surface increases (Judeikis and Stewart 1976) or as the greater roughness increases the atmospheric transport processes (Hicks 1981).

Exposure specifications such as the siting of a structure or a material's position in a structure must also be considered. The most important condition is the exposure of the material to rain. In addition to providing an aqueous medium for acidic attack, the runoff of rain water serves as a major agent in the dissolution and removal of weathering products. For example, it has been observed on the Acropolis in Athens and at the Field Museum in Chicago that the marble has reacted with SO_2 to form an even layer of calcium sulphate. This layer several centimetres thick remains intact on some surfaces that are not washed by rain while on other parts of the structure washed by rain, the layer does not exist (Gauri 1979; Skoulikidis et al. 1976).

The rate of deposition will increase with increased wind speed. Although primarily determined by the prevailing climate at the location, the wind speed at a given point on a surface can be influenced by the orientation of the structure, architectural details, and by other buildings in the vicinity (BRS 1970; Kotake and Sano 1981; Lacy 1971). For example, wind speeds around a building will vary with height and increase at corners and over cornices (Lacy 1971). The corrosion rates for galvanized wire and fencing are almost double that of galvanized sheet, indicating the influence of the geometry of a material on wind speed (Haynie 1980b). Erosion of materials by wind-borne abrasive particulates may also be significant at some locations. Finally, wind will cause rain to fall on a slant rather than perpendicularly to the ground. Thus it will drive rainfall onto vertical surfaces that otherwise would remain dry (Marsh 1977).

Finally, the conditions of thermal exposure will vary around a structure. This occurs depending on compass orientation, angle from vertical, and shading. Each part of the structure will receive differing amounts of solar radiation, thus will show differing ranges in diurnal temperature cycles. Temperature cycles are also a function of each material's thermal response characteristics. Man-made sources of heat, either within a building or from nearby sources will also modify the local thermal environment. Ranges in thermal conditions influence the atmospheric transport processes, as well as moisture content of material surfaces and thus, deposition velocities.

6.3.2 Effect of Sulphur Dioxide Pollutant/Material Interactions

There is general agreement in the literature 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 1981; Yocom and Upham 1977).

6.3.2.1 Zinc

The specific SO_2 reactions that cause metal corrosion are not fully understood. Some of the possible mechanisms involved have been discussed (Benarie 1980; USEPA 1981a). For the relatively simple case of zinc, the overall reaction is

$$SO_2 + O_2 + Zn \rightleftharpoons ZnSO_4$$

Since $ZnSO_4$ is soluble and readily lost from surfaces exposed to rain, a protective surface film is not formed. In cases where the SO_2 is converted to acidic sulphate prior to reaction with the zinc, the expected reaction would also result in the same soluble zinc species

$$H_2SO_4 + Zn \rightleftharpoons ZnSO_4 + H_2(gas)$$

Since the corrosion rate for zinc is high for solutions having a pH less than about 5 (Pourbaix 1966), many acidic species are expected to cause the corrosion of zinc. For the case of precipitation, it should be noted that the annual average pH for most of eastern North America is below 5 (see Figure 2-4).

In a recent publication (Haynie 1980b), data from six different studies for the atmospheric corrosion of zinc were reevaluated with respect to the following relationship:

$$C_z = AT_w + BT_wSO_2 \qquad (1)$$

where C_z = zinc corrosion in micrometres
T_w = time of wetness in years
SO_2 = average concentration of SO_2 in $\mu g/m^3$
A and B = regression coefficients.

The results of the coefficients evaluation (Haynie 1980b) are shown in Table 6-1.

As is typical for many atmospheric corrosion tests, intercomparisons between studies are subject to many problems due to differences in test objectives, techniques, and available environmental monitoring. In the studies examined by Haynie (1980b), the time of wetness was calculated in one of three ways: (1) by using the average relative humidity employing a previously evaluated empirical equation (Cavender et al. 1971; Haynie et al. 1976); (2) by using the total time the relative humidity exceeded 85% (Haynie et al. 1976) or 90% (Mansfeld 1980); and (3) by using a "dew-detector" (Guttman 1968; Guttman and Sereda 1968). The average concentration of SO_2 was determined by using continuous instruments (Haynie et al. 1976; Haynie and Upham 1970; Mansfeld 1980) using lead peroxide techniques (Cavender et al. 1971; Guttman and Sereda 1968) or both (Guttman 1968). In spite of the experimental differences, it is apparent that SO_2 is an important cause of degradation of zinc. The B coefficient is lower for the chamber study than for the field-determined values (Haynie et al. 1976). While this difference was attributed (Haynie 1980b) to a lower gas velocity in the chamber compared to the field studies, it has been suggested (Yocom et al. 1982) that the higher values reported for the field studies may be the result of the combined effect of SO_2 and particulate matter containing sulphates, chlorides, nitrates and other anions. The low B coefficient determined in the St. Louis study (Mansfeld 1980) may also indicate that lower particulate levels result in lower SO_2 corrosion rates. The tacit assumption being made here is that during the test period the particulate levels in St. Louis were low.

Haynie (1980b,c) has demonstrated that the average wind speed has an important influence on the SO_2 deposition velocity and, hence, the corresponding corrosion rates for zinc. Also, the deposition velocity has also been shown to be dependent on geometry. For example, the corrosion rate for galvanized wire and fencing has been shown (Haynie 1980b) to be approximately twice that of galvanized sheet exposed to the same environment. Since the lead peroxide method was used to determine total sulphur (as SO_2) in two of the studies (i.e., Cavender et al. 1971 and Guttman and Sereda 1968 as shown in Table 6-1), those values would be expected to be wind-velocity dependent (Lynch et al. 1978). In contrast, the SO_2 values measured by continuous instruments should be independent of wind velocity. The possibility that this wind-dependence affected the SO_2 coefficients should be considered before such data are used for any damage function calculations.

6.3.2.2 Steels

A number of atmospheric exposure studies have been conducted for steels (see reviews cited at beginning of Section 6.2). Only a few

Table 6-1. EXPERIMENTAL REGRESSION COEFFICIENTS WITH ESTIMATED STANDARD DEVIATIONS FOR SMALL ZINC AND GALVANIZED STEEL SPECIMENS OBTAINED FROM SIX EXPOSURE STUDIES

Reference	A μm/year	B μm/(g/m^3)year	Number of Data Sets
Cavender et al. (1971)	1.05 ± 0.96	0.073 ± 0.007	173
Guttman (1968)	1.79	0.024	large
Guttman and Sereda (1968)	2.47 ± 0.86	0.027 ± 0.008	136
Haynie et al. (1976)	1.53 ± 0.39	0.018 ± 0.002	96
Haynie and Upham (1970)	1.15 ± 0.60	0.081 ± 0.005	37
Mansfeld (1980)	2.36 ± 0.13	0.022 ± 0.004	156

studies have been conducted where simultaneous air quality and deposition measurements have been made. In general the corrosion rate for uncoated low-carbon steels has been found to depend on SO_2 concentration and exposure time. For example, in one study (Haynie and Upham 1971) the following relationship was developed

$$C_s = 9.013\ [e^{0.00161\ SO_2}][(4.768t)^{0.7512} - 0.00582\ OX] \quad (2)$$

where C_s = corrosion in micrometres
t = exposure in years
SO_2 = average concentration of SO_2 in $\mu g/m^3$
OX = total oxidants in $\mu g/m^3$ (see discussion of ozone below).

In this study, similar expressions were developed for a weathering steel. Although humidity effects were not determined, the humidity was approximately the same at all the sites used. In another study, Haynie and Upham (1974) reported a similar functional dependence

$$C_s = 325\ t^{1/2} \exp[0.00275\ SO_2 - \frac{163.2}{RH}] \quad (3)$$

where RH is the relative humidity. In this case, oxidants were not measured. Equations 2 and 3 both indicate that the corrosion rate increases with SO_2 concentration but decreases with exposure time. Equation 3 predicts very low corrosion rates for low humidity, regardless of the SO_2 level. However, at high humidity the steel would corrode even in the absence of SO_2. Although equations 2 and 3 may give a correct description of the interaction of SO_2 with low carbon steels, they have little relevance, since virtually no steels of this type are unprotected in the environment. However, studies of this material have proven useful in estimating the relative corrosivities of various exposure sites. Even in the case where a painted steel begins to rust, equations 2 and 3 probably do not accurately describe the corrosion occurring.

For a weathering steel, a material normally left uncoated, Haynie and Upham (1974) reported a relationship of the form shown in equation 2, with a lower SO_2 coefficient and a slightly different time dependence. On the other hand, studies by Copson (1945), Cramer et al. (1980), and Suzuki et al. (1980), found that sulphur incorporated into the film improved the corrosion resistance for a weathering steel, and that this sulphur could be related to the average SO_2 level in the local environment. The amount of copper and tin in the steel has been shown to influence its corrosion resistance in sulphur containing atmospheres (Cramer et al. 1980).

6.3.2.3 Copper and Copper Alloys

Copper and its alloys are among the most durable materials for exterior exposure because they form protective patinas. The pH value of precipitation is probably a significant factor determining the development of basic carbonates and/or oxide protective patina (Guttman and Sereda 1968; Mattsson and Holm 1968). Below pH of about 4, the protective coating may be rapidly dissolved exposing the bare metal (Allaino-Rossetti and Marabelli 1976; Gettens 1964; Pourbaix 1966). It is noteworthy that the mean annual pH of precipitation is near 4 in portions of northeastern United States, southern Ontario and Quebec (Figure 2-4). The presence of SO_2 in the atmosphere appears to accelerate the formation of the green patina (Mattsson and Holm 1968), normally desired on architectural copper surfaces. Analysis of the patina of the Statue of Liberty, for example, indicates that it is predominately copper sulphate, with less than 1% of copper carbonate and copper chloride (Osborn 1963). Exposure tests indicate that the most uniform patina forms on unalloyed copper. The presence of alloying elements, primarily tin and zinc for bronze and brass, respectively, interferes with patina formation and thus lowers corrosion resistance of the alloy (Scholes and Jacob 1970; Walker 1980).

6.3.2.4 Aluminum

There are no quantified damage functions reported for aluminum, although some evidence exists for both SO_2-induced damage (Benarie 1980) and for particulate-assisted SO_2 pitting damage (USEPA 1981a). Sulphur dioxide may also play a role in stress-assisted corrosion problems for aluminum (Gerhard and Haynie 1974; Haynie et al. 1976).

Several relatively new aluminum and aluminum-zinc coated steels have become available commercially in the past few years. While no damage functions have been reported, these coatings have been shown to offer superior performance to galvanized steels, with improvement in service life by a factor of from two to four times in marine, rural and industrial environments (Zoccola et al. 1978). These coatings will have a great influence on future materials selection and on estimates of future damage cost related to coated steels.

6.3.2.5 Paints

A few investigations, which have been reviewed in several recently published documents, have studied the effects of gaseous pollutants on the performance of exterior coatings (USEPA 1981a; Yocom et al. 1982). Several of these studies have shown that SO_2 can penetrate into the paint film (Svoboda et al. 1973; Walsh et al. 1977). Holbrow (1962) found sulphites and sulphates to be present after the absorption of SO_2 by the paint film. In more recent studies, the high erosion rate observed for oil base house paints was associated with the loss of calcium carbonate, an extender pigment of the paint. These controlled studies involved the exposure of several types of paints to atmospheric pollutants under a prescribed dew-light cycle (Campbell et al. 1974; Spence et al. 1975).

A clear mechanism for the deterioration of coatings by wet or dry pollutant deposition cannot be derived from these investigations. However, it is apparent that moisture on the painted surfaces plays an important role by collecting pollutants, especially SO_2, and thereby forming an acidic aqueous media that facilitates reaction with the paint film.

The study of Spence et al. (1975) is the only investigation for which pollutant dose-response relationships have been derived. Linear regression relationships were developed for two types of coatings:

Oil Base $E = 14.3 + 0.0151\ SO_2 + 0.388\ RH \quad (4)$

Vinyl Coil $E = 2.51 + 1.60 \cdot 10^{-5} \times RH \times SO_2 \quad (5)$

where E = erosion rate in μm/yr

SO_2 = average concentration of SO_2 in μg/m^3

RH = relative humidity in percent.

The oil base household paint was found to have a higher erosion rate which was strongly correlated with the concentration of SO_2 and relative humidity. However, the rate is more sensitive to changes in the humidity than SO_2. For the vinyl coating, the SO_2 effect is statistically significant but contributes less than 5% to the film erosion rates at ambient levels of concentration. These functions were obtained under controlled conditions of simulated sunlight and high temperatures and should not be applied directly to ambient conditions.

Table 6-2 provides examples of material loss in one year due to a range of sulphur dioxide concentrations and specific values of the other variables contained in equations 1 to 5. The table is intended to provide an indication of corrosion rates for a range of conditions which might be encountered at sites throughout North America.

6.3.2.6 Elastomers

A chamber study has been conducted in which samples of auto sidewall tires were exposed to two levels (0.1 and 1.0 ppm) of O_3, SO_2 and NO_2. The tires were not found to be affected by SO_2 (Haynie et al. 1976). Observations of SO_2 damage to elastomeric materials have not been reported (USEPA 1981a).

6.3.2.7 Masonry

Masonry materials are porous inorganic substances including stone and man-made composites such as brick, terra cotta, concrete,

TABLE 6-2. EXAMPLES OF MATERIAL LOSS IN ONE YEAR, L IN µm USING EQUATIONS 1 TO 5 AND TYPICAL AMBIENT VALUES.

(A) Zinc	$L_z = 1.79\ Tw + 0.024\ TwSO_2$	(Eq. 1)
(B) Steel (Low carbon)	$L_{sl} = 9.013\ EXP[0.0016\ SO_2]\ [4.768^{0.7512-0.005820X}]$	(Eq. 2)
(C) Steel (Weathering)	$L_{sw} = 325 + \frac{1}{2}\ EXP[0.00275\ SO_2 - \frac{163.2}{RH}]$	(Eq. 3)
(D) Paint (Oil base)	$L_{po} = 14.3 + 0.0151\ SO_2 + 0.388\ RH$	(Eq. 4)
(E) Paint (Vinyl)	$L_{pv} = 2.51 + 1.60\ 10^{-5} \times RH \times SO_2$	(Eq. 5)

		SO_2 µg/m^3 [a]			
		10	25	40	55
(A)[b]	Tw = 0.05	0.102	0.120	0.138	0.156
	= 0.1	0.203	0.239	0.275	0.311
	= 0.2	0.406	0.478	0.550	0.622
(B)[c]	OX = 0.05	27.84	28.52	29.22	29.93
	= 0.50	27.72	28.40	29.10	29.81
	= 1.00	27.60	28.27	28.96	29.67
(C)[d]	RH = 40	5.65	5.89	6.14	6.39
	= 60	22.01	22.93	23.90	24.91
	= 80	43.44	45.27	47.17	49.16
(D)[e]	RH = 40	29.97	30.20	30.42	30.65
	= 60	37.73	37.97	38.18	38.41
	= 80	45.49	45.72	45.94	46.17
(E)[f]	RH = 40	2.516	2.526	2.536	2.545
	= 60	2.520	2.534	2.548	2.563
	= 80	2.523	2.542	2.561	2.580

[a] SO_2 concentrations are highly variable within urban areas but normally lie within the range 10 to 50 $\mu g/m_3$ depending on city size and industrial activity.

[b] The coefficients 1.79 and 0.024 are used for illustration purposes and lie within the ranges given in Table 6-1. Note the high degree of dependence on wetness as well as SO_2 concentration. Wetness values are approximation for south central (0.05), central (0.1) and coastal (0.2) sites in North America.

[c] The function depends upon SO_2 concentrations, as stated in the text above, but appears to be not strongly dependent on OX. In this example OX is taken to mean O_3 with values given being representative of concentrations in clear air (0.05), smoggy air (0.5) and episodes (1.00).

[d] The values cited are for the first year of exposure. Relative Humidity values represent south central, central and coastal sites. This damage function is strongly dependent on RH. In addition, material loss is well correlated with SO_2 concentration. Note the much lower loss of zinc (A) compared with weathering steel (C).

[e] The erosion of oil-base paint is strongly dependent on relative humidity and much less dependent on SO_2 concentration.

[f] As noted in the text, the deterioration of vinyl paints is not strongly dependent on SO_2.

mortar, stucco, and adobe. Degradation of these materials in the atmosphere involves disruption of the interlocked mineral components through chemical and mechanical processes. Mechanical degradation disrupts the physical structure, through differential thermal expansion, freeze/thaw, salt crystallization, hydration, and migration, or by intrusion of root fibriles into the masonry matrix (Torraca 1981a; Winkler 1978). Chemical processes are those where ions react with the material and alter the mineral composition to form weathering products. If less soluble than the original material, the weathering products will remain as crusts or discolorations on the masonry surface. Soluble weathering products will be washed away with sufficient rain water flow, eroding the material surface. In the absence of runoff, the soluble salts may be transported into the body of the masonry, and there trigger mechanical weathering effects such as subflorescence and spalling.

Degradation rates depend not only on the chemical composition of the mineral composite, but also on grain size and porosity of the matrix (Jakucs 1977). These factors vary not only between general classes of masonry materials, but also from quarry to quarry, from concrete mix to concrete mix. Masonry materials of varying composition, or varying in grain size and porosity, will not exhibit similar degradation rates. Additionally, homogeneity of mineral composition plays a role in the durability of stone building materials. Inclusions and veins of minor constituents (e.g., as feldspars or micas) provide zones of preferential weathering creating microcracks and fissures and exposing interior areas to degradation processes. As such, any dose-response functions will tend to be material specific making generalizations difficult.

Commonly used masonry materials are primarily composed of carbonates or silicates. Silicates are generally more resistant to dissolution by atmospheric acids than carbonates (Loughnan 1969; Winkler 1975). Work on the interaction of SO_x and masonry material has been directed towards describing the processes and end products qualitatively (see Stambolov and van Asperen de Boer 1976 for references) and towards estimating deposition velocities (Braun and Wilson 1970; Judeikis 1979; Spedding 1969). Difficulties arise in determining dose/response relations partly because of the length of time required to produce measurable effects in both field and chamber studies (Trudgill 1977) and partly because of imperfect simulations of real-world cycles of temperature and moisture in chambers studies.

Of the commonly found construction materials, carbonate minerals have been studied more extensively than other minerals. The mechanism of SO_2 attack on calcite, the major mineral constituent of carbonate rocks and cementing materials of some sandstones, may proceed through several mechanisms according to the following equations (Gauri and Holden 1981; Torraca 1981a):

Dry conditions: $CaCO_3 + SO_2 + 1/2\ O_2 \longrightarrow CaSO_4 + CO_2$

with a possible $CaSO_3$ intermediate and

Wet conditions: $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$

Cycles of available moisture allow for conversion of anhydrite to the hydrates; gypsum ($CaSO_4 \cdot 2\ H_2O$) and bassanite ($CaSO_4 \cdot 1/2\ H_2O$). Associated changes in crystal size and pressure are significant factors in mechanical decay processes (Arnold 1976; Stambolov 1976; Winkler 1975). Similar pressures are exerted by hydration of sodium and ammonia sulphates (Torraca 1981a). The presence of these soluble sulphate salts in the subsurface of the masonry can cause spalling of the surface under freeze/thaw conditions.

Calcium sulphate is more soluble than calcium carbonate, although a range of solubilities have been reported for both minerals (Hardie 1967; Jakucs 1977; Keller 1978). In runoff conditions, calcium sulphate will dissolve and the material surface will be eroded. Calcium sulphate may also combine with other deposits (e.g., carbon particles and soot) forming black crusts (Fassina et al. 1976; Weaver 1980).

Debates concerning the contribution of biological weathering to stone deterioration have gone on since the 18th century. Bacteria on the surface of buildings convert sulphur dioxide from the atmosphere into sulphuric acid for use as a digestive fluid (Babick and Stotsky 1978; Winkler 1978). The digestive fluid attacks the calcium carbonate in the limstone, marble, or sandstone, liberates carbon dioxide, the microbe nutrient, and produces calcium sulphate as a by-product. Other studies have claimed that all deterioration can be attributed to chemical and mechanical processes, and that biological aggression is negligible (Fassina 1978; Torraca 1981b).

Several special cases of damage to stone structures subjected to extremely high local levels of pollution are noted in the literature:

1. The effect of air pollution exposure is illustrated by comparing the condition of the Elgin Marbles (removed from the Acropolis at the start of the 19th century) to the sculptures that remained exposed to the atmosphere in Athens. The Elgin marbles, kept indoors at the British Museum, are in much better condition (Skoulikidis et al. 1976), albeit some of the weathering of the exposed sculptures must be attributed to moisture and temperature cycles.

2. Some of the blocks in Cologne Cathedral were put in place in the middle of the 19th century, at the same time that sandstone from the same quarry was used in building Neuschwanstein Castle in Bavaria. The Cologne blocks are significantly more deteriorated than the Neuschwanstein, where the sulphate deposition is lower by a factor of roughly 20 (Luckat 1976).

3. The Ottawa Parliament House shows considerable deterioration caused by sodium sulphates trapped in the stone. The source of the sulphates is presumably a paper mill that operated nearby until 1973 (Stewart et al. 1981; Weaver 1980).

6.3.3 Effect of Nitrogen Dioxide and Ozone Pollutant/Material Interactions

6.3.3.1 Metals

There is little information relating NO_x concentrations to degradation rates of metals and masonry. No damage function for NO_2 on metals is given in USEPA (1981b). Haynie (1980a) assessed corrosion rates of steels exposed to NO_x, SO_2 and O_3 under varying relative humidity, temperature and wind-speed conditions. While no dose-response relation has yet been determined for steels, it was found that oxides of nitrogen (expressed as NO_2) contributed significantly to the corrosion response of zinc/copper sensors used in an "Atmospheric Corrosion Monitor".

A recent study by Byrne and Miller (1980) found that NO_x can influence the corrosion rate of aluminum more than SO_2. However, the author suggests that SO_2 may reduce nitrogen oxides to nitrogen gas in the presence of a catalytic surface (e.g., Al_2O_3). Hence, this process may reduce the potential for damage by NO_x.

Aqueous nitric acid has a more deleterious effect on most metals, than H_2SO_4 or HCl (McLeod and Rogers 1968). In addition, metal nitrate salts tend to be more soluble than the sulphate salts, so that nitrate corrosion products can be readily washed from surfaces, exposing fresh metal to attack. Conversely, sulphate products may remain on the surface to inhibit further corrosion.

The reported effects of ozone on metal corrosion appear to be contradictory. While the previously mentioned study by Haynie and Upham (1971) showed that oxidants correlated with lower steel corrosion rates (equation 2), a chamber study with ozone showed no effect on steel corrosion (Haynie et al. 1976). It has been suggested (Benarie 1980) that the effect observed in the Haynie and Upham (1971) study was either caused by some oxidant other than ozone or was related to another factor that was covariant with ozone (e.g., temperature or humidity).

6.3.3.2 Masonry

Deposition velocities have been measured for NO and NO_2 on some masonry surfaces. The measured deposition velocities for NO_x on cement appeared to be slightly lower than for SO_2. However, differences over time of exposure in the behavior of the gases makes it impossible to give direct comparison (Judeikis and Wren 1978). Since there is no proposed mechanism of ozone effects on masonry deterioration, nor published studies describing such an effect, dose-response relationships are not to be expected.

