United States
Environmental Protection
Agency

Environmental Research
Laboratory
Duluth MN 55804

EPA-600 3-80-044
May 1980

Research and Development

# Impacts of Airborne Pollutants on Wilderness Areas Along the Minnesota-Ontario Border

## RESEARCH REPORTING SERIES

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May 1980

# IMPACTS OF AIRBORNE POLLUTANTS ON WILDERNESS AREAS ALONG THE MINNESOTA-ONTARIO BORDER

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ENVIRONMENTAL RESEARCH LABORATORY
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## FOREWORD

Many of the objectives that drive efforts to improve our environment are local in nature and can be viewed as improvements in the quality of life. For example, the opportunities to swim in rivers and lakes, to catch sport fish in a beautiful lake, or to camp in a wilderness area are certainly valuable. But these objectives are not necessary for our biological requirements.

Other efforts for environmental protection are driven by the necessity to sustain the very existence of mankind. Examples of such efforts are the protection of the ozone layer, preservation of our soil for food productivity, the maintenance of our forest lands for production of wood products, and the protection of terrestrial vegetation to assure gas balance in the atmosphere.

This report presents evidence to suggest that the deposition of atmospheric pollutants is not only threatening a huge, beautiful wilderness area of the continent, but is also giving rise to another large geographical area where forests may be endangered for wood production and sustaining the atmospheric life-supporting systems.

Donald I. Mount, Director
Environmental Research Laboratory
Duluth, Minnesota

## ABSTRACT

The goal of this study was to examine previously unanswered questions concerning potential effects of the proposed Atikokan, Ontario power plant on ecosystems in the Boundary Waters Canoe Area Wilderness (BWCA) and Voyageurs National Park (VNP) of Minnesota by using the most relevant data and analytical methods. The principal steps were to focus on: (1) the ultimate deposition of emissions from the plant (rather than only on pollutant concentrations), (2) the use of a time-varying grid model with provision for atmospheric transformations, and (3) a detailed review of all available data from the region on atmospheric deposition of pollutants, water quality, and effects. The results are considered in relation to a review of responses by terrestrial and aquatic organisms to changes in the chemistry of this environment.

The sensitive aquatic and terrestrial receptors in the BWCA-VNP region are described quantitatively, and this information is assessed in terms of what is currently known about the impacts of atmospheric pollutants. Specific conclusions based on factual information, probable consequences, and possible impacts of the proposed coal-fired power generating station at Atikokan are presented.

The study supports, in part, the conclusions reached previously concerning the predicted air concentrations of sulfur dioxide, but differs significantly with the conclusions concerning the significance of future