6.3.3.3 Paints

In a chamber study conducted by Spence et al. (1975), ozone was found to be the most likely factor to affect the erosion rates of acrylic coil coatings. The following dose-response relationship was derived:

$$E = 0.159 + 0.000714\, O_3 \tag{6}$$

where E = erosion rate in μm/yr

O_3 = concentration of O_3 in $\mu g/m^3$

As indicated by the relationship, the effect of ozone on the erosion rate is negligible, even though it was found to be statistically significant.

Vinyl and acrylic coil coatings were not significantly affected by NO_2 at ambient levels.

6.3.3.4 Elastomers

The cracking of rubber products results from the combined effects of ozone and stress on sensitive elastomeric material. Sensitive elastomers contain olefin structures (carbon double bonds) which are susceptible to chemical attack by ozone (Bailey 1958). Natural rubber and certain synthetic elastomers (e.g., styrene-butadiene, polybutadiene, and polyisoprene) contain these chemical structures. The ozone-olefinic reaction can result in chain scissioning as well as cross-linking of the elastomeric material. In the case of chain scissioning, the molecular weight is decreased and a loss of tensile strength of the elastomeric material is observed. When cross-linking occurs, the elastomeric material becomes brittle with a loss of elasticity. If no tensil stress is applied, these elastomers can be exposed to high concentrations of ozone for long periods of time without the formation of cracks. However, when stressed as little as 2 - 3% in extension and exposed to 20 $\mu g/m^3$ of ozone in extension, surface cracks are observed at right angles to the direction of the stress (Crabtree and Malm 1956).

The major use of these synthetic elastomers is in the production of tires. Antiozonants are added to the tire formulation and provide a protective film against ozone degradation (Fisher 1957; Mueller and Stickney 1970; USEPA 1978). These additives are expensive and their cost is passed on to the consumer. Other synthetic elastomers are commercially available which have no olefinic structures and are chemically resistant to ozone (e.g., silicones, chlorosulphated polyethylenes and polyurethanes). Although these elastomers are expensive, they have captured the special-application market especially for use in hazardous chemical environments.

Dose-response relationships for exposure of elastomeric materials to ozone have been developed. Unfortunately, most of the work has involved high ozone levels and elastomeric materials without antiozonants. Hence, the results do not have an application for tires in a normal urban environment. An exponential function was obtained when two styrene-butadiene formulations with several levels of antiozonant were exposed to 490 $\mu g/m^3$ of ozone (Edwards and Storey 1959). The function relates the dose of ozone needed to produce visible cracks at certain levels of antiozonant.

6.3.4 Effect of Ammonia Pollutant/Material Interactions

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 Callaghan 1966).

Ammonia also plays a prominent role in the atmospheric chemistry of SO_2 resulting in the formation of ammonium sulphate aerosols (Bos 1980; Georgie 1970). While there is no information on the effect of this aerosol on the corrosion of materials, the chemistry of metal-ammonia complexes would suggest the possibility of such effects. The primary process would be the modification of stable corrosion films by the selective dissolution or retention of specific alloy constituents.

6.3.5 Effect of Particulate Pollutant/Material Interactions

While particulates obviously play a major role in soiling of surfaces, there appears to be no conclusive correlation between particulates and materials degradation (Del Monte et al. 1981; Fassina et al. 1976; USEPA 1981a; Vittori and Fuzzi 1975). In some cases the particulates serve to increase the effect of other pollutants by serving as catalysts (Hegg and Hobbs 1978).

However, since particulates probably deliver to surfaces of the order of 20% of the sulphate and, under certain conditions, up to 50% of the nitrate (in cities) the role they play in corrosion processes must not be underestimated (see for example Lindberg and Hosper 1982). Once the dry particles are deposited, wetting events will produce the effects described above.

6.4 IMPLICATIONS OF TRENDS AND EPISODICITY

Estimates are that atmospheric emissions of NO_x will increase in the order of 35% over the next 20 years (Altshuller and McBean 1980) while projections show that SO_2 emissions will remain the same or increase only slightly. This means that nitric acid in rain will substantially increase resulting in increases in potential deterioration of materials.

Episodicity encompasses the variations in levels of air pollutants occur at a given site. For example, in the northeast, the yearly peaks of SO_2 occur during the winter months. Thus, resulting deposition rates may vary through the year.

Episodicity also includes cycles of available moisture, specifically cycles of condensation and precipitation. In the northeast, the specific humidity and temperature of the atmosphere is lower in the winter. This condition may effect the time of wetness of material surfaces in the absence of other sources of moisture.

The frequency and intensity of rainfall in relation to dry periods is another aspect of episodicity. The erosion caused by the dissolving of reaction products (e.g., calcium sulphate) in rain runoff may be more severe in intense rainfall (Trudgill 1976). Thus, for two locations having the same total annual rainfall, the erosion in the one with heavier, but less frequent rain events may be greater than the other, where rain occurs more frequently.

Furthermore, the situation in the episodes between rain events should also be considered. In those cases where the damage occurs primarily by particulate induced attack (e.g., pitting of aluminum), more frequent rain events may wash off the particulates actually reducing the overall rate of damage. Variations in the pH of the rain can influence the solubility of corrosion and weathering products (further details available in Section 6.3.2).

6.5 DISTRIBUTION OF MATERIALS AT RISK

Most buildings, structures, and statuary subjected to the deteriorating process associated with atmospheric transport and deposition are found in urban areas. Hence, the spatial distribution will tend to follow industrial and demographic patterns, rather than the sensitive regions identified in aquatic and terrestrial impact sections (see Sections 3.5 and 4.5). However, this is not to imply that materials at risk are distributed as a simple function of population. Attempts to estimate quantities of exposed materials as a function of aggregate population may lead to erroneous results (Haynie 1980c; Koontz et al. 1981; Stankunas et al. 1981). Results from field surveys in two cities indicate that the period of urban development and the local availability of materials are important factors determining the distribution of material quantities for rural areas. Estimates of material distribution have not yet been attempted.

Inventories of historic structures and monumental statuary have been undertaken by both the American and the Canadian governments. The Canadian inventories are maintained by federal, provincial and municipal agencies and list thousands of structures of cultural significance. The National Register of Historic Places (U.S.) includes approximately 25,000 properties. These inventories warrant closer attention in terms of geographic distribution.

Determination of materials at risk must take into consideration both the susceptibility of the material as well as the availability and expense of measures to respond to the incremental damage caused by air pollution. The principal effect of air pollution damage is to reduce the length of time the material can serve its intended purpose. The intended purpose of house paint, for example, is primarily to protect the underlying wall material. The paint's expected life may be several years. The purpose of statuary marble, however, is to display the artistic inspiration of the sculptor and is intended to last for many generations. Therefore, even though the paint may be more sensitive to a given level of air pollution than the marble, the marble statue is more at risk.

Considering the expense and availability of remedial measures, sculptured stone and bronze are perhaps the most sensitive materials at risk. Dimension stone is next on the list since it is expensive to replace once it has been built into a structure. Sheet metals, brick and block, and concrete lie on the scale somewhere between dimension stone and surface coatings. The labour and raw materials involved are less expensive than dimension stone, but more costly than paints and surface coatings.

6.6 DATA NEEDS AND RESEARCH REQUIREMENTS

Although the examination of the deterioration of materials is a well established discipline, dose-response relationships, taking account of atmospheric variables as well as concentrations, are rather poorly documented. Selection of materials to be investigated should consider gaps in existing knowledge and significance of materials.

Dose-response relationships need to be better delineated for the range of pollutants and materials determined in field studies, controlled environments (including accelerated studies), and in laboratory models. There needs to be a study of the roles and possible damage caused by SO_4^{2-}, SO_2, NO_3^+, NO_2, O_3 and particulates, both individually and synergistically. Other agents in material deterioration need to be studied to determine which constituents are active on selected materials (e.g., the impact of ammonia on the corrosion of carbon steels, low-alloy steels and copper alloys), the effect of background levels of chloride ions and carbonyl sulphide (Gradel et al. 1981) on the corrosion of materials, and the effects of biological activity on building materials. Further, the role of microclimate, including rainfall, cycles and episodes of temperature and moisture, and wind regime needs to be evaluated. Finally, study should be made to assess mechanical degradation of masonry, soil sensitivity and underground corrosion, and stress corrosion cracking of Al and Cu alloys.

Many of these needs were discussed in a report to the Electric Power Research Institute (Yocom and Grappone 1976). In addition to these areas of study there are certain data sets which would help develop an impact assessment. Pollutant loads should be estimated for susceptible structures, giving relative contributions by local sources and distant sources. Also, there needs to be more study of the dose-response relationships for pollutants and materials of interest as well as an inventory of the distribution of the construction materials and cultural resources sites at risk. Unit cost data for cleaning, maintenance repair and replacement as well as the human response functions for maintenance and replacement need to be developed.

6.7 METHODOLOGIES

Testing of materials to determine their resistance to atmospheric corrosion or degradation has been conducted for many years at a number of established sites around the world (Committee G-1 1968, for metals). Approximately 15 of these sites are in the United States located east of the 100° meridian with additional sites being maintained on a proprietary basis by individual organizations. Meteorological and air quality monitoring have not generally been performed at these sites. Instead, the sites are typically characterized as rural, urban, industrial, or marine, to reflect the perceived quality of the environment at each site. Recently, measurements of temperature, rainfall, humidity, wind speed and direction, solar radiation, SO_2 and cloride ion concentration, were begun at the marine site at Kure Beach, North Carolina (F.L. La Que Corrosion Laboratory). There has been no report of acidic deposition, nitrogen oxides, oxidants, particulate matter and ammonia being measured at any of the other material test sites.

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. The tests for atmospheric corrosion of metals range from the preparation, cleaning and evaluation of specimens to the way tests are conducted and data are recorded (ASTM 1980a). Several methods have been developed to characterize pollutant levels in the atmosphere. For example, sulphur dioxide may be determined by using lead peroxide candles (ASTM 1977) or lead peroxide plates (APHA 1977). A standard for measuring time-of-wetness for surfaces exposed to the atmosphere has been prepared in draft form (ASTM 1980b; Sereda et al. 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 acidic 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 materials 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 nonmetallic 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 some laboratory studies of the mechanisms, kinetics, and thermodynamics of materials corrosion and degradation processes, and of the effect of specific atmospheric constituents on these processes, experimental conditions have been well controlled and a wide variety of sampling and analytical techniques are available

(Duncan and Spedding 1973a,b; Haynie et al. 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 (ASTM Standard Practice, ASTM 1980c for short-term accelerated tests methodology). Hence, they are often limited to simple conditions involving the initiation of corrosion 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. However, it has not 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.

New building components and systems are constantly being designed and manufactured. The operating and stress conditions to which they will be subjected are difficult to predict. Although many tests have been developed to accelerate degradation processes of building materials, they are seldom fully adequate for reliability predicting long-term performance. A recommended practice, ASTM (1980c) provides a framework for the development of improved durability tests. Probabilistic concepts have not been applied extensively to materials durability problems in the construction industry but these concepts offer new opportunities for obtaining improved quantitative predictions of the service life of building materials in polluted environments.

By far the greatest amount of work on atmospheric corrosion and the degradation of materials has involved field exposures at regional test sites. Here 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). 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 (Ashton and Sereda 1981; Haynie 1980a).

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. Among other reasons, 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. 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 1980a). All these variations have an influence on the ultimate impact of atmospheric components.

Although it is rarely done, it is highly desirable to collect and analyze the runoff from material exposure samples whenever possible. These samples provide a direct measure of the amount of material actually eroded and serve as a check against other techniques such as measuring the weight loss of the exposure sample. In some cases, the runoff sample can provide a reliable measurement of material loss over a much shorter exposure time than possible with other techniques.

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; Yocom 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 a 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. For a given exposure time, the second approach more readily identifies the important variables and interactions at a specific site. However, the response function is nonlinear. Therefore, the results obtained by the second approach for different test sites are not generally comparable and should not be used for interpolating to other conditions.

An essential difficulty particularly for heavily used test sites (e.g., Kearny, NJ.; State College, PA.; and Kure Beach, NC.), has been the absence of meteorological, air quality and acidic 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 not always correspond to those at the test site (Haynie 1980a; Haynie and Upham 1970, 1971; Mansfeld 1980).

It is now generally recognized that meteorological, acidic 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 acidic deposition on materials corrosion and degradation.

In a study in St. Louis, Missouri, concurrent environmental and meteorological measurements were made (Mansfeld 1980). Materials exposure sites were located at nine stations where air quality, including total suspended particulates (i.e., sulphate and nitrate), and meteorological data were recorded. Precipitation chemistry was not obtained. These measurements will allow the correlation of material damage as a function of the recorded environmental parameters.

In a second study begun in 1980, a temporary monitoring station was established at the Bowling Green U.S. Customs House in New York City. This was a joint NPS-EPA contribution to the NATO-Committee on Challenges to a Modern Society monitoring project (Livingston 1981). The objectives of this study were to intercompare site specific measurements with the permanent Manhattan monitoring station measurements, correlate these measurements with material deterioration, and investigate a variety of methods to measure stone damage.

A study for investigating material degradation rates over long exposure periods is being supported by the U.S. Environmental Protection Agency. The approach is to measure the erosion of marble gravestones in national cemetaries across the United States (Baer and Berman 1980). These standard stones, provided by the Veterans Administration, are obtained from only three marble quarries, providing three sets of chemically uniform indicators. The national cemetary system provides over 100 exposure sites throughout the country. Since 1873, the stones have recorded the cumulative environmental effects at each site.

6.8 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. Damage cost is a measure of material, energy and labour consumption. Premature consumption of products wastes limited natural resources and consumes labour in nonproductive 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 these variables are difficult or expensive to quantify and some relate indirectly to damage costs. The values of many of these variables can only be estimated, because no hard data are available. In cases where a material is part of a work of art, or has other cultural value, difficulties arise because of the lack of methodology for the assignment of an economic value. Some attempts have been made to estimate damage costs, using conservation and restoration costs as a surrogate for cultural value. Although this approach neglects the loss of unquantifiable artistic value originally present in the structure or object, at least it allows the costs of restoration to be compared with other control measures.

The literature on effects of pollutants on materials describes various approaches to determining unit costs of extra maintenance, such as more frequent painting, and earlier replacement resulting from air pollutants and acidic deposition (Haynie 1980c; Liu and Yu 1976; Yocom and Grappone 1976; Yocom and Upham 1977). These studies typically involve broad assumptions about the kinds of materials which are exposed in a given area and are generally based on a limited variety of materials. 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. 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 must be known. The deterioration rate in the absence of the pollutants must also be known so that the incremental effects of air pollution (Yocom and Grappone 1976) and the dose-response relationship can be determined. The distribution of the material in the environment needs to be catalogued including how the material is used and whether or not it is protected or exposed. There needs to be accurate data on pollutant loadings coincident with the material distribution. Finally, human response to materials damage must be predicted. In the latter component, there is variability on how and when to clean, paint, or replace as well as on the selection of substitute materials which may offer improved performance. There is also variability as to the extent structures are replaced prior to the time significant damage would have occurred due to pollutants. The accuracy of economic estimates is compromised by uncertainties in all of the above factors.

The economic assessments available today are crude. In the future the damage functions for new and old construction materials will be determined, and methodologies for determining materials distribution will be refined. Then the range of uncertainty in the aggregate cost of pollution-induced materials damage undoubtedly will be narrowed. These damage functions and distribution inventories are urgently needed.

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SECTION 7

THE FEASIBILITY OF ESTIMATING THE ECONOMIC BENEFITS OF CONTROLLING THE TRANSBOUNDARY MOVEMENT OF AIR POLLUTANTS

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 section 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. This section focuses on techniques to estimate benefits.

The objectives of this section are threefold. The first is to present an overview of economic methodologies which may be 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 section 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 matter. Another Work Group, 3B, is summarizing state of the art technology and costs.

This review draws upon published works in an attempt to synthesize theory and application. In particular, Freeman (1979) and Crocker et al. (1981) 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 acidic 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 noneconomic techniques do not provide a systematic and nonarbitrary 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 nonmarketed 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: (1) <u>activity</u> value which is derived from the direct use of goods and services affected by environmental quality; (2) <u>option</u> value which is derived from the possibility that people might use these goods and services in the future; and (3) <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 section, 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, (e.g., SO_x and NO_x), and monetary benefits is complex, and varies among receptor categories. However, the general 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.

Quadrant I shows a transformation function which relates emission levels to deposition (used here as inverse for environmental quality). In the case of acidic 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. There is actually a complex affect on the aquatic ecosystem. The amount of change in pH (and metal ions) varies with the buffering capacity (sensitivity) of the waterbody. The change in pH will have various effects on the fish population (i.e., rough , warm and cold species). Finally, recreational fishing may be affected by the changes in species types available as well as a reduction in the number of days fishing is permitted. This assumes that the stock of fish is independent of fishing pressures.

Where the effects are direct (e.g., 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, total economic value increases. This function could illustrate the relationship between activities and both its primary and secondary economic value.

In the quadrant IV, a benefits function can be drawn which relates the dollar value of benefits to particular LRTAP emission levels by

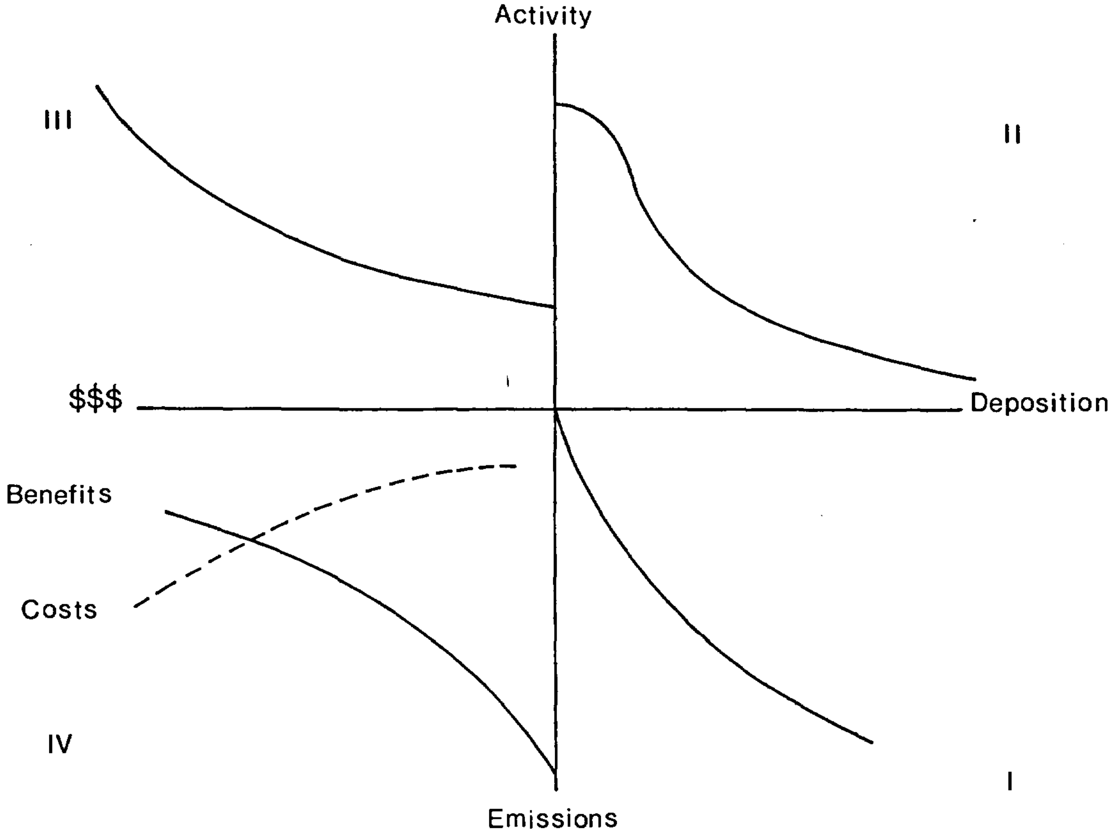

Figure 7-1. Conceptual relationship between emissions and economic effects.

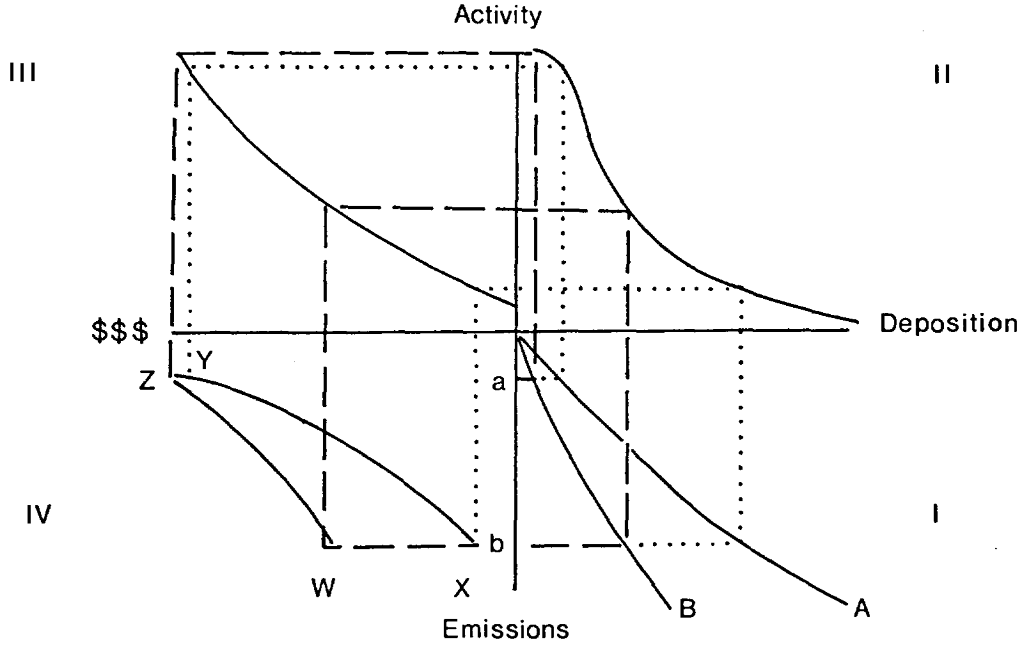

Figure 7-2. Variation in effects due to different emission-deposition relationships.

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).

Actually the functions are not as straightforward as shown in this quadrant diagram. There are elements of uncertainty, which may result from inaccuracies in measurement or from the use of assumptions drawn from insufficient data.

For example, the best estimate of the relationship between emissions and deposition (i.e., the transformation function) is represented by a range. The upper limit is A and the lower limit is B. The benefits range in quadrant IV is no longer a curve. It is now the area WXYZ (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.

In the case of LRTAP, this section reviews the economic methodologies for assigning monetary values to benefits for the activity categories shown in Table 7-1.

A critical link in this process is the relationship between dose and response (Quadrant II). Until more consistent research data 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 benefits 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.

It is often possible to reallocate resources, (e.g., spend more or less on environmental protection) to increase 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 associated with environmental damages or environmental protection activities sometimes may 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.

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 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 may be more significantly affected than others by social choices to abate or not to abate LRTAP. They may be located in source or sensitive receptor regions or they may have a preference for goods and services related to air quality in these regions. A decision to maintain existing air quality management practices produces gains to individuals who use the environment for production (e.g., 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), 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 reversed if LRTAP abatement is contemplated.

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 and lakes with fish populations to the coal-burning utilities and the nonferrous smelting industry. A political jurisdiction may surrender these rights from one area to another 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 in the collective good that may result from the transfer. 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. A benefit/cost analysis shows a particular course of action worthwhile if the gains 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. It has been noted 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).

There is disagreement 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. A series of welfare-weighted calculations could be used as an alternative to the 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 recommends weighting functions. These weighting functions are then reviewed and approved by the central budget agency (e.g., Office of Management and Budget, or Treasury Board) to ensure weighting consistency among programs 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. Therefore, the 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 the area under a demand curve. Consumer surplus is the difference between willingness to pay and actual expenditures. It is the change in consumer surplus resulting from changes in LRTAP which provides a useful measure of benefits to consumers. The willingness to supply on the part of producers is described graphically as the area under a supply curve. Producer's surplus is the difference between the price line and the supply curve and it is the change in producer surplus due to LRTAP which provides a useful measure of benefits to producers. (For those unfamiliar with economics, see the Appendix which gives a few key concepts of economic theory). Most of this section will describe the three basic approaches (i.e., market, imputed market and nonmarket) 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. These are not usually contributions to national economic efficiency, but are transfers from one region to another. Nonetheless, they are important at the regional level.

7.2.1 Primary Benefits

7.2.1.1 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. One way to measure changes in producer's income is 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, 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.

An innovative application of the Net Factor Income approach is to determine the change in input costs rather than output. Changes in producer's income are measured by the difference in the cost of production to sustain the same yield at different levels of LRTAP deposition. The advantage of this approach is that estimates can be made in the absence of specific dose-response data.

Partial Budgeting, a technique similar to net factor income, 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 from 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. Economic gains are estimated 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 incorrectly 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 acidic deposition. The *a priori* implications of change in these aspects can be noted, but the empirical verification of these hypotheses in some cases is difficult. The market price may generally be used as the relevant measure of unit value. However, where government support or other policies which raise prices is in effect, use of this (supported or other) price may overstate the value of benefits.

7.2.1.2 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 accurately reflect the adjustment. Therefore, 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 rather broad set of circumstances is the demand function derived as an accurate measure of willingness to pay for environmental quality.

Complementary Expenditure is yet a third imputed market technique. Variation in travel cost is the most frequently used expenditure and 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 (e.g., expenses for fishing equipment) may be used to impute values.

Risk Premium is the imputed market technique most frequently used in valuing mortality. These risk premiums may include 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.

7.2.1.3 Nonmarket 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 (e.g., visibility changes), this approach is an alternative to another major approach (e.g., imputed market). In cases where no markets exist for estimating option value, it is the only approach for valuation.

The Bidding Game is a nonmarket approach to preference revelation. The technique consists of constructing an artificial (i.e., contingent) market and simulating market transactions. The interviewer/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 is asked whether he or she concurs with a price for each possibility. 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 nonmarket technique requiring similar information about hypothetical environmental situations to the bidding game. Also some measure of the costs or price of a visit was required. Individuals are asked to rank the hypothetical situations from the least to the most desirable. These rankings reveal tradeoffs among the environmental services, other attributes of an area and price of admission. These tradeoffs 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 occurs 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 (Brookshire et al. 1976). 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 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. However, the benefits of environmental improvement are 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 respending patterns (multipliers) and the direct, indirect, and induced effects on other economic sectors (linkages) and 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 nonmarket 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. It comments on the technique's specific application to the valuation of benefits associated with LRTAP abatement 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 tradeoffs or concessions. Ultimately, it is desirable to obtain the most useful results at reasonable cost for the purpose at hand.

7.3.1 Aquatic

7.3.1.1 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 socioeconomic 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, (i.e., $OBCD_1$).

Now, if acidic 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.

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 and estimates 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. However, this method is 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. Also 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

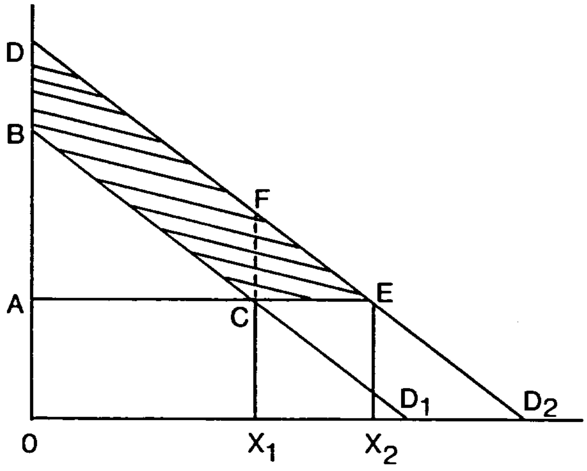

Figure 7-3. Change in demand due to water quality improvement.

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 socioeconomic 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, (e.g., travel cost). Then one component of recreation benefits (i.e., the value to new users) can be estimated by multiplying the increase in recreation days (quantity) by the assumed value per day (price) (Figure 7-3). This approach is limited in 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 acidic 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. However, 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 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 acidic deposition and general species type (rough, warm water and cold water). In addition, they would have to provide dose-response data, such as 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 acidic deposition.

For recreational fisheries a <u>contingent market</u> 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 behaviour 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 Section 2.

There are two limitations to the above techniques. They fail to capture option and legacy values of the recreational fishery or the aquatic ecosystem. They also place 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).

7.3.1.2 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 acidic deposition. If the fishery is being appropriately managed to maximize net economic yield, the benefit of reducing acidic deposition is equal to the market value of the increased yield. This is net of any changes in expenditure on variable factors of production. For 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 there is free access to the fishery, 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. This is because there are higher levels of congestion 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.

7.3.1.3 Aquatic Ecosystem

Any valuation of the benefits of reducing acidic 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 acidic 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. These changes should therefore be stated in qualitative terms.

7.3.2 Terrestrial

7.3.2.1 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 increases or as surplus income increases above the fixed factor of production.

In the case of acidic deposition, there is limited information about effects on agricultural productivity. A satisfactory estimate of the change in net factor income can 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 is assumed that producers have neither undertaken mitigation measures (e.g., liming), nor changed cropping patterns in response to acidic deposition.

If acidic 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 (i.e., 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. In the absence of dose-response data, an alternative estimate of net income changes due to differences in LRTAP is nonetheless possible. This approach requires measuring the difference in the cost of producing a given level of agricultural output under different environmental quality conditions.

7.3.2.2 Forestry

The conceptually correct procedure for estimating the value of changes in the forestry sector is similar to the agriculture sector where the market approach is used. Since knowledge of production, demand, and market structure suggest that the benefits of reducing acidic deposition will accrue to producers, benefits may be estimated from observed or predicted changes in net factor income.

In the case of acidic 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). The procedure is less complex for the forestry sector than in the agriculture sector, because there is less government intervention. Also there are fewer known uses of mitigation measures or changes in tree planting patterns due to acidic deposition.

7.3.2.3 Ecosystem

Any valuation of the benefits of reducing acidic deposition should reflect the value of all changes in the terrestrial ecosystem, not 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 have some affect on activity, option and existence values. Although these are best measured by means of a survey, it is unlikely that individuals would be able to assign accurate options or values to the terrestrial ecosystem considering the dearth of dose-response information.

7.3.3 Water Supply

The conceptually correct procedure for valuing a reduction in the direct effects of acidic 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 acidic deposition effects. Even if there were no acidic 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 atmospheric acidic deposition.

7.3.4 Effects on Buildings and Structures

The conceptually correct procedure for valuing the reduction in the effects of acidic 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 acidic 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. However, this method will result in an underestimate of total value in that 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 (e.g., recreation and visibility), additional research would be required prior to their application to derive historical values.

7.3.5 Human Health

7.3.5.1 Mortality

An understanding of the dose-response relationship between air pollutants and mortality and morbidity is needed to value changes. Animal and clinical studies provide a basis for confirming a relationship between air pollution and health. Some epidemiological studies estimate a dose-response between air pollutants and mortality and morbidity. Epidemiological and clinical studies can therefore be used to indicate the probability or risk of mortality or morbidity under different environmental conditions. These types of data must also be matched with changes in population exposed to determine changes in mortality or morbidity.

The amount that an individual must be paid to accept additional risk is conceptually the correct procedure for estimating the value of human life. When aggregated over many individuals, this willingness-to-pay, 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 behaviour 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%. Although this study measured willingness to pay, it differed from the behavioural approach in that it placed a value on a known human life. 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. Therefore, it is 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.

7.3.5.2 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 also ask 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 nonworking day). Their earning measures do not reflect loss in productivity and the pain and discomfort they suffer.

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 respectively be valued at $40-$50 per day and $10-$20 per day to provide a range, the latter being the (U.S.) average gross daily earning in the private nonagriculture sector in 1980.

Other measures of the value of health effects can be obtained from changes in medical expenditures for health care. In addition, the costs, (e.g., relocation) incurred to avoid unhealthy situations can also be used.

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 such things as income and tastes (Figure 7-4). If the number of days of satisfactory visibility is OA, the value of visibility is the entire area under the demand curve, because there is no expenditure for visibility. This assumes the initial level of visibility is maintained.

Using a dose-response relationship specified by the effects group, a reduction in LRTAP with improved visibility increases the number of days of satisfactory visibility. 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 nonmarket 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, (e.g., the choice of residential location). This approach further assumes that the intensity of these preferences is revealed by individuals' behaviour and their demand for associated market goods (e.g., how much more individuals pay for homes in neighbourhoods with clean air, and the degree to which vacationers change their travel plans reveal how much they value visibility). Technical measures of pollution concentrations or visibility levels must be reasonable representations of the environmental attributes that individuals value. These measures must be able to be used to identify that part of an individual's behaviour attributable to the component of environmental quality being studied.

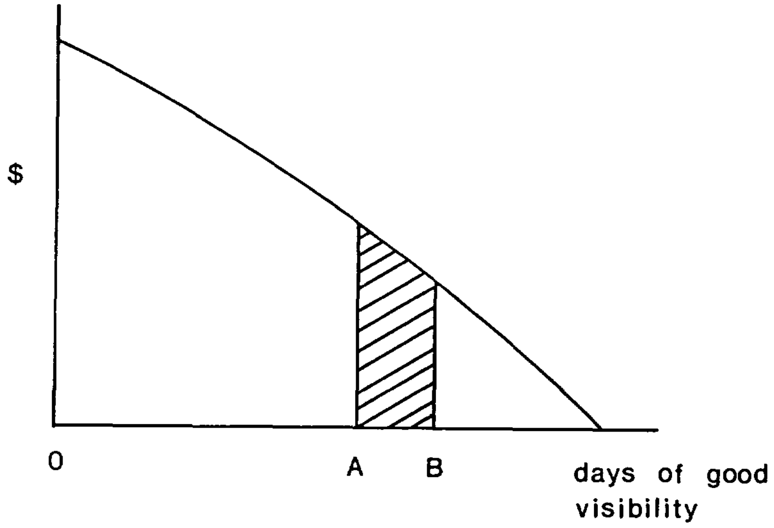

Figure 7-4. Change in demand due to visibility improvement.

The nonmarket approaches (e.g., Bidding Game and 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, nonmarket 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 respond 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 and willing to predict their response behaviour to a hypothetical situation that they may not have ever 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 $\underline{X}$ denotes the method which is recommended as most appropriate. The methods capture only the primary values and that regional econometric analysis is necessary to draw out the secondary economic effects (e.g., jobs and income) in a given sector and in a specific area.

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:

TABLE 7-2. SUMMARY OF METHODS

	Market		Imputed Market			Nonmarket
	Factor Income	Substitutes	Travel Cost	Property Value	Observed Behaviour	Survey
A. Aquatic						
1. Sports Fishery			X		$\underline{X}$[a]	X
2. Commercial Fishery	$\underline{X}$[a]					
3. Ecosystem						$\underline{X}$[a]
B. Terrestrial						
1. Crops	$\underline{X}$[a]			X		
2. Forests	$\underline{X}$[a]			X		
3. Ecosystem						$\underline{X}$[a]
C. Buildings, Structures						
1. Materials	$\underline{X}$[a]			X		
2. Historic						$\underline{X}$[a]
D. Water Systems		$\underline{X}$[a]				
E. Health						
1. Morbidity					$\underline{X}$[a]	
2. Mortality					$\underline{X}$[a]	
F. Visibility				X		$\underline{X}$[a]

[a] $\underline{X}$ denotes the method is recommended as the most appropriate.

1) there is a lack of dose-response relationship information;
2) there is difficulty in capturing all benefit values; and
3) there needs to be an evaluation of irreversibilities and the all or nothing feature.

7.4.1.1 Dose-Response Relationship

The need for data from the Effects Groups for the various receptor categories has been stressed at several points. Although some data are available, a clear statement is needed 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 (Table 7-3).

In the absence of these data, meaningful benefit estimates are impossible. Changes in producer cost would provide an alternative estimate of benefits of LRTAP control with yield and catch held constant.

7.4.1.2 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 only 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 (e.g., 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 where measurable values are sufficient to indicate the desired choices.

7.4.1.3 Irreversibilities and the All or Nothing Feature

There are additional limitations to conventional economic analysis. The physical dose-response relationships with respect to LRTAP deposition may be irreversible and the rate of damage may not be monotonically related to deposition. This is called the all or nothing feature or nonconvexities.

First, 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, it is imperative

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-}

that option, existence, and legacy values be included in the estimates.

Second, 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 nonconvexity would suggest that benefits of LRTAP control are much higher, increasing at a faster rate in a relatively unpolluted environment. Once the rate of damages starts to decline, the benefits of abatement would be commensurately lower. The limitation of this suggestion is that it is based on the adverse effect on a few species. If acidic deposition affects numerous species, any mitigation effort even at high levels of pollution could show significant benefits.

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. However, many of the latter have not dealt specifically with the effects of LRTAP.

Four 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. The values are underestimated since they fail to include option and legacy values for some effects. However, the lack of data on dose-response relationships limits the application of these techniques at this time.

2. Even in the absence of dose-response data, a variation in the factor income approach is available to estimate the benefits of changes due to reduced LRTAP deposition. This approach provides benefit estimates on the basis of the differences due to various levels of LRTAP in production costs for a given level of output and could be applied to commercial fisheries, agriculture, forestry, and buildings and structures.

3. 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.

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

The following recommendations can be made:

1. Dose-response data are available for the aquatic receptor and the geographically - specific studies now being undertaken tend to ignore substitution among fishing sites. Therefore, the participation model should be applied on a U.S./Canada basis to sports fishing to determine the value of primary benefits due to LRTAP reduction.

2. A regional economic analysis should 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).

3. To develop benefit estimates for LRTAP reduction for commercial fisheries, agriculture, forestry, and buildings and structures, a variation on the standard factor income approach should be used. Here the differential in the cost of producing a given level of output is determined.

4. Further research should be undertaken to determine the most appropriate value for changes in morbidity.

5. Further research needs to 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.

6. Further work needs to be undertaken with respect to the issues relating to property rights. These are an important part of the distributional aspect of the long range transport of pollutants.

7. The relationship between activity and other (option and legacy) values for the various receptor categories should be further investigated in order to derive a sense of the underestimate of the total benefits due to the omission of the latter values.

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APPENDIX - 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.

A.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.

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

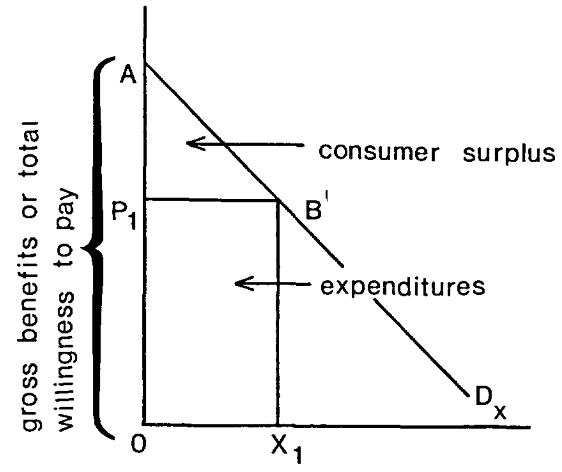

Figure 7-5. Measure of consumer surplus.

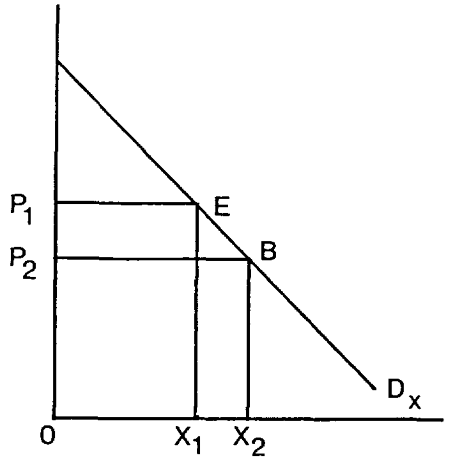

Figure 7-6. Change in consumer surplus.

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. Then, one must 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 which, given the price decrease, 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. 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 nonzero 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). This type of commodity is not traded in an organized market but it does have a 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. Demand is derived through other means as discussed in Sections 2 and 3. Again, the measure of consumer's surplus is the area under the demand curve. In this case, consumer's surplus is 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 (Figure 7-7).

While willingness-to-pay is used to determine demand curves, this is not the real test of the value of visibility. However, 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 (Figure 7-8). Equivalent surplus is a change in income which produces a change in utility equal to the change in quantity, at the original quantity level.

A.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.

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. 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

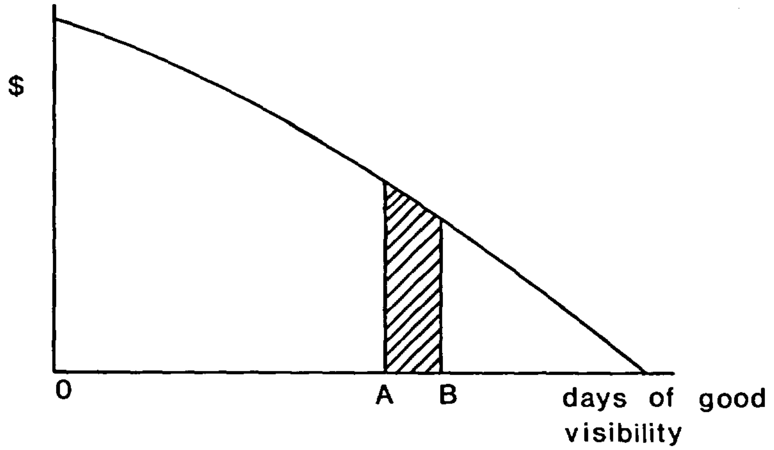

Figure 7-7. Change in demand due to visibility improvement.

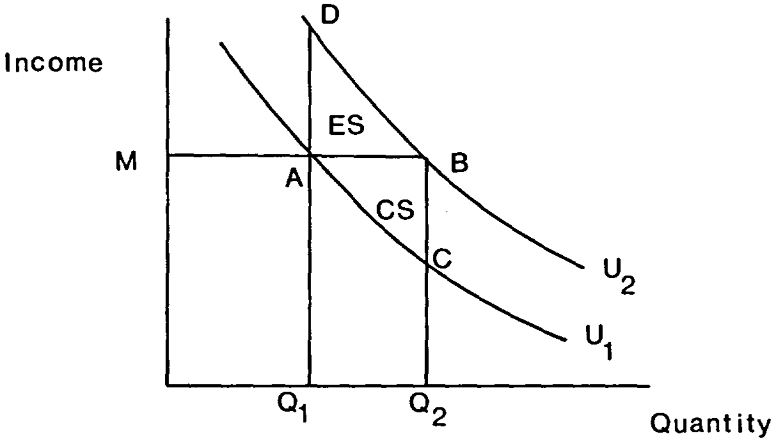

Figure 7-8. Compensating and equivalent surplus.

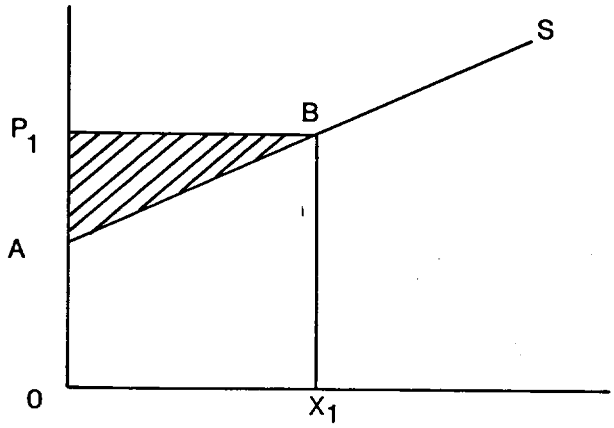

Figure 7-9. Producer's surplus.

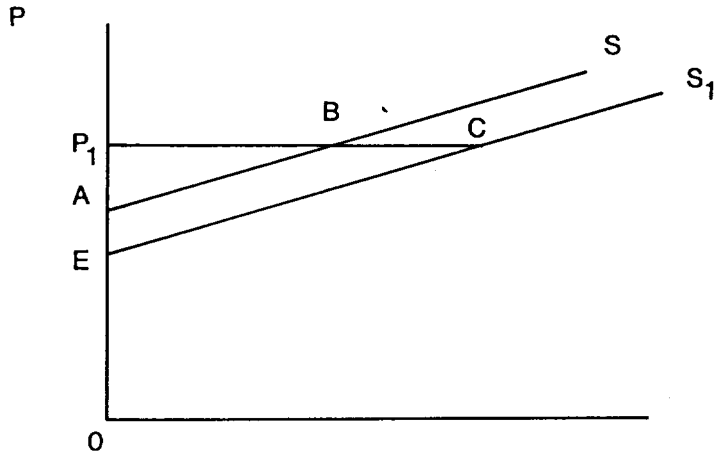

Figure 7-10. Change in producer's surplus due to change in supply.

same price and the producer gains on all unit levels which are lower than the total sale. This is because the market price exceeds the minimum the producer needs. This gain is called producer's surplus, and is represented by the area AP_1B, the area above the supply curve bounded by the market price (Figure 7-9).

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 (Figure 7-10).

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, (Figure 7-11).

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.

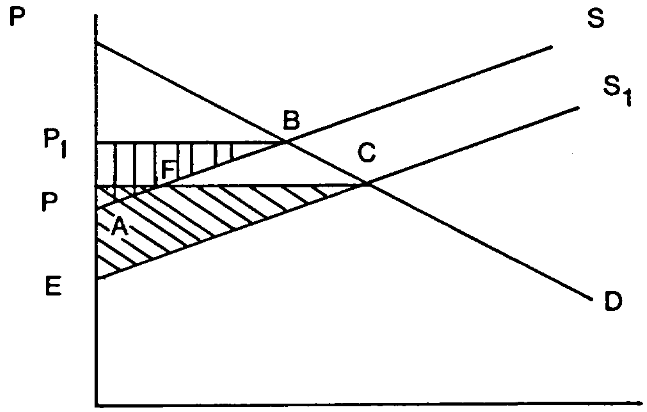

Figure 7-11. Hypothetical change in producer's surplus due to reduction in LRTAP deposition.

SECTION 8

NATURAL AND MATERIAL RESOURCES INVENTORY

SECTION 8

NATURAL AND MATERIAL RESOURCES INVENTORY

8.1 INTRODUCTION

The objective of an economic evaluation of acidic deposition is to estimate the value of reduced adverse effects achieved by a given reduction in emissions. This objective is pursued in six steps:

1. Inventory: Identify the totality of the resource of interest.
2. Sensitivity: Divide the resource inventory into sensitivity classes.
3. Exposure: Subdivide each sensitivity class by the severity of some indicator of deposition.
4. Response: Measure the adverse response expected absent of mitigative measures, for each sensitivity-exposure subdivision.
5. Mitigation: Determine reduction in deposition resulting from mitigation measures and calculate the fraction of the adverse effects estimated in (4) that would be reduced.
6. Valuation: Estimate the value of the adverse effects reduced.

The long-range transport of air pollutants (LRTAP) inventory of resources potentially at risk includes aquatic, terrestrial, and man-made resources. In all cases, the inventories now available are incomplete and generally lacking in the detail needed for a benefit/cost evaluation. The aquatic inventory is limited to large streams and lakes, and does not include potentially affected fish populations or the many plants, insects and animals living in or adjacent to water bodies. The terrestrial ecosystem consists of two major components, agriculture and forestry. The inventory of each will be conducted separately. Only major crop values and production are surveyed for the agricultural inventory. The forest inventory differentiates only between major forest types and does not include any information on shrubs and grasses. The materials inventory is far from complete in that it does not include common construction materials, such as galvanized steel and chain link fence. It lacks detail in describing historic places, landmarks and parks, and is the least comprehensive of the three categories.

This LRTAP inventory of resources potentially at risk does not include all natural and man-made resources in eastern North America. Wherever data are available, the inventory is geographically selective by two important criteria: (1) sensitivity, and (2) deposition regime.

The first criterion is the sensitivity of the various natural and man-made systems to acidic deposition. (The concept of sensitivity is explained in more detail in sections 3.5 and 4.5 of this report). The sensitivity of aquatic ecosystems is a function of soil characteristics, bedrock geology, topography, and alkalinity of the receiving waters. The sensitivity of terrestrial ecosystems is a function of soil characteristics and management practices and bedrock geology. It should be noted that even if a forest ecosystem is not in a sensitive area, its foliar system may still be affected by acidic deposition. The sensitivity of man-made structures is a function of the specific material and the mitigation measures undertaken by man. For example, the sensitivity of metals is a function of their composition and of the surface platings or coatings of corrosion resistant materials. Calcareous stone and masonry are sensitive materials unless protected.

The second criterion is the intensity of acidic deposition. Wet sulphate deposition is used herein as an indicator because data are available and because wet sulphate deposition is clearly an important contribution to overall acidification. Other factors, (e.g., dry deposition, nitrates, and seasonability of deposition), are known to affect the acidification potential of deposition, but an indicator which combines all of those factors is not yet available. It is known that ambient sulphur dioxide concentration is a more appropriate indicator of the potential damage to materials than wet sulphate, so SO_2 is used in place of sulphate when considering materials. Wet sulphate deposition is divided into three ranges as shown in Figures 8-1a and 8-1b: low (10-20 kg/ha.yr), moderate (20-40 kg/ha.yr), and high (greater than 40 kg/ha.yr).

The use of the data on resource distribution, sensitivity and deposition intensity to define resources potentially at risk is best explained by a simple graphic (Figure 8-2). Each data category (e.g., resource distribution, sensitivity and deposition) constitutes one set. Any overlap of the three sets defines the resource potentially at risk. Thus, the inventories provide information on the quantity and nature of resources within each of the three deposition zones. In the case of aquatic resources, this is supplemented by estimates of the potential of the soils and bedrock to reduce (or buffer) acidity.

The estimates of resources at risk presented in the following sections are based on steps 1 to 3, (i.e., inventory, sensitivity, and exposure; page 8-1) and are illustrated in Figure 8-2. Steps 4 to 6 (i.e., response, mitigation, valuation), as well as better data for steps 1 to 3, will further reduce the amount of the resource of interest in evaluating an emission reduction measure. It should be clear from the other sections in this report that our ability to perform steps 4 to 6 is limited at present. Therefore, the estimates below should not be interpreted as representing the value attributable to a deposition control measure, but rather as categories of

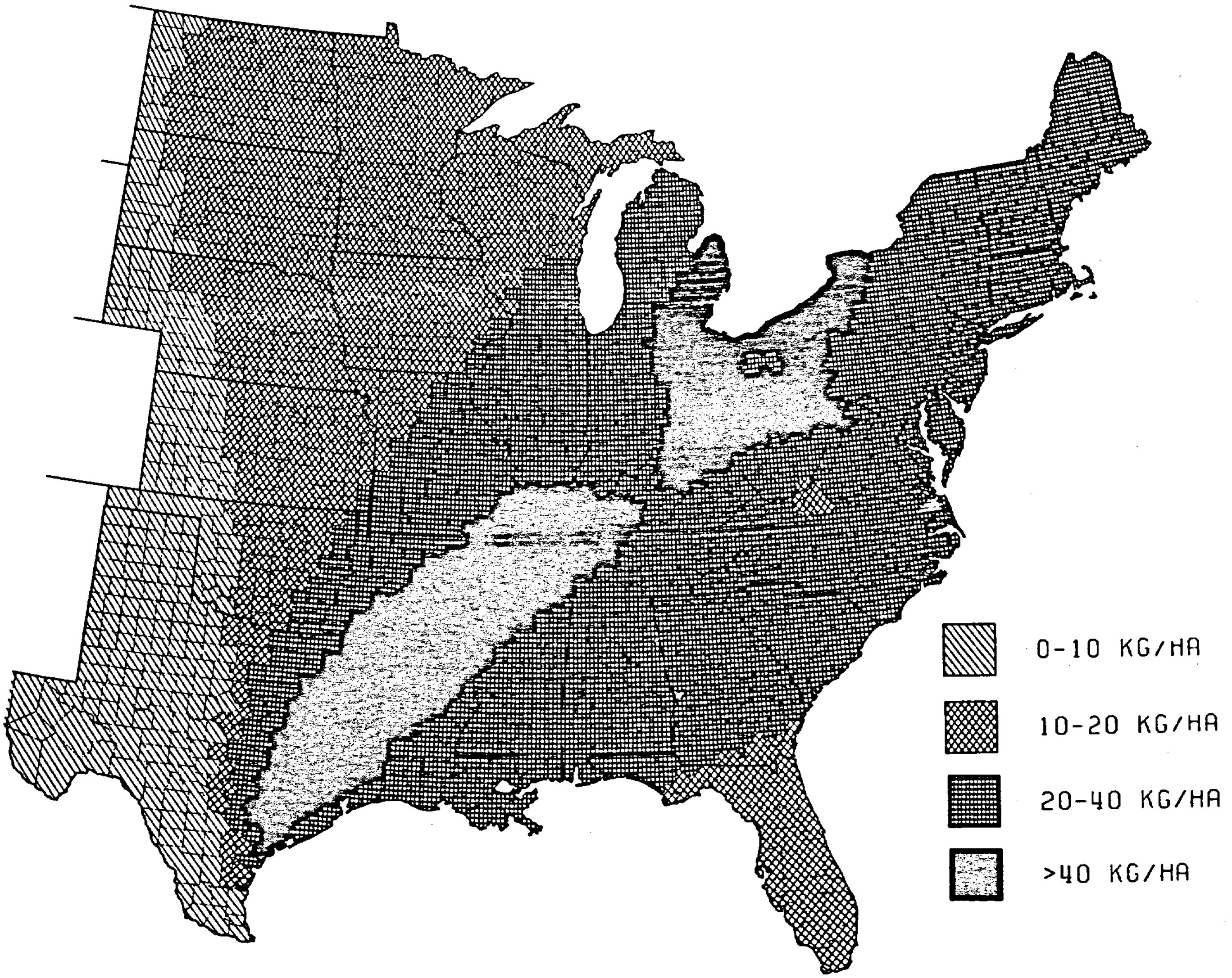

Figure 8-1a. Annual sulphate deposition regime for eastern United States, based on NADP data covering April 1979 to March 1980.

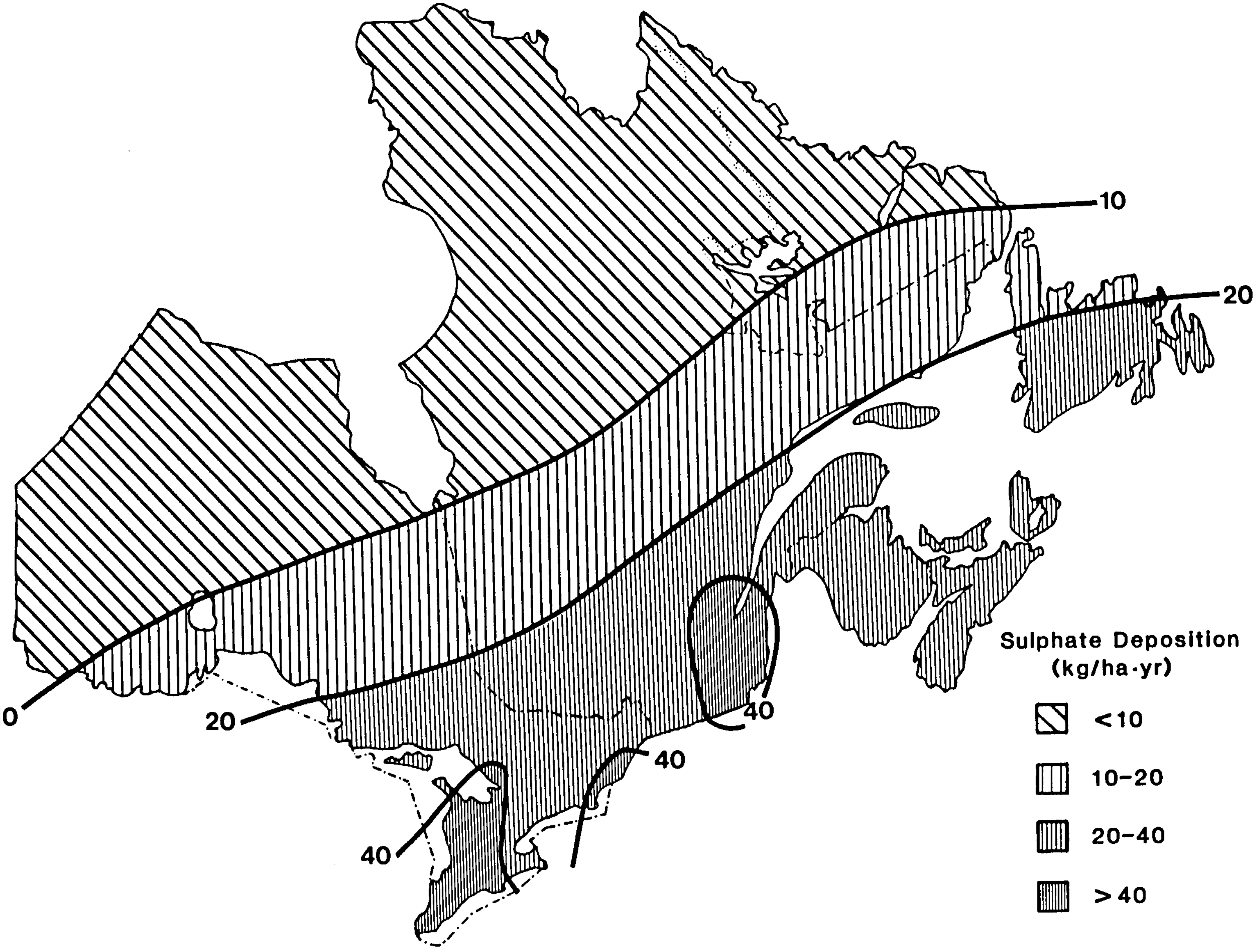

Figure 8-1b. Annual sulphate deposition regime for eastern Canada based on CANSAP 1980 data.

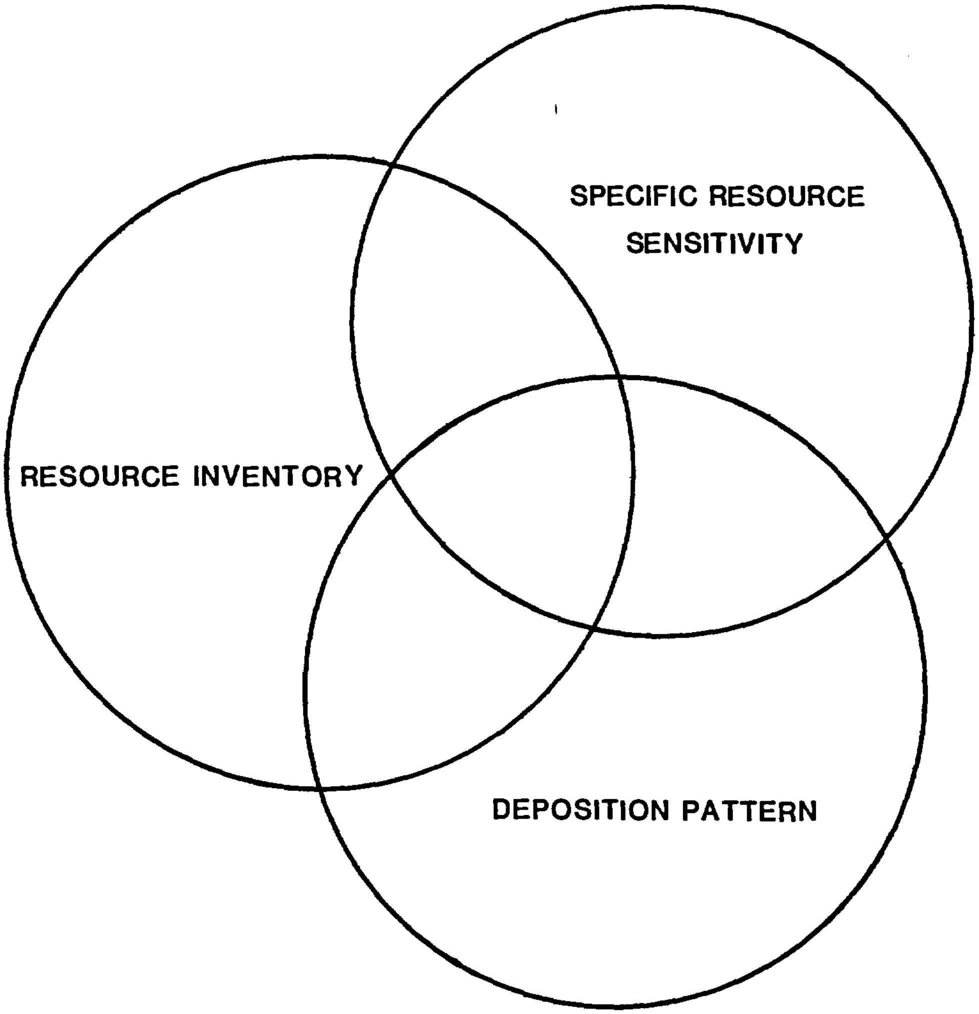

Figure 8-2. Conceptual scheme for identifying resources potentially at risk.

resources potentially at risk from which actual damages remain to be derived.

The resource inventory has drawn on data from a variety of sources. Although none of it was compiled specificially for acidic deposition, the best estimates have been made using this information compiled for different purposes, in different ways and for various years. Attempts were made to ensure that the U.S. and Canadian inventories are reasonably comparable. Despite the minor differences it is believed that the inventory presented here represents the best data available. Additional data collection will be necessary to improve the inventory both in coverage and specificity (e.g., tree species).

8.2 AQUATIC ECOSYSTEM

For the purpose of defining potential resources at risk, the aquatic ecosystem identified here pertains only to lake and stream area measures. A census of surface water resources within each combination of sensitivity/deposition regimes has been taken to provide quantitative estimates of the total area of surface waters (i.e., lakes and streams) potentially at risk.

8.2.1 U.S. Aquatic Resources

The Work Group took as its starting point for an inventory of surface water areas the Geoecology Data Base maintained by Oak Ridge National Laboratory (ORNL). The surface water inventory in the Geoecology Data Base includes all lakes greater than 2 acres and permanent streams. The primary advantages of using the inventory in the Geoecology Data Base are the completeness of the surface water inventory and that ORNL prepared the map of sensitive areas for the Aquatics Subgroup (Figure 3-10; Olson et al. 1982). The primary disadvantages of using the Geoecology Data Base are the absence of data on surface water chemistry (i.e., alkalinity) and the inability to discriminate among various sizes of lakes and streams. The inventory includes several large lakes and streams which even in sensitive areas would probably not be adversely affected by acidic deposition.

The Work Group limited its inventory effort to 38 states; those east of the 100° meridian. The surface water area in all counties with 50% of the land area in urban and agriculture uses was assigned to a special category rather than one of the three sensitivity categories. Surface water in this category were assumed to be more adversely affected by urban and agricultural activities than by acidic deposition. The remaining surface water area was assigned to one of four deposition categories. The disaggregated results of the classification are included in Appendix Tables 8-1 to 8-3.

Approximately 25% of the U.S. surface water area is located in areas with limited (low and moderate) potential to reduce acidity and of deposition greater than 20 kg SO_4^{2-}/ha.yr (Table 8-1). Only 10% are located in areas with the most limited (low only) potential to reduce acidity and of deposition greater than 20 kg SO_4^{2-}/ha.yr. The actual surface water area would be more limited if data were available on surface water chemistry (i.e., alkalinity). Additional refinements of the inventory should include data on this variable as well as more accurate measurements of surface water area.

Although the aggregate 38-state data show that approximately 25% of the U.S. surface water area is potentially at risk, data disaggregated at the state level show a much higher percentage in some states (Table 8-2). All of the New England states have at least 70% or more of the surface waters potentially at risk. Three mid-Atlantic states (Maryland, New Jersey, and New York) and three southern states (Georgia, North Carolina, and Virginia) have at least 50% or more of their surface water potentially at risk. Most of the states in the mid-west, west and southwest have very limited, if any, surface water potentially at risk except for Michigan and Arkansas. In some states with low potential to reduce acidity and numerous lakes, such as Wisconsin and Minnesota, the annual sulphate deposition loading is less than 20 kg/ha.yr, so the surface water area is not considered at risk. In all cases, these estimates of surface water potentially at risk will be reduced to some degree when data on stream chemistry are available.

8.2.2 Canadian Aquatic Resources

The basis for the inventory was provided by the map indicating the potential of soils and bedrock to reduce the acidity of atmospheric deposition (Figure 3-9; Lucas and Cowell 1982). This was overlaid with the map of sulphate deposition (Figure 8-1b). Finally, data on the proportion of surface water area for each province was combined with the deposition/acidity reduction capability information to derive estimates of the total area of surface waters at risk.

The data on surface waters were drawn from two main sources. In Ontario, detailed lake counts and measurements (Cox 1978) provided data on a watershed basis. For Quebec and the Maritimes, the Ecodistrict Data Base developed by Environment Canada (1981a,b) was utilized. The data presented here provide an estimated ratio of water to land for each Ecodistrict. No data were available for Newfoundland and Labrador. Two other serious omissions of this inventory are a lack of information on lake alkalinity and data on specific aquatic biota associated with the various deposition regimes on a provincial basis.

Table 8-3 provides a provincial summary of the aquatic resources at risk based on surface water sensitivity (as estimated by the

TABLE 8-1. SUMMARY OF EASTERN U.S. SURFACE WATER AREA (km^2) CROSS CLASSIFICATION BY SENSITIVITY AND DEPOSITION (USDA 1971, 1978a)

Sulphate Deposition (kg/ha.yr)	Urban and Agricultural Area	AREA km^2 (Percent of Total)			
		Potential to Reduce Acidity			
		Low[a]	Moderate	High	Total[b]
0-10	2,290(2)	10(<1)	1,240(1)	3,950(3)	7,490(5)
10-20	17,240(12)	5,410(4)	11,470(8)	15,740(10)	49,860(35)
20-40	11,120(8)	13,940(10)	19,970(14)	27,400(19)	72,430(50)
40	5,070(3)	210(<1)	2,190(1)	7,620(5)	15,090(10)
TOTAL[b]	35,720(25)	19,570(15)	34,870(25)	54,710(35)	144,870(100)

[a] A low potential to reduce acidity is interpreted as a high sensitivity.

[b] Rounded to the nearest 5%.

TABLE 8-2. SURFACE WATER AREA WITH LOW AND MODERATE POTENTIAL TO REDUCE ACIDITY RECEIVING GREATER THAN 20 kg/ha.yr SULPHATE DEPOSITION (USDA 1971, 1978a)

	km^2 (Percent of State Total)	
	Low Potential to Reduce Acidity	Moderate Potential to Reduce Acidity
REGION I		
Connecticut	340 (70)	0 (0)
Maine	6,010 (100)	0 (0)
Massachusetts	970 (90)	0 (0)
New Hampshire	860 (100)	0 (0)
Rhode Island	340 (75)	0 (0)
Vermont	720 (70)	0 (0)
REGION II		
New Jersey	150 (15)	660 (75)
New York	1,930 (40)	1,250 (20)
REGION III		
Delaware	0 (0)	0 (0)
Dist. of Columbia	0 (0)	0 (0)
Maryland	20 (<5)	1,020 (50)
Pennsylvania	40 (<5)	550 (35)
Virginia	70 (<5)	1,660 (55)
W. Virginia	120 (25)	20 (5)
REGION IV		
Alabama	10 (<5)	1,280 (35)
Florida	0 (0)	410 (5)
Kentucky	30 (<5)	400 (15)
Georgia	250 (10)	1,660 (55)
Mississippi	60 (<5)	810 (40)
North Carolina	310 (5)	9,010 (85)
South Carolina	0 (0)	640 (25)
Tennessee	90 (<5)	110 (<5)
REGION V		
Illinois	0 (0)	0 (0)
Indiana	10 (<5)	40 (<5)
Michigan	1,690 (40)	0 (0)
Minnesota	0 (0)	0 (0)
Ohio	0 (0)	0 (0)
Wisconsin	0 (0)	0 (0)
REGION VI		
Arkansas	130 (5)	1,350 (35)
Louisiana	0 (0)	0 (0)
Oklahoma	0 (0)	1,090 (25)
Texas	0 (0)	10 (<5)

TABLE 8-2. CONTINUED

	km^2 (Percent of State Total)	
	Low Potential to Reduce Acidity	Moderate Potential to Reduce Acidity
REGION VII		
Iowa	0 (0)	0 (0)
Kansas	0 (0)	0 (0)
Missouri	0 (0)	0 (0)
Nebraska	0 (0)	0 (0)
REGION VIII		
North Dakota	0 (0)	0 (0)
South Dakota	0 (0)	0 (0)

TABLE 8-3. SUMMARY OF SURFACE WATER AREA (km^2) IN EASTERN CANADA CROSS CLASSIFICATION BY SENSITIVITY AND DEPOSITION

	Sulphate Deposition (kg/ha.yr)	AREA km^2 (Percent of Total)[a] Potential to Reduce Acidity Low[b]	 Moderate	 High	Total
Ontario	10-20	11,254(12)	4,142(4)	1,672(2)	17,068(18)
	20-40	8,452(9)	1,890(2)	2,120(2)	12,462(13)
	>40	408(<1)	98(<1)	408(<1)	914(1)
Quebec	10-20	20,474(22)	2,532(3)	2,972(3)	25,978(27)
	20-40	10,137(11)	730(<1)	3,006(3)	13,873(15)
	>40	-	456(<1)	252(<1)	708(<1)
Maritimes	10-20	-	-	-	-
	20-40	8,719(9)	13,447(14)	1,482(2)	23,648(25)
	>40	-	-	-	-
TOTAL		59,444(63)	23,295(25)	11,912(13)	94,651(100)

[a] Total surface water area receiving more than 10 kg/ha.yr sulphate deposition.

[b] A low potential to reduce acidity is interpreted as a high sensitivity.

potential of surrounding soils and bedrock to reduce acidity) and sulphate deposition.

Of the total estimated surface water area of 51,605 km^2 located in regions sustaining over 20 kg/ha.yr of sulphate deposition, 44,337 km^2 (86%) are in areas with either low or moderate potential to reduce acidity. More than half of this (27,716 km^2) are in areas of low potential alone. Within the moderate and high deposition zones, the majority of surface water is receiving between 20 and 40 kg/ha.yr of sulphate; only 1.9% (962 km^2) both receive more than 40 kg/ha.yr sulphate and have low or moderate potential to reduce acidity.

The provincial breakdown indicates that 94% (22,166 km^2) of the surface water surveyed (i.e., receiving more than 10 kg/ha.yr sulphate) in the Maritimes both receive at least 20 kg/ha.yr of sulphate and have a low or moderate potential to reduce acidity. Although Quebec has the greatest total surface water area (40,559 km^2) only 28% (11,323 km^2) are within areas of low and moderate potential to reduce acidity receiving more than 20 kg/ha.yr sulphate. Thirty-six percent (10,848 km^2) of surface water surveyed in Ontario are in a moderate or high deposition zone combined with a low or moderate potential to reduce acidity.

8.3 AGRICULTURAL RESOURCES

The majority of crops listed in the inventory have been selected due to their significance in terms of value or production. The six most important crops are corn, soybeans, wheat, hay, tobacco and potatoes. This basic list has been supplemented by other crops which individually ranked high in the U.S. (cottonlint and sorghum) and Canada (barley and vegetables). Maps which provided crop data on a county or census tract basis were overlaid with deposition information to provide the quantitative crop information. The inventory presented here provides data on crop yields and values by state or province for each of the three deposition zones.

8.3.1 U.S. Agricultural Resources

The growing of agricultural crops is a major economic industry in the United States. Farms in the U.S. in 1978 produced over $64.9 billion worth of crops (USDA 1980).

The U.S. Department of Agriculture each year publishes its estimates of the previous three years crop statistics in Agricultural Statistics (USDA 1980). In addition to data on agricultural supplies, consumption, costs, and returns, this reference book lists data on acreage, production, yield, and value of 99 crops grown in the U.S. Of these crops, about 34 have been studied for their yield response to acidic deposition. The inventory in this section was limited to those crops of major economic importance among the 34 crops.

The major crops were identified by ranking all of the crops by their 1978 estimated value of production (USDA 1980). Table 8-4 presents this ranking for the entire U.S. and each crop's cumulative percentage of the total. It was found that the top eight accounted for almost 75% of the total value of all U.S. crops.

Of these eight crops, there are research studies on the effects of acidic deposition on the yields of six. There are no effects data on cottonlint and sorghum. Consequently, yield of only the six crops studied is matched with sulphur deposition patterns.

Data on yield of these six crops in the states east of the 100° meridian (38 states) is displayed in Appendix Tables 8-4 to 8-7. The four tables describe yield for the six crops by deposition pattern (i.e., 10-20 kg/ha.yr, 20-40 kg/ha.yr and greater than 40 kg/ha.yr) and total yield. Many states produce some of these crops under all three deposition patterns.

The total yield of each crop under four deposition patterns shows considerable variation (Table 8-5). Soybeans and tobacco are the only crops with any significant proportion of their yield in areas with sulphur deposition greater than 40 kg/ha.yr. For the remainder of the crops, less than 15% of their total yield is grown in areas of high deposition.

Although the aggregate 38-state data show that only 20% or more of the yield of two of the six major crops receives sulphate deposition greater than 40 kg/ha.yr, disaggregated data show that a higher percentage of crops in some states receive a high rate of sulphate deposition (Table 8-6). More than 50% of soybean yield in five states and of tobacco yield in two states receive sulphate deposition greater than 40 kg/ha.yr. In addition, a significant portion of the six crops in some states receive a high rate of deposition. At least 50% of three crops in the states of Arkansas, Kentucky, Michigan, Ohio and Tennessee receives 40 kg SO_4^{2-}/ha.yr.

8.3.2 Canadian Agricultural Resources

Agriculture is an important economic activity for all provinces in eastern Canada with most of the yield and value centred in Ontario and Quebec. Data have been assembled from Statistics Canada and provincial agriculture ministries to provide an overview of the types, yields, and values of crops at risk within each of the three identified deposition regimes. The crops of importance are primarily grains, but data on certain vegetables are also included, although they represent only about 1% of the total value of production.

TABLE 8-4. RANKING OF U.S. CROPS BY 1978 VALUE OF PRODUCTION (USDA 1980)

CROP	1978 \$ Value (10^6)	Percent of Total	Cumulative Percent	Production (Metric Tons 10^6)
Corn	15,900	24	24	177.2
Soybeans	12,500	19	43	50.9
Hay	6,600	10	53	126.6
Wheat	5,400	8	61	48.9
Cottonlint	3,000	5	66	2.4
Tobacco	2,700	4	70	.9
Sorghum	1,500	2	72	19.0
Potatoes	1,200	2	74	16.3
TOTAL	48,800			

TABLE 8-5. 1978 YIELD OF SIX CROPS IN 38 STATES BY DEPOSITION REGIME (USDC 1979)

	Metric Tons 10^6 (Percent of 38-State Total)[a] Sulphate Deposition kg/ha.yr				
CROP	<10	10-20	20-40	> 40	Total
Corn	7.2 (5)	76.7 (45)	68.4 (40)	16.7 (10)	169.0
Soybeans	.2 (0)	13.7 (30)	21.7 (45)	11.3 (25)	46.9
Hay	4.6 (5)	41.4 (45)	32.2 (35)	13.8 (15)	92.0
Wheat	7.5 (25)	17.6 (60)	3.1 (10)	2.2 (5)	30.4
Tobacco	0 (0)	<.1 (0)	.7 (80)	.2 (20)	.9
Potatoes	<.1 (0)	2.7 (50)	2.3 (45)	.3 (5)	5.3

[a] To the nearest 5%.

TABLE 8-6. SELECT U.S. AGRICULTURAL CROPS BY STATE RECEIVING GREATER THAN 40 kg/ha.yr SULPHATE DEPOSITION (USDC 1979)

	Metric Tons 10^3 (Percent of State Total)[a]					
	Corn	Soybeans	Hay	Wheat	Tobacco	Potatoes
REGION II						
New York	404.7 (30)	0 (0)	963.6 (20)	25.3 (40)	0 (0)	110.5 (20)
REGION III						
Maryland	7.9 (< 5)	0 (0)	49.4 (10)	.2 (<5)	0 (0)	0 (0)
Pennsylvania	392.9 (15)	2.7 (5)	95.5 (<5)	15.0 (10)	0 (0)	45.5 (20)
W. Virginia	52.2 (35)	0 (0)	365.0 (55)	1.8 (40)	.3 (0)	2.0 (40)
REGION IV						
Kentucky	2,027.3 (70)	839.5 (85)	1,604.7 (65)	140.0 (85)	142.0 (70)	0 (0)
Mississippi	21.5 (15)	805.7 (40)	101.6 (10)	34.2 (70)	0 (0)	0 (0)
Tennessee	621.6 (60)	1,133.1 (85)	470.7 (30)	96.7 (70)	19.3 (35)	0 (0)
REGION V						
Illinois	390.8 (<5)	263.4 (5)	147.8 (5)	45.9 (5)	0 (0)	0 (0)
Indiana	1,107.6 (5)	405.9 (10)	1,604.7 (10)	110.3 (20)	1.9 (30)	0 (0)
Michigan	2,268.1 (50)	316.6 (55)	1,209.6 (40)	218.3 (55)	0 (0)	57.3 (15)
Ohio	8,565.1 (95)	3,276.9 (100)	2,722.9 (90)	967.6 (95)	19.3 (100)	0 (90)
REGION VI						
Arkansas	26.5 (95)	2,850.2 (100)	780.9 (65)	232.2 (100)	0 (0)	0 (0)
Louisiana	3.2 (5)	200.3 (10)	244.4 (40)	5.0 (50)	0 (0)	0 (0)
Oklahoma	.1 (< 5)	8.0 (5)	44.0 (< 5)	1.4 (< 5)	0 (0)	0 (0)
Texas	312.9 (10)	176.2 (40)	1,978.2 (40)	37.4 (< 5)	0 (0)	0 (0)
REGION VII						
Missouri	430.1 (10)	991.8 (25)	268.2 (5)	27.7 (5)	0 (0)	0 (0)

[a] To the nearest 5%.

Table 8-7 provides a ranking on the basis of production value of all crops included in the inventory. From this table it is clear that grain, corn and hay are most important, accounting for just over 50% of total production value in eastern Canada.

A breakdown of the value and yield for each of these twelve crops by deposition zone are provided in Tables 8-8a and 8-8b, respectively. For many of the crops, more than 50% of their total yield is grown in areas of high sulphate deposition, (over 40 kg/ha.yr). By contrast, very small proportions (4% or less) are grown in areas experiencing only 10 - 20 kg/ha.yr of sulphate deposition. It is evident that a very significant proportion of Canada's agricultural crops are grown in areas experiencing high deposition levels.

In order to obtain a better understanding of the geographical distribution of these crops, Table 8-9 was prepared. This provides a breakdown of production values for each province receiving more than 40 kg/ha.yr sulphate deposition. Appendix Tables 8-12 through 8-14 provide more detail.

Only Ontario and Quebec, which are significant agricultural producers of all crops, have areas exposed to sulphate deposition in excess of 40 kg/ha.yr. The most important crops in these areas (based on value of production), are grain corn, hay and soybeans. In the case of soybeans which is a small crop by volume, 95% of its total volume of production is in the high deposition zone. This is the highest proportion for any single crop, and all of this production takes place in southwestern Ontario.

Overall, the most important crops in terms of value which are grown in areas receiving 20 - 40 kg/ha.yr sulphate are hay, grain corn, potatoes and tobacco. On a provincial basis, hay and grain corn are a greater proportion of total value of production in Ontario and Quebec, where potatoes are an important crop in the Maritime provinces.

It is evident even from this preliminary analysis that a very large proportion of eastern Canada's agricultural yields are grown in areas of high and moderate deposition. In turn, the geographic distribution of crops varies so that certain crops represent a more significant proportion of total value of production in each province. This inventory has provided a preliminary overview of the agricultural resources at risk, particularly in the high and medium deposition zones. Better data on the responses of individual crop species to these deposition regimes will provide the basis for a more accurate quantification of the extent of risk.

TABLE 8-7. RANKING OF CROPS IN EASTERN CANADA BY 1980 VALUE OF PRODUCTION (1980 $ Cdn)

CROP	1980 $ Value (10^3)	Percent of Total	Cumulative Percent	Production (Metric Tons)
Grain Corn	794,173	28	28	5,990.0
Hay	658,550	24	52	13,278.0
Tobacco	333,821	12	64	115.0
Potatoes	279,940	10	74	1,843.6
Soybeans	228,499	8	82	962.9
Fodder Corn	253,084	6	88	12,984.4
Wheat	128,605	5	92	1,207.2
Oats	100,595	4	96	796.9
Barley	88,756	3	99	714.6
Cabbage	15,878	<1	100	119.6
Lettuce	9,332	<1	100	35,793.0
Spinach	1,222	<1	100	3,003.0
TOTAL	2,892,495			

Source: Appendix Tables 8-12 and 8-13

TABLE 8-8a. VALUE AND PERCENTAGE OF TOTAL 1980 YIELD OF EACH CROP IN EASTERN CANADA BY DEPOSITION REGIME

	Value 1980 $ 10^3 (Percent of 1980 Yield)				
	Sulphate Deposition kg/ha.yr				
CROP	<10	10–20	20–40	>40	Total
Grain Corn	0 (0)	0 (0)	226,982 (38)	567,191 (62)	794,173
Hay	0 (0)	21,271 (4)	354,095 (53)	283,184 (43)	658,550
Tobacco	0 (0)	0 (0)	159,492 (49)	174,329 (51)	333,821
Potatoes	0 (0)	1,607 (<1)	217,210 (79)	61,123 (21)	279,940
Soybeans	0 (0)	0 (0)	10,429 (5)	218,070 (95)	228,499
Fodder Corn	0 (0)	25 (<1)	104,610 (44)	148,449 (56)	253,084
Wheat	0 (0)	460 (<1)	40,125 (33)	88,020 (67)	128,605
Oats	0 (0)	3,636 (3)	62,587 (66)	34,372 (31)	100,595
Barley	0 (0)	3,422 (4)	35,796 (44)	49,538 (52)	88,756
Cabbage	0 (0)	39 (<1)	12,972 (80)	2,867 (20)	15,878
Lettuce	0 (0)	0 (0)	6,351 (75)	2,981 (25)	9,332
Spinach	0 (0)	0 (0)	848 (66)	374 (34)	1,222

TABLE 8-8b. 1980 YIELD OF MAJOR CROPS IN EASTERN CANADA BY DEPOSITION REGIME

	Metric Tons 10^3 (Percent of 1980 Yield) Sulphate Deposition kg/ha.yr				
CROP	<10	10-20	20-40	> 40	Total
Grain Corn	0 (0)	0 (0)	2,274.0 (38)	3,716.0 (62)	5,990.0
Hay	0 (0)	419.0 (3)	7,087.0 (53)	5,772.0 (44)	13,278.0
Tobacco	0 (0)	0 (0)	57.0 (50)	58.0 (50)	115.0
Potatoes	0 (0)	7.6 (<1)	1,452.0 (79)	384.0 (21)	1,843.6
Soybeans	0 (0)	0 (0)	43.9 (5)	919.0 (95)	962.9
Fodder Corn	0 (0)	1.4 (<1)	5,667.0 (44)	7,316.0 (56)	12,984.4
Wheat	0 (0)	4.2 (<1)	394.0 (33)	809.0 (67)	1,207.2
Oats	0 (0)	24.9 (3)	524.0 (66)	248.0 (31)	796.9
Barley	0 (0)	24.6 (4)	316.0 (44)	374.0 (52)	714.6
Cabbage	0 (0)	.2 (<1)	96.0 (80)	23.4 (20)	119.6
Lettuce	0 (0)	0 (0)	26.7 (75)	9.1 (25)	35.8
Spinach	0 (0)	0 (0)	2.0 (66)	1.0 (34)	3.0

TABLE 8-9. VALUE (1980 $ Cdn 10^3) OF MAJOR CROPS BY PROVINCE RECEIVING GREATER THAN 40 kg/ha.yr SULPHATE DEPOSITION

	Value 1980 $ 10^3 (Percent of Provincial Total)[a]								
	Wheat	Oats	Barley	Grain Corn	Fodder Corn	Soybeans	Potatoes	Tobacco	Hay
Ontario	84,348	20,958	45,104	560,864	130,447	218,070	44,438	174,329	186,171
	(81)	(44)	(65)	(78)	(70)	(95)	(78)	(59)	(52)
Quebec	3,672	13,414	4,434	6,327	18,002	-	16,685	-	97,013
	(16)	(27)	(12)	(8)	(28)	-	(29)	-	(38)
Maritimes	- no deposition of greater than 40 kg/ha.yr -								

[a] Total value of each crop in eastern Canada.

8.4 FOREST RESOURCES

Data on forest resources are aggregated and information on individual tree species are not provided in any terms. For the U.S., the forests are differentiated into two categories (i.e., hardwood and softwood), while in Canada there are three categories (i.e., hardwood, mixed and softwood). Quantitative information of the total volume of forest resources (yield), its growth (or annual yield) and value is provided in the inventory for each state or province and deposition regime.

8.4.1 U.S. Forest Resources

As of 1977, total commercial forest land in the U.S. was 197 x 10^6 hectares, and the total timber volume was 22.6 x 10^9 m^3 (USDA 1978b). The annual growth was 350 x 10^6 m^3 of softwoods and 270 x 10^6 m^3 of hardwoods. The average stumpage price in 1978 dollars was $27.50 per m^3 for softwoods and $8.60 per m^3 for hardwoods (Ulrich 1981). Combining the annual growth and appropriate value estimates gives a value of $11.9 billion to the net annual growth.

The total forest land area in those states east of the 100° meridian was 145 x 10^6 hectares, and the total timber volume was 9.8 x 10^9 m^3. The annual growth was 224 x 10^6 m^3 of softwood and 252 x 10^6 m^3 of hardwoods. Combining the annual growth and appropriate value estimates results in a value of $8.3 billion for the net annual growth in the eastern United States.

The total forest volume and annual growth grouped by the two higher deposition categories are displayed in the Appendix to this section. Note that the data on annual growth are incomplete for several states. These data are not available on a county basis, so they did not appear in the data summary.

The volume and growth increments show a similar distribution among the four deposition categories (Table 8-10). Approximately 10% of the hardwood and softwood growth is found in areas of highest depositions and over 75% of the hardwood and softwood growth is found in areas of moderate deposition.

Although the aggregate 38 state data show that only 15% of the forest volume is exposed to sulphate deposition greater than 40 kg/ha.yr, individual state data show a different picture (Table 8-11). A significant portion of the forest areas in the states of Arkansas, Ohio and Texas receives sulphate deposition greater than 40 kg/ha.yr. In nine states 30% or more of the forest area receives sulphate deposition greater than 40 kg/ha.yr.

TABLE 8-10. U.S. HARDWOOD AND SOFTWOOD VOLUME AND GROWTH (Olson et al. 1980)

	m^3 10^6 (Percent of 38 State Total)[b] Sulphate Deposition kg/ha.yr				
	<10	10-20	20-40	>40	Total
Volume					
Hardwood Volume[a]	0 (0)	780 (10)	4,040 (70)	940 (15)	5,750
Softwood Volume[a]	40 (0)	480 (15)	2,690 (75)	480 (10)	3,690
Total Volume	40 (0)	1,290 (10)	6,930 (70)	1,540 (15)	9,800
Growth					
Hardwood Growth[a]	<10 (0)	10 (10)	110 (80)	20 (10)	140
Softwood Growth[a]	<10 (0)	20 (15)	140 (75)	20 (10)	190
Total Growth	<10 (0)	30 (15)	250 (75)	40 (10)	330

[a] These numbers may not add to total numbers because data for some states do not distinguish between hardwood and softwood.

[b] To the nearest 5%.

TABLE 8-11. U.S. FOREST VOLUME BY STATE RECEIVING GREATER THAN 40 kg/ha.yr SULPHATE DEPOSITION (Olson et al. 1980)

	Volume $m^3 \cdot 10^3$	(Percent of State Total)[a]
REGION II		
New York	41,900	(10)
REGION III		
Maryland	7,800	(10)
Pennsylvania	180,200	(30)
West Virginia	125,400	(35)
REGION IV		
Kentucky	123,300	(40)
Mississippi	45,400	(10)
Tennessee	102,000	(35)
REGION V		
Illinois	14,200	(20)
Indiana	5,300	(5)
Michigan	25,800	(5)
Ohio	113,300	(95)
REGION VI		
Arkansas	195,300	(80)
Louisiana	194,200	(40)
Oklahoma	18,500	(30)
Texas	308,900	(100)
REGION VII		
Missouri	35,000	(20)

[a] See Appendix Table 8-11 for growth data.

8.4.2 Canadian Forest Resources

The wood industry is an important component of the Canadian economy. Forest industries valued at $22 billion Cdn. annually constitute Canada's largest manufacturing industry as well as the largest single contributor to the positive side of our balance of payments (Sidor 1981). One in ten Canadian jobs depends on the forestry sector.

The importance of the forest industry in the eastern Canadian provinces to the wood industry is substantial. Approximately 35% of the country's total productive forest land lies within the boundaries of eastern Canada. Further, the eastern Canadian provinces accounted for about 64% ($3.5 billion Cdn.) of Canada's total value added in the forest industry (Sidor 1981). Total value of the annual forest growth of 150,241,000 m^3 is estimated to be $3.9 billion Cdn. This is based on an average wood value of $26.25 Cdn. per m^3 (1981).

Figure 8-3 illustrates the pattern of acidic deposition (kg SO_4^{2-} /ha.yr) and forest type. In eastern Canada higher levels of SO_4^{2-} are most often associated with deciduous forests and lower SO_4^{2-} levels with coniferous.

Table 8-12 lists the annual growth by forest type and deposition regime. Although only 4% (5,436 $m^3.10^3$) of the annual growth occurs in areas receiving more than 40 kg/ha.yr sulphate deposition this does represent 10% of the hardwood annual yield. Although deposition exceeding 40 kg/ha.yr sulphate affects the smallest area of forested land (2,048,000 ha), this is the area of highest mean annual increment (2.1 m^3/ha) affecting mixed and hardwood forests. The bulk of hardwood and mixed wood growth occurs in areas receiving 20 - 40 kg/ha.yr sulphate, representing 64% and 70% of annual growth by forest type, respectively.

The provincial summary (Table 8-13) illustrates the geographic variation in annual growth. While only 41% and 30% of the annual growth for Quebec and Ontario are receiving more than 20 kg/ha.yr of sulphate, 100% of the annual growth in the Maritime provinces are under the moderate deposition regime. Sixty-seven percent of Newfoundland's forest growth occurs under similar conditions receiving 20 - 40 kg/ha.yr of sulphate.

8.5 MAN-MADE STRUCTURES

Man-made materials can be grouped into three classes (i.e., metals, masonary and organic materials). Organic materials include paints, coatings, textiles and wood. Materials within each one of these classes behaves differently when exposed to air and water pollutants.

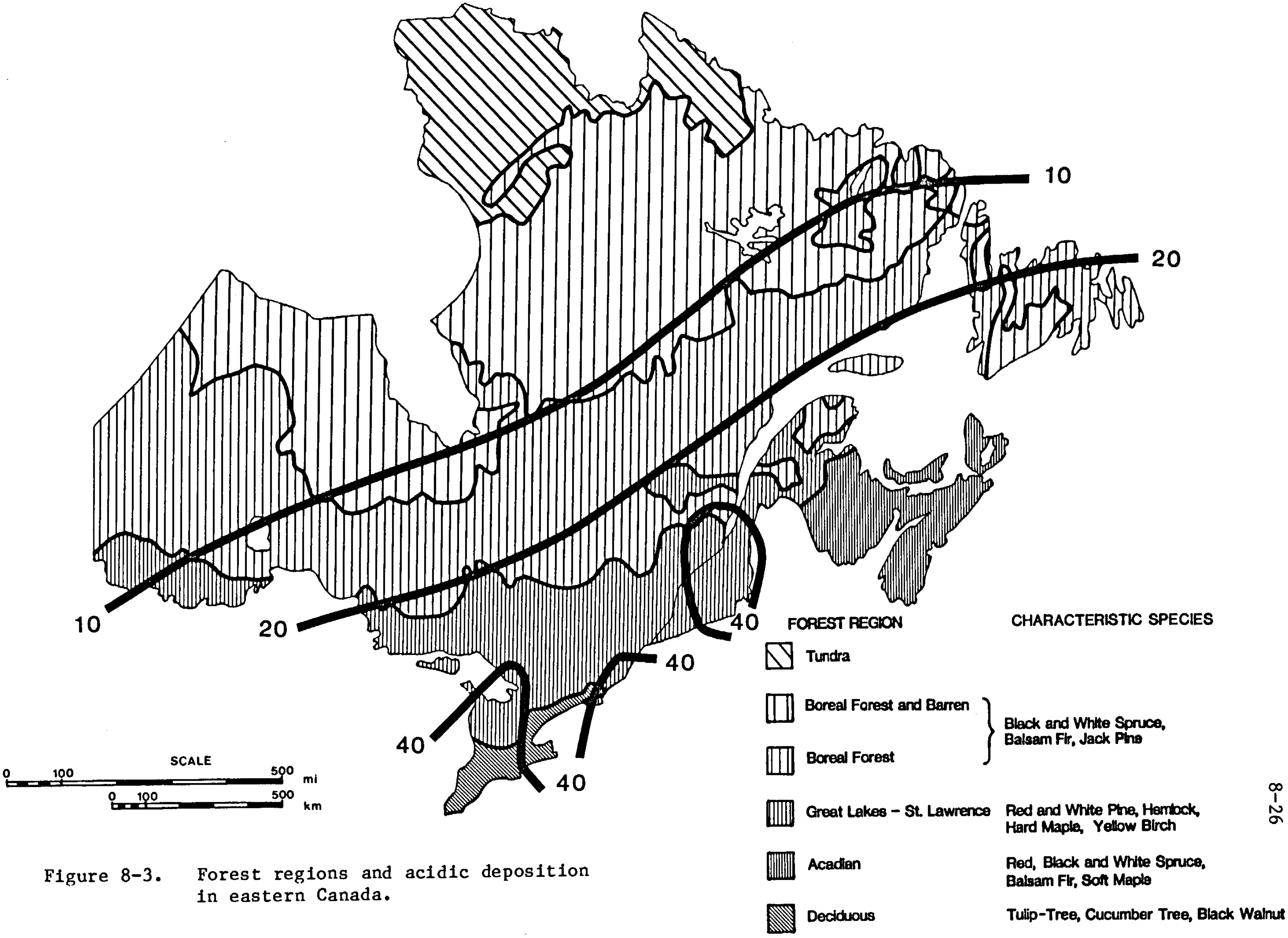

Figure 8-3. Forest regions and acidic deposition in eastern Canada.

TABLE 8-12. HARDWOOD, SOFTWOOD AND MIXED WOOD ANNUAL GROWTH ($m^3.10^3$) IN EASTERN CANADA BY DEPOSITION REGIME

	Annual Growth $m^3.10^3$ (Percent of Total) Sulphate Deposition kg/ha.yr 10-20	20-40	>40	Total[b]
Hardwood[a]	5,082 (26)	12,491 (64)	1,825 (10)	19,398
Softwood[a]	66,753 (71)	26,814 (28)	815 (1)	94,382
Mixed Wood[a]	8,327 (23)	25,341 (70)	2,760 (8)	36,428
Total Annual Growth	80,162 (53)	64,646 (43)	5,400 (4)	150,208

[a] Hardwood and softwood forests contain 70% or more of the specified type. Mixed wood forests contain less than 70% of either hardwood or softwood species.

[b] Total annual growth does not include data on regions receiving less than 10 kg/ha.yr sulphate desposition.

TABLE 8-13. ANNUAL FOREST GROWTH ($m^3.10^3$) BY PROVINCE RECEIVING GREATER THAN 20 kg/ha.yr SULPHATE DEPOSITION

	Annual Growth $m^3.10^3$ (Percent of Provincial Total)	
	Sulphate Deposition kg/ha.yr	
	20-40	>40
Ontario	12,544(28)	998(2)
Quebec	29,659(36)	4,438(5)
New Brunswick	11,474(100)	0(0)
Nova Scotia	7,077(100)	0(0)
Prince Edward Island	443(100)	0(0)
Newfoundland	3,456(67)	0(0)

An inventory of man-made structures must distinguish between renewable materials and cultural materials. Renewable materials are those which are easily replaceable. They include such items as surface coatings (paint), chain link fence and galvanized roofing. Cultural materials are those which are difficult to replace because of the scarcity of material and requirements for skilled craftsmen to recreate the resource. They include such items as sculptured stone and metals and dimension stone. There are several materials (e.g., adobe, plaster concrete and unit masonry) which could fall into either category depending on the craftsmanship requirements.

There is no national inventory of renewable materials which are susceptible to acidic deposition. Past efforts to create a national inventory for urban areas have combined per capita material estimates, based on limited survey data, and census data on population distribution. Although this approach to creating an inventory of renewable resources has been used, the resulting urban inventories are of questionable value due to the uncertainties associated with the per capita material estimates (Koontz et al. 1981; Stankunas et al. 1981). Results in two Standard Metropolitan Statistical Areas (SMSA) indicate that the area of urban development and local availability of materials are important factors in the distribution of material quantities. There are no estimates of renewable materials in rural areas. Until additional survey work is complete, the Work Group cannot provide an acceptable national inventory of renewable materials or an estimate of materials by sulphur deposition regimes.

Complete national inventories of cultural materials are not available for either Canada or the U.S. Such national inventories would include all significant cultural materials, both historic and contemporary. The only inventory of cultural materials that can be assembled at this time is one of major historical resources. Both the U.S. and Canada maintain lists of significant historic sites and artifacts. The limitations of these sources are that they are incomplete in not listing all significant materials, such as sculpted stone and metals in urban areas and that the data on those items is not always adequate for an analysis of potential damage from air pollution.

8.5.1 U.S. Historic Inventory

The Work Group compiled a general U.S. inventory of historic resources based on Federal data sources. These sources were the National Register of Historic Places (U.S. Federal Register 1979, 1980, 1981, 1982), National Historic Landmarks (USDI 1976) and National Historic Parks (USDI 1982). The National Register of Historic Places includes sites because of their association with an event or person, of their architectural or engineering qualities, or of their potential contribution to historic studies. It consists of approximately 26,000 sites and is the most comprehensive of all three sources. National Historic Landmarks are those historic places designated by the Secretary of Interior to be of national significance. It consists of about 1,500 sites. National Historic Parks is used as a generic designation of properties of national sigificance owned by the Federal government. It includes historic sites, military battlefields and historic monuments and numbers about 150 sites.

The Work Group cross-classified historical resources by three ambient SO_2 categories at the county level. The three ambient categories at the county level were chosen arbitrarily because there is no SO_2 standard designated for protecting materials resources nor did the Material Effects Work Group establish damage functions for material damages (see Section 5). The results of the tabulation are summarized by state in Table 8-14. The sum of all such sites in the three ambient categories is the total for each state. No attempt was made to distinguish a major and minor site within each category so the numbers should be interpreted with great care.

Only historic sites in seven out of the 38 states under consideration experience ambient SO_2 concentrations greater than 80 $\mu g/m^3$. Within those states, the majority of historic places, landmarks and monuments are located in counties with ambient SO_2 concentrations less than 60 $\mu g/m^3$. Only in the states of Illinois and New York are there more than 20% of the historic sites in counties with ambient concentrations greater than 80 $\mu g/m^3$. In total, approximately 3% of the historic places, 3% of the historic landmarks and 2% of the historic parks and monuments are located in counties with ambient concentrations greater than 80 $\mu g/m^3$.

8.5.2 Canadian Historic Inventory

For the purposes of this inventory, there are three categories (i.e., national historic sites, buildings and museums, and monuments and parks). Data for all of these categories are available only for Ontario. For the other provinces of eastern Canada, only national historic sites are included. These have been further subdivided into two deposition regimes; under 40 and over 40 kg/ha.yr. Although with structures, concentrations of SO_2 (in $\mu g/m^3$) is perhaps more appropriate, no ambient air quality data are available from which areas of uniform concentrations can be drawn. Generally, higher levels (i.e., above 55 $\mu g/m^3$ of SO_2) are found in the major cities, and even then the annual averages are much lower.

The inventory data presented in Table 8-15 indicate that the majority of national historic sites in areas of high deposition are found in Ontario, with the balance in Quebec, in the vicinity of Quebec City, the oldest settlement in eastern North America.

TABLE 8-14. U.S. HISTORIC SITES BY AMBIENT SO_2 ($\mu g/m^3$) (USDI 1976; USEPA 1980)

	Historic Places			Historic Landmarks			Historic Parks		
	<60	60-80	>80	<60	60-80	>80	<60	60-80	>80
REGION I									
Connecticut	459	-	-	29	-	-	-	-	-
Maine	384	170	36	23	-	1	-	-	-
Massachusetts	649	-	-	105	-	-	9	-	-
New Hampshire	226	-	6	16	-	12	1	-	-
Rhode Island	324	-	-	23	-	-	2	-	-
Vermont	297	-	-	10	-	-	-	-	-
REGION II									
New Jersey	485	-	-	23	-	-	4	-	-
New York	827	126	211	87	-	16	9	1	3
REGION III									
Delaware	273	-	-	11	-	-	-	-	-
Dist. of Col.	224	-	-	37	-	-	12	-	-
Maryland	510	-	-	42	-	-	9	-	-
Pennsylvania	1,201	-	163	66	-	-	12	5	-
Virginia	916	-	-	78	-	-	12	-	-
W. Virginia	255	-	2	3	-	-	2	-	-
REGION IV									
Alabama	303	-	-	14	-	-	2	-	-
Florida	363	-	-	15	-	-	-	-	-
Georgia	705	-	-	25	-	-	6	-	-
Kentucky	543	142	-	11	3	-	3	-	-
Mississippi	426	-	-	15	-	-	3	-	-
North Carolina	617	-	-	19	-	-	5	-	-
South Carolina	460	-	-	59	-	-	3	-	-
Tennessee	465	1	-	18	-	-	6	-	-
REGION V									
Illinois	419	-	148	18	-	12	1	-	-
Indiana	326	27	9	7	-	1	1	-	-
Michigan	468	-	-	7	-	-	-	-	-
Ohio	1,193	404	16	25	-	1	1	-	-
Wisconsin	603	-	-	12	-	-	-	-	-
REGION VI									
Arkansas	409	-	-	2	-	-	3	-	-
Louisiana	367	-	-	34	-	-	3	-	-
Oklahoma	357	-	-	13	-	-	1	-	-
Texas	731	-	-	21	-	-	5	-	-

TABLE 8-14. CONTINUED

	Historic Places			Historic Landmarks			Historic Parks		
	<60	60-80	>80	<60	60-80	>80	<60	60-80	>80
REGION VII									
Iowa	497	22	-	9	-	-	1	-	-
Kansas	292	-	-	14	-	-	2	-	-
Missouri	550	20	-	19	2	-	3	-	-
Nebraska	279	-	-	14	-	-	1	-	-
REGION VIII									
North Dakota	106	-	-	1	-	-	2	-	-
South Dakota	209	-	-	10	-	-	-	-	-
TOTAL	18,766	912	591	948	5	33	124	6	3

TABLE 8-15. CANADIAN HISTORIC INVENTORY BY PROVINCE AND DEPOSITION (OMCR 1978; Parks Canada 1981)

	Sulphate	National Historic Sites		Buildings and Museums		Monuments and Parks	
Province	Deposition (kg/ha.yr)	<40	>40	<40	>40	<40	>40
Ontario		21	23	129	72	8	3
Quebec		13	5	N/A		N/A	
Prince Edward Island		4		N/A		N/A	
Nova Scotia		13		N/A		N/A	
New Brunswick		2		N/A		N/A	
Newfoundland		6		N/A		N/A	
TOTAL		59	28				

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APPENDIX TABLE 8-1. U.S. AQUATIC RESOURCES BY STATE AND SENSITIVITY CATEGORY (km^2) 10-20 kg/ha.yr SULPHATE DEPOSITION (USDA 1971, 1978)

	Low Potential to Reduce Acidity	Moderate Potential to Reduce Acidity	High Potential to Reduce Acidity	Total Surface Water Area in the State
REGION III				
Virginia	10	20	40	2,950
West Virginia	10	0	0	480
REGION IV				
Florida	0	100	9,560	13,130
Georgia	280	210	180	3,000
REGION V				
Illinois[a]	0	0	0	2,110
Michigan	1,350	0	190	4,180
Minnesota	1,460	8,440	890	13,810
Wisconsin	2,310	1,240	240	5,420
REGION VI				
Oklahoma	0	0	1,170	4,440
Texas	0	0	1,060	15,260
REGION VII				
Iowa[a]	0	0	0	990
Kansas	0	0	1,000	3,140
Missouri[a]	0	0	0	2,770
Nebraska[a]	0	0	0	2,330
REGION VIII				
North Dakota	0	620	200	4,540
South Dakota	0	410	1,210	4,240
TOTAL	5,420	11,040	15,740	82,790

[a] These states are included, even though they do not have surface water area in counties falling into one of the three sensitivity categories, because they have surface water area falling into the urban/agricultural category receiving 10-20 kg sulphate/ha.yr.

APPENDIX TABLE 8-2. U.S. AQUATIC RESOURCES BY STATE AND SENSITIVITY CATEGORY (km^2) 20-40 kg/ha.yr SULPHATE DEPOSITION (USDA 1971, 1978)

	Low Potential to Reduce Acidity	Moderate Potential to Reduce Acidity	High Potential to Reduce Acidity	Total Surface Water Area in the State
REGION I				
Connecticut	340	0	0	500
Maine	6,010	0	0	6,010
Massachusetts	970	0	0	1,100
New Hampshire	860	0	0	860
Rhode Island	340	0	0	460
Vermont	720	0	0	1,000
REGION II				
New Jersey	150	660	10	920
New York	1,930	1,050	520	5,260
REGION III				
Delaware	0	0	0	330
Dist. of Columbia[b]	0	0	0	0
Maryland	0	1,020	80	1,900
Pennsylvania	40	300	400	1,620
Virginia	70	1,600	840	2,950
W. Virginia	110	20	120	480
REGION IV				
Alabama	10	1,280	1,590	3,040
Florida	0	410	960	13,130
Georgia	250	1,660	560	3,000
Kentucky	30	140	410	2,320
Mississippi	60	970	620	2,470
North Carolina	310	9,010	1,110	10,480
South Carolina	0	640	2,100	2,750
REGION V				
Illinois	0	0	90	2,110
Indiana	0	40	150	930
Michigan	1,650	0	140	4,180
Ohio	0	0	20	970
Wisconsin[b]	0	0	0	5,420
Tennessee	90	100	1,440	3,140
REGION VI				
Arkansas	0	180	500	3,670
Louisiana	0	0	10,050	11,390
Oklahoma	0	880	1,330	4,440
Texas	0	10	3,040	15,260

APPENDIX TABLE 8-2. CONTINUED

	Low Potential to Reduce Acidity	Moderate Potential to Reduce Acidity	High Potential to Reduce Acidity	Total Surface Water Area in the State
REGION VII				
Iowa[b]	0	0	0	990
Kansas[b]	0	0	0	3,140
Missouri	0	0	1,320	2,770
TOTAL	13,940	19,970	27,400	107,890

[a] The states of Minnesota (13,810 km^2), Nebraska (2,330 km^2), North Dakota (4,540 km^2) and South Dakota (4,240 km^2) received less than 20 kg/ha.yr sulphate deposition in 1979-80.

[b] These states are included, even though they do not have surface water area in counties falling into one of the three sensitivity categories because they have surface water area falling into the urban/ agricultural category receiving 20-40 kg sulphate/ha.yr.

APPENDIX TABLE 8-3. U.S. AQUATIC RESOURCES BY STATE AND ACID SENSITIVITY CATEGORY (km^2) FOR GREATER THAN 40 kg/ha.yr SULPHATE DEPOSITION (USDA 1971, 1978)

	Low Potential to Reduce Acidity	Moderate Potential to Reduce Acidity	High Potential to Reduce Acidity	Total Surface Water Area in the State
REGION II				
New York	0	200	0	5,260
REGION III				
Maryland	20	0	0	1,900
Pennsylvania	0	250	220	1,620
W. Virginia	10	0	210	480
REGION IV				
Kentucky	0	260	480	2,320
Mississippi	0	90	10	2,470
Tennessee	0	10	640	3,140
REGION V				
Illinois	0	0	80	2,110
Indiana	10	0	0	930
Michigan	40	0	40	4,180
Ohio	0	0	360	970
REGION VI				
Arkansas	130	1,170	400	3,670
Louisiana	0	0	1,050	11,390
Oklahoma	0	210	0	4,440
Texas	0	0	4,050	15,260
REGION VII				
Missouri	0	0	80	2,770
TOTAL	210	2,190	7,620	62,910

APPENDIX TABLE 8-4. U.S. AGRICULTURE RESOURCES IN AREAS RECEIVING 10-20 kg/ha.yr OF SULPHATE DEPOSITION (YIELDS IN KILOGRAMS 10^3) (USDC 1979)

	Corn	Soybean	Hay	Wheat	Tobacco	Potatoes
REGION III						
Virginia	23,300	100	126,700	1,500	1,900	100
W. Virginia	4,300	0	23,300	300	300	200
REGION IV						
Florida	277,300	466,200	500,500	0	9,500	223,200
Georgia	123,600	26,300	33,800	500	6,200	223,200
REGION V						
Illinois	216,500	5,400	180,300	400	0	0
Michigan	16,100	50	249,100	700	0	40,500
Minnesota	14,470,700	3,332,600	6,614,600	2,202,900	0	734,000
Wisconsin	4,735,700	60,800	9,397,200	1,900	0	67,000
REGION VI						
Oklahoma	16,800	32,500	1,325,200	2,165,800	0	0
Texas	61,600	100	401,900	102,300	0	0
REGION VII						
Iowa	33,192,600	6,886,300	5,836,000	20,900	0	0
Kansas	1,299,400	605,900	3,003,300	4,282,500	0	0
Missouri	1,830,200	1,286,500	1,418,100	105,600	0	0
Nebraska	15,826,200	1,022,600	4,741,700	797,500	0	0
REGION VIII						
North Dakota	507,000	113,100	3,936,700	6,367,800	0	1,050,100
South Dakota	4,234,300	310,400	5,537,200	1,581,900	0	0
TOTAL	76,745,700	13,729,300	43,325,700	17,649,700	17,600	2,724,200

APPENDIX TABLE 8-5. AGRICULTURE RESOURCES IN AREAS RECEIVING 20-40 kg/ha.yr OF SULPHATE DEPOSITION (YIELDS IN KILOGRAMS 10^3) (USDC 1979)

	Corn	Soybean	Hay	Wheat	Tobacco	Potatoes
REGION I						
Connecticut	0	0	173,000	0	211,400	23,100
Maine	0	0	333,200	0	0	1,127,100
Massachusetts	0	0	221,973	0	0	29,300
New Hampshire	0	0	155,100	0	0	0
Rhode Island	0	0	19,000	0	0	0
Vermont	0	0	769,000	0	0	0
REGION II						
New Jersey	199,000	143,800	268,400	19,100	0	0
New York	881,900	0	3,400,200	34,300	0	410,499
REGION III						
Delaware	378,300	202,800	41,700	15,400	0	0
District of Columbia	-	-	-	-	-	-
Maryland	1,406,700	312,600	486,900	70,600	11,900	0
Pennsylvania	2,492,600	60,500	3,017,000	156,600	9,700	171,600
Virginia	1,267,300	353,300	1,264,500	11,900	57,500	108,800
W. Virginia	87,100	0	261,300	2,700	600	0
REGION IV						
Alabama	577,200	849,600	933,600	39,000	0	100,300
Florida	104,300	164,400	80,600	0	200	1,000
Georgia	1,826,600	710,600	821,700	84,300	44,800	0
Kentucky	768,300	132,800	872,500	22,800	61,200	0
Mississippi	103,100	1,201,000	768,900	14,100	0	0
North Carolina	2,887,600	953,700	611,700	117,100	372,200	0
South Carolina	743,100	792,200	367,900	47,800	64,600	0
Tennessee	447,900	202,300	1,192,100	41,600	37,800	0

APPENDIX TABLE 8-5. CONTINUED

	Corn	Soybean	Hay	Wheat	Tobacco	Potatoes
REGION V						
Illinois	29,420,400	7,921,500	25,115,200	804,800	0	0
Indiana	14,898,600	3,262,500	1,568,800	492,800	44,000	0
Michigan	2,407,200	258,400	1,806,800	179,900	0	291,900
Ohio	351,800	16,500	372,800	27,700	0	11,900
Wisconsin	2,590,400	118,800	2,314,000	22,200	0	27,100
REGION VI						
Arkansas	2,100	22,700	457,400	4,600	0	0
Louisiana	4,500	1,844,400	374,500	4,700	0	0
Oklahoma	6,400	93,700	877,700	54,700	0	0
Texas	100,700	105,700	1,073,300	300,900	0	0
REGION VII						
Iowa	22,008,900	345,400	268,600	4,200	0	0
Kansas	13,100	85,100	53,700	49,900	0	0
Missouri	2,286,300	155,300	3,497,300	343,800	0	0
TOTAL	68,404,000	21,708,300	31,240,200	3,094,000	666,900	2,304,600

APPENDIX TABLE 8-6. U.S. AGRICULTURE RESOURCES IN AREAS RECEIVING MORE THAN 40 kg/ha.yr SULPHATE DEPOSITION (YIELDS IN KILOGRAMS 10^3) (USDC 1979)

	Corn	Soybean	Hay	Wheat	Tobacco	Potatoes
REGION II						
New York	404,700	0	963,600	25,300	0	110,500
REGION III						
Maryland	7,900	0	49,400	200	0	0
Pennsylvania	392,900	2,700	95,500	15,000	0	45,500
W. Virginia	52,200	0	365,000	1,800	300	2,000
REGION IV						
Kentucky	2,027,300	839,500	1,604,700	140,000	142,000	0
Mississippi	21,500	805,700	101,600	34,200	0	0
Tennessee	621,600	1,133,100	470,700	96,700	19,300	0
REGION V						
Illinois	390,800	263,400	147,800	45,900	0	0
Indiana	1,107,600	405,900	1,604,700	110,300	1,900	0
Michigan	2,268,100	316,600	1,209,600	218,300	0	57,300
Ohio	8,565,100	3,276,900	2,722,880	967,600	9,100	47,700
REGION VI						
Arkansas	26,500	2,850,200	780,900	232,200	0	0
Louisiana	3,200	200,300	244,400	5,000	0	0
Oklahoma	100	8,000	44,000	1,400	0	0
Texas	312,900	176,200	1,978,200	37,400	0	0
REGION VII						
Missouri	430,100	991,800	268,200	27,700	0	0
TOTAL	16,742,300	11,270,400	12,186,600	2,208,300	263,100	172,700

APPENDIX TABLE 8-7. U.S. AGRICULTURAL RESOURCES - STATE TOTALS FOR SIX CROPS (YIELD IN KILOGRAMS 10^3) (USDC 1979)

	Corn	Soybean	Hay	Wheat	Tobacco	Potatoes
REGION I						
Connecticut	0	0	0	0	2,113	23,059
Maine	0	0	33,320	0	0	0
New Hampshire	0	0	155,100	0	0	0
Rhode Island	0	0	19,000	0	0	0
Vermont	0	0	769,000	0	0	0
REGION II						
New Jersey	199,000	143,800	268,400	19,100	0	0
New York	1,286,500	0	4,363,800	59,600	0	520,900
REGION III						
Delaware	378,300	202,800	41,700	15,300	0	0
District of Columbia	-	-	-	-	-	-
Maryland	1,414,600	312,600	536,000	70,800	11,900	0
Pennsylvania	2,885,500	63,100	3,971,500	171,600	9,700	217,200
Virginia	1,290,600	353,400	1,391,200	120,000	59,400	109,000
W. Virginia	143,600	0	649,800	4,800	900	5,300
REGION IV						
Alabama	5,771,200	849,600	933,600	39,000	0	100,300
Florida	381,600	211,000	58,100	0	9,600	223,300
Georgia	1,950,300	736,900	855,500	84,800	51,000	0
Kentucky	21,795,500	972,300	2,477,200	162,900	203,200	0
Mississippi	124,700	2,006,600	870,500	48,300	0	0
North Carolina	288,800	953,700	611,700	117,100	372,200	0
South Carolina	743,100	792,200	367,900	47,800	64,500	0
Tennessee	1,069,500	1,335,300	1,662,800	138,300	57,100	0

APPENDIX TABLE 8-7. CONTINUED

	Corn	Soybean	Hay	Wheat	Tobacco	Potatoes
REGION V						
Illinois	30,027,600	8,190,300	2,843,300	851,100	0	0
Indiana	15,916,200	3,668,400	1,849,500	603,200	6,300	0
Michigan	4,691,400	575,100	3,265,600	399,000	0	389,700
Minnesota	144,070,700	3,332,600	6,614,600	2,202,099	0	734,000
Ohio	8,916,900	3,293,500	3,095,200	995,300	9,100	59,600
Wisconsin	7,326,100	179,500	11,711,300	41,400	0	703,200
REGION VI						
Arkansas	28,600	2,872,900	1,238,300	236,800	0	0
Louisiana	48,600	2,044,700	618,900	9,600	0	0
Oklahoma	94,600	135,700	2,637,700	3,389,200	0	0
Texas	2,916,900	424,600	4,700,500	1,495,200	0	0
REGION VII						
Iowa	35,303,500	7,231,600	6,104,600	25,100	0	0
Kansas	3,862,000	717,900	4,620,300	7,305,000	0	0
Missouri	4,656,600	3,831,300	5,183,600	736,300	0	0
Nebraska	17,915,100	1,024,900	6,121,500	1,979,700	0	0
REGION VIII						
North Dakota	511,100	113,300	4,456,000	7,301,300	0	1,052,800
South Dakota	4,282,800	310,400	6,206,400	1,747,100	0	0
TOTAL	169,096,200	46,889,300	91,968,600	30,417,400	857,200	5,294,600

APPENDIX TABLE 8-8. U.S. FOREST RESOURCES IN AREAS RECEIVING 20-40 kg/ha.yr SULPHATE DEPOSITION - VOLUME ($m^3.10^3$) (Olson et al. 1980)

	Total Volume	Softwood Volume	Hardwood Volume	Total Volume in State[a]
REGION I				
Connecticut	66,600	10,100	56,500	66,600
Maine	601,800	418,000	183,800	601,800
Massachusetts	96,100	35,900	60,200	96,100
New Hampshire	186,300	88,900	97,400	186,300
Rhode Island	9,800	2,100	7,700	9,800
Vermont	133,900	48,600	85,300	133,900
REGION II				
New Jersey	41,600	7,300	34,300	41,600
New York	303,600	84,100	219,500	345,400
REGION III				
Delaware	16,600	5,200	11,400	16,600
District of Columbia	-	-	-	-
Maryland	91,100	22,000	69,000	98,900
Pennsylvania	445,600	28,500	417,200	625,800
Virginia	509,600	144,000	365,600	548,600
W. Virginia	251,800	17,300	234,500	382,700
REGION IV				
Alabama	572,300	319,500	252,800	572,300
Florida	75,900	48,100	27,800	367,100
Georgia	647,000	370,300	276,700	714,600
Kentucky	200,700	-	-	324,000
Mississippi	440,600	239,700	201,000	486,000
North Carolina	702,400	294,000	408,400	702,400
South Carolina	486,500	252,800	233,700	486,500
Tennessee	192,400	44,300	148,100	294,400
REGION V				
Illinois	51,200	100	51,100	66,400
Indiana	93,900	1,700	92,200	99,200
Michigan	184,800	33,400	151,500	425,400
Ohio	5,200	100	5,100	118,500
Wisconsin	8,200	500	7,700	315,400

APPENDIX TABLE 8-8. CONTINUED

	Total Volume	Softwood Volume	Hardwood Volume	Total Volume in State[a]
REGION VI				
Arkansas	56,700	11,200	45,500	252,000
Louisiana	278,600	132,500	146,100	472,800
Oklahoma	39,900	17,300	22,600	58,400
Texas	6,900	3,800	3,100	315,800
REGION VII				
Iowa	3,500	-	-	29,900
Kansas	600	0	600	8,400
Missouri	127,600	6,600	121,000	172,100
TOTAL	6,929,500	2,688,000	4,037,400	9,435,700

[a] Under all deposition regimes.

APPENDIX TABLE 8-9. U.S. FOREST RESOURCES IN AREAS RECEIVING 20-40 kg/ha.yr SULPHATE DEPOSITION - GROWTH ($m^3.10^3$) (Olson et al. 1980)

	Total Growth	Softwood Growth	Hardwood Growth	Total Growth in State[a]
REGION I				
Connecticut	1,700	300	1,400	1,700
Maine	18,000	14,000	4,000	18,000
Massachusetts	3,100	1,200	2,000	3,200
New Hampshire	6,700	3,600	3,140	6,700
Rhode Island	300	100	200	300
Vermont	3,000	1,300	1,700	3,000
REGION II				
New Jersey	700	200	500	700
New York	-	-	-	-
REGION III				
Delaware	500	1,300	400	500
District of Columbia	-	-	-	-
Maryland	-	-	-	-
Pennsylvania	-	-	-	-
Virginia	21,400	6,500	14,900	23,000
W. Virginia	-	-	-	-
REGION IV				
Alabama	33,600	22,300	11,300	33,600
Florida	4,400	3,400	1,000	21,500
Georgia	40,800	29,400	11,400	44,500
Kentucky	-	-	-	-
Mississippi	26,100	15,800	10,300	28,700
North Carolina	31,900	15,200	16,700	31,900
South Carolina	27,300	17,500	9,800	27,300
Tennessee	9,400	2,500	6,900	14,400
REGION V				
Illinois	1,900	0	1,900	2,400
Indiana	-	-	-	-
Michigan	-	-	-	-
Ohio	-	-	-	-
Wisconsin	-	-	-	-

APPENDIX TABLE 8-9. CONTINUED

	Total Growth	Softwood Growth	Hardwood Growth	Total Growth in State[a]
REGION VI				
Arkansas	-	-	-	-
Louisiana	14,300	8,400	5,900	26,300
Oklahoma	2,400	1,000	1,400	3,400
Texas	300	200	100	18,300
REGION VII				
Iowa	-	-	-	-
Kansas	-	-	-	-
Missouri	2,700	300	3,400	5,100
TOTAL	251,500	143,100	108,400	314,500

[a] Under all deposition regimes.

APPENDIX TABLE 8-10. U.S. FOREST RESOURCES IN AREAS RECEIVING GREATER THAN 40 kg/ha.yr SULPHATE DEPOSITION - VOLUME ($m^3.10^3$) (Olson et al. 1980)

	Total Volume	Softwood Volume	Hardwood Volume	Total Volume in State[a]
REGION II				
New York	41,900	6,000	35,900	345,400
REGION III				
Maryland	7,800	400	7,400	98,900
Pennsylvania	180,200	8,600	171,600	625,800
W. Virginia	125,400	10,500	114,900	382,700
REGION IV				
Kentucky	123,300	-	-	324,000
Mississippi	45,400	13,200	32,200	486,000
Tennessee	102,000	6,600	95,300	294,400
REGION V				
Illinois	14,200	400	13,800	66,400
Indiana	5,300	0	5,300	99,200
Michigan	25,800	1,000	24,800	425,400
Ohio	113,300	3,200	110,100	118,500
REGION VI				
Arkansas	195,300	80,900	144,400	252,000
Louisiana	194,200	123,500	70,700	472,800
Oklahoma	18,500	11,300	7,200	58,400
Texas	308,900	205,700	103,200	315,800
REGION VII				
Missouri	35,000	3,900	31,100	172,100
TOTAL	1,536,500	475,300	937,800	45,378,000

[a] Under all deposition regimes.

APPENDIX TABLE 8-11. U.S. FOREST RESOURCES IN AREAS RECEIVING GREATER THAN 40 kg/ha.yr SULPHATE DEPOSITION - GROWTH ($m^3.10^3$) (Olson et al. 1980)

	Total Growth	Softwood Growth	Hardwood Growth	Total Growth in State[a]
REGION II				
New York	-	-	-	-
REGION III				
Maryland	-	-	-	-
Pennsylvania	-	-	-	-
W. Virginia	-	-	-	-
REGION IV				
Kentucky	-	-	-	-
Mississippi	2,600	900	1,700	28,700
Tennessee	5,100	500	4,600	14,400
REGION V				
Illinois	400	0	400	2,400
Indiana	-	-	-	-
Michigan	-	-	-	-
Ohio	-	-	-	-
REGION VI				
Arkansas	-	-	-	-
Oklahoma	900	500	400	3,400
Louisiana	12,000	8,700	3,300	26,300
Texas	18,000	12,000	6,000	18,300
REGION VII				
Missouri	1,100	100	1,000	5,100
TOTAL	40,100	22,800	17,300	98,600

[a] Under all deposition regimes.

APPENDIX TABLE 8-12. 1980 CANADIAN AGRICULTURAL PRODUCTION BY CROP AND PROVINCE FOR DEPOSITION ZONE 10-20 kg/ha.yr

Deposition Zone 10-20 kg/ha.yr	Wheat	Oats	Barley	Grain Corn	Fodder Corn	Soybeans	Potatoes	Tobacco	Cabbage	Lettuce	Spinach	Hay
ONTARIO												
Crops grown 1976 (hectares)	205	8,159	2,437	-	75	-	466	-	6.5	-	-	40,095
Yield 1980 ('000 metric ton)	.26	17.1	15.0	-	1.4	-	4.4	-	.12	-	-	175
Farm Value (1980 $000)	$28	$2,568	$2,143	-	$25	-	$1,038	-	$32	-	-	$9,207
QUEBEC												
Crops grown 1976, (hectares)	605	9,508	1,391	27	32	-	166	2	2.5	-	-	49,958
Yield 1980 ('000 metric ton)	4.0[b]	7.7[a]	9.6[b]	not available	not available	-	3.3[a]	-	.06[b]	-	-	244[b]
Farm Value[c] (1980 $000)	$432	$1,068	$1,279	-	-	-	$569	-	$6.5	-	-	$12,064
TOTAL Zone 10-20 kg/ha.yr												
Crops grown 1976 (hectares)	810	17,667	3,823	27	107	-	632	2	9	-	-	90,053
Yield 1980 ('000 metric ton)	4.2	24.9	24.6	-	1.4	-	7.6	-	.18	-	-	419
Farm Value (1980 $000)	$460	$3,636	$3,422	-	$25	-	$1,607	-	$38.5	-	-	$21,271

[a] Based on 1977 regional totals and 1980 province wide figures

[b] Production based on provincial total and assumed in proportion to hectares grown

[c] Dollar values based on Ontario 1980 average value per unit crop

Source: OMAF 1981a,b
QBS 1978
Statistics Canada 1976a,b, 1981a,b

APPENDIX TABLE 8-13. 1980 CANADIAN AGRICULTURAL PRODUCTION BY CROP AND PROVINCE FOR DEPOSITION ZONE 20-40 kg/ha.yr

Deposition Zone 20-40 kg/ha.yr	Wheat	Oats	Barley	Grain Corn	Fodder Corn	Soybeans	Potatoes	Tobacco	Cabbage	Lettuce	Spinach	Hay
ONTARIO												
Crops grown 1976, (hectares)	52,651	106,268	39,822	123,105	113,671	1,708	4,046	13,400	774	268	174	532,044
Yield 1980 ('000 metric ton)	185	16.8	168	1,797	2,829	44	73	40	31	6.130	1.196	3,245
Farm Value (1980 $000)	$20,188	$24,391	$22,508	$154,211	$55,795	$10,429	$11,819	$120,906	$5,013	$2,276	$588	$164,136
QUEBEC												
Crops grown 1976 (hectares)	25,747	183,464	11,857	56,931	73,914	216	11,167	3,816	2,234	1,172	129	595,240
Yield 1980 ('000 metric ton)	170[c]	258[a]	82[c]	478[c]	2,546[c]	not available	226[a]	13.2[d]	56	19.953	.775	2,890
Farm Value[b] (1980 $000)	18,560	$35,854	$10,895	$72,771	$46,315	-	$39,310	$29,906 (1977)	$6,072	$3,702	$260	$143,009
NEW BRUNSWICK												
Crops grown 1976 (hectares)	2,304	18,617	2,823	108	2,427	4	22,308	138	117	32	-	70,000
Yield 1980 ('000 metric ton)	12.3	26.5	9.6	-	74	-	526	.25	2.3	.225	-	321
Farm Value (1980 $000)	$353	$1,274	$378	-	not available	-	$66,402	not available	$588	$225	-	$15,859

APPENDIX TABLE 8-13. CONTINUED

Deposition Zone 20-40 kg/ha.yr	Wheat	Oats	Barley	Grain Corn	Fodder Corn	Soybeans	Potatoes	Tobacco	Cabbage	Lettuce	Spinach	Hay
NOVA SCOTIA												
Crops grown 1976 (hectares)	1,498	9,545[f]	1,823[f]	1,620	4,050	17[f]	1,459[e]	243	142	28	-	73,000
Yield 1980 ('000 metric tons)	9.8	16.2	5.9	not available	122	-	33	.54	3.1	.207	-	361
Farm Value (1980 $000)	$604	$187	$72	-	$2,500 est	-	$3,678	$1,680	$405	$96	-	$17,830[b]
PRINCE EDWARD ISLAND												
Crops grown 1976 (hectares)	6,501	17,742	10,542	262	3,240[f]	-	20,818	1,620[g]	45[e]	12[e]	-	53,000
Yield 1980 ('000 metric tons)	15.8	46	50	not available	94	-	591	2.2	1.1	.167	-	269
Farm Value (1980 $000)	$420	$881	$1,943	-	not available	-	$95,236	$7,000	$236	$52	-	$13,261[b]
NEWFOUNDLAND												
Crops grown 1976 (hectares)	17	245	11	-	10	-	741	-	158[e]	-	-	2,239
Yield 1980 ('000 metric tons)	-	not available	-	-	-	-	3.0	-	3.0	-	-	not available
Farm Value (1980 $000)	-	-	-	-	-	-	$765	-	$688	-	-	-"-

APPENDIX TABLE 8-13. CONTINUED

Deposition Zone 20-40 kg/ha.yr	Wheat	Oats	Barley	Grain Corn	Fodder Corn	Soybeans	Potatoes	Tobacco	Cabbage	Lettuce	Spinach	Hay
TOTAL Zone 20-40 kg/ha.yr												
Crops grown 1976 (hectares)	88,718	339,751	66,878	181,569	199,687	1,945	60,992	18,974	3,470	1,512	303	1,325,520
Yield 1980 ('000 metric tons)	394	524	316	2,274	5,667	43.9	1,452	57	96	26.686	1.995	7,087
Farm Value (1980 $000)	$40,125	$62,587	$35,796	$226,982	$104,610	$10,429	$217,210	$159,492	$12,972	$6,351	$848	$354,095

[a] Based on 1977 regional totals and 1980 province wide figures

[b] Dollar values based on Ontario 1980 average value per unit crop

[c] Production based on provincial total and assumed to be in proportion to hectares of crops grown

[d] 1977.

[e] 1979.

[f] 1981.

[g] 1980.

Source: N.B. Telephone Inquiry
Nfld. Telephone Inquiry
N.S. Telephone Inquiry
P.E.I. Telephone Inquiry
OMAF 1981a,b
QBS 1978
Statistics Canada 1976a-f, 1981a,b

APPENDIX TABLE 8-14. 1980 CANADIAN AGRICULTURAL PRODUCTION BY CROP AND PROVINCE FOR DEPOSITION ZONE >40 kg/ha.yr

Deposition Zone >40 kg/ha.yr	Wheat	Oats	Barley	Grain Corn	Fodder Corn	Soybeans	Potatoes	Tobacco	Cabbage	Lettuce	Spinach	Hay
ONTARIO												
Crops grown 1976 (hectares)	159,917	92,495	105,000	536,598	237,731	149,377	13,955	20,758	489	315	114	520,600
Yield 1980 ('000 metric tons)	775	152	340	3,675	6,326	919	288	58	19.4	7.654	.949	3,808
Farm Value (1980 $000)	$84,348	$20,958	$45,104	$560,864	$130,447	$218,070	$44,438	$174,329	$2,424	$2,711	$355	$186,171
QUEBEC												
Crops grown 1976 (hectares)	5,084	102,011	4,836	4,597	28,762	14	4,932	5	163	86	10	405,767
Yield 1980 ('000 metric tons)	33.7[c]	97[a]	33.3[c]	41.5[c]	989[c]	-	96[a]	-	4.1[c]	1.457[c]	.059[c]	1,964[c]
Farm Value[b] (1980 $000)	$3,672	$13,414	$4,434	$6,327	$18,002	-	$16,685	-	$443	$270	$19	$97,013
MARITIMES		- no deposition of 40+ kg/ha.yr -										
TOTAL Zone 40+ kg/ha.yr												
Crops grown (1976 hectares)	165,001	194,506	109,836	541,555	266,493	149,391	18,887	20,763	652	401	124	926,367
Yield 1980 ('000 metric tons)	809	248	374	3,716	7,316	919	384	58	23.4	9.107	1.008	5,772
Farm Value (1980 $000)	$88,020	$34,372	$49,538	$567,191	$148,449	$218,070	$61,123	$174,329	$2,867	$2,981	$374	$283,184

[a] Based on 1977 regional totals and 1980 province wide values
[b] $ values based on Ontario 1980 average value per unit crop
[c] Production based on provincial total; production assumed in proportion to hectares grown

Source: OMAF 1981a,b
QBS 1978
Statistics Canada 1976a,b; 1981a,b

APPENDIX TABLE 8-15. SULPHATE DEPOSITION FOR FOREST RESOURCES BY PROVINCE[a]

Province	Sulphate Deposition (kg/ha.yr)	Absolute Area ('000 ha)	Mean Annual Increment[b] m^3/ha	Total Annual Yield (000s)m^3	Annual Yield by Type ('000 m^3)			Value $000 ($ 1981 Cdn.)
					Soft	Mixed	Hard	
Ontario	10-20	18,600	1.7	31,065	26,219	124	4,722	815,456
	20-40	7,095	1.8	12,544	4,855	2,007	5,682	329,280
	>40	444	2.9	998	425	-	573	26,198
Quebec	10-20	34,061	1.2	47,363	39,074	7,957	332	1,243,279
	20-40	15,998	1.9	29,659	10,648	15,423	3,589	778,549
	>40	2,048	2.1	4,438	426	2,760	1,252	116,498
New Brunswick	10-20	-	-	-	-	-	-	-
	20-40	5,928	2.1	11,474	4,475	5,278	1,721	301,193
	>40	-	-	-	-	-	-	-
Newfoundland	10-20	2,570	.7	1,734	1,460	246	28	45,518
	20-40	2,637	1.3	3,456	2,976	370	111	90,720
	>40	-	-	-	-	-	-	-
Nova Scotia	10-20	-	-	-	-	-	-	-
	20-40	4,441	1.6	7,077	3,730	2,003	1,345	185,771
	>40	-	-	-	-	-	-	-
Prince Edward Island	10-20	-	-	-	-	-	-	-
	20-40	247	1.7	433	130	260	43	-
	>40	-	-	-	-	-	-	-
TOTALS		94,069		150,241	94,418	36,428	19,398	3,943,826

[a] Aggregated information from Bickerstaff et al. 1981.

[b] Average values.

SECTION 9

LIMING

SECTION 9

LIMING

9.1 INTRODUCTION

This chapter reviews the potential of adding neutralizing or buffering materials to correct or modify the adverse effects associated with acidic deposition. Such activities are commonly called "liming" and they are limited in practice to correcting to some degree adverse effects on aquatic, terrestrial and drinking water systems. It is not possible to use liming to mitigate effects on materials, visibility, and adverse health effects resulting from direct inhalation of airborne pollutants. Each section of this chapter discusses the effectiveness of liming for the particular system and then the unit cost associated with liming that system.

9.2 AQUATIC

It has been shown in many areas of the world that acid loadings due to long range transport are capable of acidifying surface waters. In theory however, even the most acidic loadings could periodically be neutralized if limestone were added to the affected systems in amounts ranging from 50 to 100 kg/ha.yr. In areas with calcareous soils, this amount of neutralizing capacity is available inherently for very long periods of time (i.e., 1 cm of soil covering 1 ha is about 150 metric tons, which is capable of neutralizing present maximum acid loading for about 3,000 years). In hard rock areas with little or no calcareous soil some present acid loadings cannot be neutralized fast enough resulting in acidic runoff. In order to reverse or prevent the resulting effect, at least five different jurisdictions (Sweden, Norway, New York State, Nova Scotia, and Ontario) have added neutralizing agents to surface water systems. The numbers of lakes and rivers treated and the methods used in the application of neutralizing agents vary greatly from area to area. Limestone is most often used although other chemicals have been tried. The term "liming" is used to describe artificial neutralization regardless of the chemical or chemicals actually used.

9.2.1 Liming as a Mitigative Measure

In certain cases, a species or a unique race of organisms may be threatened by acidification of its natural habitat. In these cases, liming or other mitigative measures might be undertaken on lakes, rivers or parts of rivers in order to preserve a population of the endangered organism. Very small populations become inbred and so the preserved habitat must be large enough to support a reasonably large population. The populations saved in this way might play an important part in the restoration of fisheries to waters where fish have been exterminated by acidification or other causes.

The future value of any species or organism cannot be foreseen. Therefore, the extinction of any species could be a great loss to man. As the extinction of a species can never be remedied, the threat of extinction of any species by acid rain would justify lake liming or virtually any other feasible protective measure regardless of immediate costs or benefits.

If a population of fish is considered an especially suitable source of stock for the rehabilitation of acidified rivers or lakes, then liming or other measures to protect its natural habitat would be justified to protect it from acidification. Liming of an acidified habitat would also be justified if it were inhabited by a population which was genetically unique and consequently for which no replacement could be found if it were exterminated.

9.2.2 Liming Programs

9.2.2.1 Sweden

Sweden has conducted the greatest number of experiments on lake liming of any country. A 5-year program designed to evaluate both lake and stream liming was completed in 1981 and a final summary report was prepared (National Fisheries Board and National Environmental Protection Board 1981). During the 5-year period, 304 projects were started which involved over 700 lakes and streams. While there were some negative aspects to the results, the program was deemed to be a success by the National Board of Fisheries. Success was generally measured in terms of a favourable response in the sport fish, mainly salmon, trout and arctic char, although some lakes were treated with environmental conservation as the prime objective. Limestone has been applied at rates of 100-200 kg/ha of lake surface which corresponds to 50-75 kg/ha of watershed per year. Application on land required up to 100 times this amount to give an acceptable runoff quality. Application directly to water was found to be the most economical treatment method (Bengtsson et al. 1980).

Hultberg and Andersson (1982) reported detailed studies on six lakes in two areas of Sweden. Four lakes were limed and two held as reference lakes. Although they reported favourable biological results, there was concern over continued biological and chemical damage from liming, resulting from the input of aluminum in acidified runoff from the watershed. Most of the lakes and streams had a relatively small number of species of fish (three or four). The improved water quality generally resulted in increased numbers of fish, and hence an improved sport fishery. Bengtsson (pers. comm.)

reported that, in some cases, nonsport fish species responded the most dramatically.

Bengtsson et al. (1980) summarized some of the problems with lake neutralization as follows:

> "Obtaining yearly leaching of a certain amount of bicarbonate or an acceptable yearly pH-medium value is not the problem. The problem is to keep an acceptable value at high flow (i.e., during snowmelt). At this time the lake waters become highly stratified with the cold acid melting-water on top. As a result it does not mix with the water below which is of better quality.
>
> The running waters carrying this melting-water represent an even greater problem. To neutralize the acidified melting-water, either large overdosing is needed when applied to water or on land or every year lime has to be applied on the snow pack.
>
> Moreover, the acidification is not just a pH-problem but is also coupled to the anthropogenic pollution of metals deposited from the atmosphere and the increased leaching of metals from acidified soils.
>
> The toxicity of most metals is higher in neutral than in acid water. Thus, when liming an acid lake the organisms suffer a transition period before the metals have precipitated. Aluminum leached from the soil is highly aggressive to fish gills in the pH range 4.5 - 6 and liming has even killed salmon and trout when the aim was to save the fish."

The situation in North America may be even more complicated because generally, the lakes contain more species of fish than many of the Scandinavian lakes. The potential for disruption of the aquatic food chain is greater. It could happen that fish populations would survive in the treated lakes but the normal distribution of species might be altered. For example, inputs of aluminum might disrupt the life cycle of some species more than others, changing the ecological balance among species.

9.2.2.2 Norway

The Norwegian government is conducting a liming project at Lake Hovvatn in southern Norway. The lake is about one square kilometre and has a mean residence time of 1.1 years. The drainage basin is interspersed forest and bog with numerous granite outcroppings. The project was begun in May 1980 with background sampling at two month intervals at five lake stations and five inlet streams. Analyses include pH, alkalinity, conductivity, all major ions and metals. Zooplankton and phytoplankton are also being monitored. In March 1981, the lake was treated with 240 metric tons of agricultural limestone spread on the ice near the shore. As the ice melted in

April the pH went from 4.5 to 6.0. Sampling and analyses are expected to continue for years. The lake was stocked with brown trout in June 1981. A smaller lake draining into Hovvatn was not limed and serves as a control.

9.2.2.3 United States

A paper by Pfeiffer (1982) reported results of a January 1981 questionnaire he circulated to Fisheries Chiefs or Directors in the 50 United States. Forty states responded to his acidic deposition questions. Nonrespondents included the states of Florida, Louisiana, Maryland, Michigan, Missouri, New Mexico, North Carolina, North Dakota, Vermont and Virginia. Seven of 40 states replied that they are presently engaged in a liming program for ponded waters. The summary is as follows:

State	Ponded Waters Treated Per Average Year	
Kansas	5	(10 ha)
Massachusetts	2-3	(81 ha)
New Jersey	2	(8 ha)
New York	7	(81 ha)
West Virginia	1	(17 ha)
Wisconsin	2	(12 ha)

West Virginia was the only state that indicated that they were liming streams. The figures provided were 16 km, representing approximately 12 ha. There were no questions on future considerations for liming programs.

Festa (pers. comm.) reported that the New York Department of Environmental Conservation had treated 16 small ponds (0.5 to 3.0 ha) which were operated mainly as put-grow-and-take brook trout fisheries. The treated lakes had a simple food chain with only one fish species stocked. Fish growth was good and the fish were harvested by angling in the autumn. There was no attempt to establish a self-sustaining population.

9.2.2.4 Ontario, Canada

Limestone and slaked lime were added to Middle, Hannah, Lohi and Nelson Lakes, four acidic lakes near Sudbury, Ontario between 1973 and 1976. Contamination by metals, especially Cu and Ni, prevented reestablishment of trout populations in the first three lakes which are situated within 13 km of Sudbury (Yan et al. 1979), even though pH was increased from about 4.4 to >6.0. Nelson Lake (3.09 km^2) was acid-stressed (pH ~5.5-6.0) prior to additions of crushed limestone (51 metric tons) and slaked lime (68 metric tons) in the fall of 1975 and the spring of 1976 (Yan et al. 1977). The decline of the lake's fisheries was indicated by the dominance of yellow perch and the disappearance of smallmouth bass. Lake trout populations were low but by the winter of 1979-1980 winter fishing for lake trout was very successful (summarized in Yan and Dillon 1982).

9.2.3 Economic Aspects of Lake Liming

Estimating the total cost of liming aquatic systems is very difficult but some unit cost figures are available for Sweden, New York State, Norway and Nova Scotia. Generally there are three categories of cost associated with liming programs: supply of chemicals, distribution of chemicals, and monitoring of the systems before and after the applications.

9.2.3.1 Costs in Sweden

Although the costs in Sweden cannot be expected to apply directly in North America, they serve as a guide in estimating North American costs. Results from their 5-year experimental program which dealt with over 700 lakes (Bengtsson et al. 1980) have given good cost estimates. The cost of limestone application, including materials and distribution ranged from 500 to 1100 Skr ($115-253 Cdn.) per metric ton using eight different spreading methods. The average cost for the whole program was about $140 Cdn. per metric ton. Manual applications had the lowest cost of about $115 Cdn. per metric ton while aerial applications were the most expensive at about $250 Canadian per metric ton (National Fisheries Board and National Environmental Protection Board 1981). The cost of scientific surveys to document effects can range from a very small amount for some pH and alkalinity measurements to several thousand dollars. In Sweden, the average cost of research has been about $16,000 for each project. However, each project may have more than one lake or river involved.

9.2.3.2 Costs in Norway

Limited cost information is available but a total experimental cost of $80,000 for each of the five study lakes has been projected. In addition there is support from universities with separate funding and support from local residents.

9.2.3.3 Costs in New York State

New York State Department of Environmental Conservation has been adding limestone to 16 small lakes (0.5 to 3 ha) and started a 40 ha lake in 1979. They found the costs of limestone application to range from $60 U.S. to $225 U.S. per hectare for a 3-year treatment ($20 to $75 U.S./ha.yr). They conducted a very limited technical evaluation of the lakes. The lakes were essentially devoid of fish to start with and the objectives were to establish put-and-take brook trout fisheries.

9.2.3.4 Costs in Canada

Watt (pers. comm.) has recorded actual cost figures for purchase, delivery and distribution of crushed bagged limestone to Sandy Lake in Nova Scotia. The loading rate was about one metric ton/ha. The experiment was designed to protect salmon populations in downstream rivers. The lake was easily accessible, and crushed limestone was readily available. The total cost for liming the 70 ha lake was in excess of $11,000, or about $160 Cdn. per hectare.

Although costs per lake will vary according to dose required, generally application rates for lakes appear to vary from about 380 (Yan and Dillon 1982) to 1000 kg/ha which Watt has used in Nova Scotia. The Ontario example given by Yan and Dillon (1982) has maintained the lake pH for at least five years. Generally, average application rates of about 500 kg/ha are necessary to give multi-year pH stability.

9.2.4 Technical Evaluations Necessary in Liming Programs

The calculation of costs associated with neutralization programs must be accompanied by the necessary technical evaluations. Any system, considered for liming must be studied in a variety of ways (e.g., depth, flushing time, water chemistry, and biota). Swedish treatment and research costs of about $16,000 Cdn. per project are based on 304 projects which cover at least 700 individual lakes (Bengtsson et al. 1980). Therefore, average monitoring costs appear to be about $8,000 per lake. A minimum sample program of only twice per year would still cost at least $1,000 per lake including labour, analyses and data reporting. Meaningful evaluation of chemical and biological conditions would cost in the order of $10,000 per lake per year.

Control and management of the fisheries in treated systems would also add substantially to overall costs.

It is worth noting that the situation concerning fishing rights in Scandinavia and North America is quite different. In Sweden the rights to fish are privately owned, with the owners on some rivers issuing fishing licenses and to some extent controlling fish harvest. This element of "self interest" allows for easier control of fishing activities which can affect the success of fish survival and reproduction.

9.3 TERRESTRIAL LIMING

The addition of alkaline materials has been proposed as a means for ameliorating the effects of acidic deposition on terrestrial ecosystems. While lime applications have an important place in the efficient management of agricultural soils and much research has been conducted to determine optimum dosages for different crops and soils, the scope for lime in temperate and boreal forestry is much more limited. Moreover, few field trials have been concerned with entire forested catchments. In this sub-section positive and negative aspects of the liming technique will be discussed.

Numerous calcium-based alkaline materials are available for the neutralization of acidified soil. However, for most situations, crushed limestone ($CaCO_3$), flaked or hydrated lime ($Ca(OH)_2$), and unslaked lime or quicklime (CaO) are the most readily available and effective materials. A variety of substances have been proposed for use as neutralization agents (Grahn and Hultberg 1975).

The data available up to now do not indicate obvious effects on forest ecosystems caused by acid deposition. However, the potential of the available techniques for remedial action warrant examination in the event that subsequent data indicate forest degradation.

9.3.1 The Application of Lime to Agricultural Soils

Microorganisms and higher plants respond to their chemical environment, and soil kinetics are a key factor in determining agricultural soil productivity. There are two major groups of factors which bring about large changes in soil pH: (1) those which result in increased adsorbed hydrogen and in turn release aluminum, and (2) those which increase the content of adsorbed bases. Both organic and inorganic acids are formed when organic matter is decomposed. The simplest and perhaps the most widely found is carbonic acid (H_2CO_3) which results from the reaction of CO_2 and water. The solvent action of H_2CO_3 on the mineral constituents of the soil is exemplified by its dissolution of limestone or calcium carbonate. Because carbonic acid is relatively weak, it cannot account for the low pH values found in many soils. Inorganic acids such as H_2SO_4 and HNO_3 are suppliers of hydrogen ions in the soil. These acids, along with the organic acids, contribute to the development of acid conditions. Sulphuric and nitric acids are formed, not only by the organic decay processes, but also from the microbial action on certain fertilizer materials such as sulphur and ammonium sulphate. In the latter case both nitric and sulphuric acids are formed.

Podzolization is an example of a process by which strong organic acids are formed. The organic debris is attacked largely by fungi which have among their important metabolic end products relatively complex but strong organic acids. As these are leached into the mineral portion of the soil, they not only supply hydrogen for adsorption, but they also replace bases and encourage their solution from the soil minerals. Leaching also encourages acidity. Therefore, bases which have been replaced from the colloidal complex or which have been dissolved by percolating acids are removed in the drainage waters. This process encourages the development of acidity in an indirect way by removing those metallic cations which might compete with hydrogen and aluminum on the exchange complex.

When lime is added to the soil, two changes occur:

1) the calcium and magnesium compounds applied undergo solution under the influence of a variable partial pressure of carbon dioxide; and

2) an acid colloidal complex will adsorb considerable amounts of calcium and magnesium ions.

When lime, whether the oxide, hydroxide, or the carbonate, is applied to an acid soil, the movement, as solution occurs, is toward the bicarbonate form. This is because the partial pressure of carbon dioxide, usually several hundred times greater than that of atmospheric air, generally is intense enough to prevent the existence of the hydroxide or even the carbonate. The reactions, written only for the purely calcium limes, are as follows:

$$CaO + H_2O \rightleftharpoons Ca(OH)_2$$

$$Ca(OH)_2 + 2H_2CO_3 \rightleftharpoons Ca(HCO_3)_2 + 2H_2O$$

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2$$

The above equations represent only the solution of the lime in carbonated water. However, the soil situation is not as simple as these reactions might lead one to assume. This is because the soil colloidal matter upsets the equilibrium tendencies by adsorbing the ions of calcium and magnesium. These ions may be taken from the soil solution proper or directly from the solid phase if the contact is sufficiently close (Buckman and Brady 1969).

The changes of lime in the soil are many and complicated. If a soil of pH 5.0 is limed to a more suitable pH value (e.g., pH 6.5) then a number of significant chemical changes occur. For example: (1) the concentration of H^+ ions will decrease; (2) the concentration of OH^- ions will increase; (3) the solubility of iron, aluminum and manganese will decline; (4) the availability of phosphates and molybdates will be augmented; (5) the exchangeable calcium and magnesium will increase; (6) the percentage base saturation will increase; and (7) the availability of potassium may be increased or decreased, depending on soil conditions.

Overliming is an important phenomemon which must be considered. A potential problem is the addition of lime until the pH of the soil is above that required for optimum plant growth. Under such conditions, many crops that ordinarily respond to lime are detrimentally affected, especially during the first season following the lime application. With heavy soils, and when farmers can afford to apply only moderate amounts of lime, the danger is negligible. But on sandy soils (low in organic matter and therefore lightly buffered) it is easy to injure certain crops, even with a relatively moderate application of lime (Buckman and Brady 1969). Some of the detrimental influences of excess lime are:

1. Deficiencies of available iron, manganese, copper, or zinc may be induced.

2. Phosphate availability may decrease due to the formation of complex and insoluble calcium phosphates.

3. The absorption of phosphorus by plants and especially its metabolic use may be interfered with.

4. The uptake and utilization of boron may be hindered.

5. The drastic change in pH may, in itself, be detrimental.

9.3.2 Economics of Agricultural Liming

On judging the amounts of lime to apply, a number of factors should be considered: (1) cost of liming material; (2) the soil surface pH, texture and structure, and the amount of organic matter; (3) the subsoil pH, texture and structure; (4) the crops to be grown; (5) the length of the rotation; (6) the kind of lime used and its chemical composition; (7) the fineness of the limestone; and (8) operational experience.

9.3.3 Forest Liming

While much is known about agricultural liming practices (materials, techniques, beneficial effects, and potential problems), much less is known about liming forested ecosystems. For the boreal, north temperate and temperate forests, such as are present in northeastern North America, Scandinavia and northwestern Europe, liming has considerable tradition for many centuries (Evelyn 1776).

Where forest liming is viewed more as a fertilizer or nutritional measure, rather than as an aid to soil restoration, its promise is far less re-assuring. This is because calcium deficiencies have seldom been demonstrated and fertilizer trials embodying a calcium treatment have rarely shown a positive response by tree growth. Thus major reviews of fertilizer research for Canada (Rennie 1972), the United States (Bengtsson 1977; Mustanoja and Leaf 1965), Sweden (Holmen 1976), Great Britain (Everard 1974) and Germany (Baule and Fricker 1970), show calcium trials to be extremely few compared with those for nitrogen, potassium and phosphorus, with very few indications of positive growth responses.

Forest liming has not been widely implemented because it has not yet been shown statistically that acidic deposition has caused adverse effects in forest growth. Forest liming is further complicated because the inaccessibility of forests makes application difficult (Bache 1980).

Sweden is one of the few countries where forest liming is practised. The first attempts to lime forest lands in Sweden were made 67 years ago. The most recent lime applications were made at a rate of 5 - 10 metric tons/ha on 0.2 hectare plots in 12 areas. Various combinations of fertilizer were also applied. It was pointed out (Fraser et al. 1982) that after 25 years 50% of the lime was not leached from the soil. Research from 1971 to 1978 at Lisselbo (Fraser et al. 1982) where sulphuric acid and lime were applied to plots, was described. Annual precipitation of 700 mm leaches between 2.0% and 11.6% of the lime since application. Two preliminary conclusions from these studies are important: (1) liming has little effect on the growth of forest trees and (2) lime persists in undisturbed forest soils, despite 700 mm of annual precipitation.

Tveite and Abrahamsen (1980) report the results of field experiments located in two different areas of southern Norway. The authors present results from the Norwegian field experiments with artificial acidic deposition and liming added to pine and spruce forests. All experiments included treatment with 25 or 50 mm/month of artificial acidic deposition with different pH, applied during the frost-free time of the year. After five years of treatment no negative growth effects of the acid applications are apparent and there were no effects of liming found.

No useful purpose would be served by documenting here a comprehensive list of such trials, but a few typical published results exemplify the unattractiveness of the approach. For 45-year old jack pine (Pinus banksiana Lamb.) in the Boreal Forest of Ontario, calcium at 448 kg/ha gave no response except where nitrogen, phosphorus and potassium had also been applied (Morrison et al. 1977b). A further trial with 55-year old but poorer quality jack pine, also north of Lake Superior, again only showed a growth response to lime where nitrogen, phosphorus and potassium has also been applied. Indeed, the suggestion was the lime by itself exercised a depressive effect upon growth by adversely affecting soil microbiological processes (Morrison et al. 1977a). The complexity of lime effects is apparent from the work of Adams and his colleagues (1978) on the acid peaty gleys of Northern Ireland. There, lime did not increase the growth of Sitka spruce (Picea sitchensis Carr.), but it did affect the soil microbiology and the viability of the mycorrhizal root association. As might be expected, the pH of the litter was raised from 4.0 to 6.0 - 6.5, a result that has been of serious concern to those aware of the optimum soil conditions for the spread of rot fungi such as Formes annosus (de Azevedo and Moniz 1974).

The possible effects associated with liming forested ecosystems are still unknown but experiments of watershed liming may provide some insight. Bengtsson et al. (1980) report on experiments of watershed liming conducted in Sweden. Agricultural lime (i.e., powdered $CaCO_3$) is generally transported to the watershed in large trucks and applied as a slurry with a sprayer truck. The $CaCo_3$ dose required to achieve adequate neutralization of watershed systems is generally two orders of magnitude greater than that of direct water addition which is due to the many base consuming processes that occur within the forest soil systems (Bengtsson et al. 1980). There have been application rates reported in the range of 5,000-7,000 kg $CaCO_3$/ha.yr. Hultberg and Andersson (1982) reported that some damage to the terrestrial environment may be associated with liming. Sphagnum moss was severely damaged with $CaCO_3$ addition. Damage to lichens, mosses and spruce needles was also observed.

Smelters at Sudbury, Ontario, represent the greatest single source of sulphur dioxide emission in the world. Over the past several years, a terrestrial liming/reclamation program has been operated (Fraser et al. 1982). The affected lands have a pH of approximately 4.0 and concentrations of copper and nickel were measured up to 10 ppm. To reclaim this land, crushed agricultural limestone is applied at a rate of 12.4 short tons/ha, then fertilized with a nitrogen-phosphorus-potash mixture (6-24-24, respectively), and seeded with a variety of blended grasses. The limestone application is labor intensive with 400 students adding the limestone by hand. Over 1000 hectares have been reclaimed to date. According to the authors, this terrestrial liming project has been extremely successful in raising the pH of the soil and complexing the heavy metals (although there is still some minor nickel toxicity). The authors report that grass is now able to grow on barren areas and the resultant shading and lowering of ground temperature has enabled some natural vegetation (e.g., quaking aspen seedlings) to become reestablished. The newly established vegetation is monitored and analyzed, as is the recovery of populations of insects, birds, and small mammals.

Limited information is available on the changes to terrestrial flora and fauna after the addition of lime to forested soils. Tamm (1976) stated that when lime was added to forest soils in small-scale experiments, tree growth rates typically was not enhanced, because of the tendency of lime to immobilize the nitrogen in organic matter and thereby reduce its availability to trees. Fraser et al. (1982) report that lime had little effect on the growth of forest trees, based on preliminary conclusions from forest liming studies conducted in Sweden from 1971 to 1978. Abrahamsen et al. (1980) reported that soil animal populations nearly always fail to increase when soil acidity was reduced by liming. Hultberg and Andersson (1982) report that the liming of watersheds in addition to lakes and streams would release additional phosphorous to the waterbodies and enable these aquatic systems to increase their primary productivity.

9.3.4 Terrestrial Liming Summary

In conclusion, although in principle the liming of land might neutralize an acidifying pollutant (Ulrich 1972) it has the following serious limitations. First, it would not prevent direct injury to plant tissues, even where in agricultural situations it is already being used as a soil amendment. Secondly, in the typical forest situation it would be very difficult to apply. Thirdly, the effects of lime in the boreal and north temperate forest are complex and often far from beneficial.

9.4 DRINKING WATER SUPPLY

Low pH conditions in municipal water supplies can cause corrosion of the plumbing materials. The estimated costs for controlling corrosion were based on adding lime to water to stabilize it. This should control corrosion of lead pipes as well as corrosion of cast iron water mains, and is the corrosion control technique most likely to be used by water utilities.

9.5 COSTS OF CORROSION CONTROL

Costs for corrosion control by lime stabilization were estimated by Hudson and Gilcreas (1976) to total $0.30 U.S. per capita for operation and amortization costs in 1976. Average per capita costs for lime stabilization were estimated by Davis et al. (1979) to range from $0.18 to $0.57 U.S., depending on the extent of chemical treatment provided to stabilize the water.

Corrosion control by calcium carbonate stabilization and deposition of a protective calcium carbonate film has been suggested by EPA as an effective approach to nonselectively provide protection to a number of materials, including asbestos cement, lead, iron, galvanized steel, copper, and alloys that may be used in water distribution systems or plumbing. Annual per capita costs for corrosion control by addition of lime were estimated by USEPA (1979). Costs are a function of plant size, as shown in Table 9-1.

The methods used to calculate corrosion costs in the USEPA Statement of Basis and Purpose were developed by Gumerman et al. (1979). An example of calculation of cost for corrosion control by addition of lime at 30 mg/L for pH control in a 5 million gallons per day (MGD) plant is given in Table 9-2. The costs are shown for operation at 70% of capacity (3.5 MGD). The principle items of expense are capital amortization, labor, and chemical used. Chemical consumption is the cost category most sensitive to water quality changes.

TABLE 9-1. COST OF CORROSION CONTROL BY LIME ADDITION AS A FUNCTION OF PLANT SIZE

Plant Size Gallons Per Day	¢/1,000 Gallons Treated - 70% Capacity	Annual Per Capita Cost[a] - $
2,500	56.9	20.50
50,000	16.4	6.00
5,000,000	2.7	1.00
100,000,000	1.1	0.40

[a] Cost stated in $ U.S. 1981, December.

TABLE 9-2. EXAMPLE OF COST CALCULATION FOR FEEDING LIME AT A 5 MILLION GALLONS PER DAY PLANT

	\$/Year[a]
Amortized Capital at 10%, 20 years	11,944
Labor, 702 hrs at \$12/hr (includes fringes and benefits)	8,424
Electricity, 26,770 kw-hr at \$0.05/kw-hr	1,339
Maintenance Material	1,037
Chemica, Lime 153 ton/yr at \$75/ton	11,475
	34,219

[a] Cost per 1,000 gallons treated = 2.68¢ U.S. when operating at 70% capacity

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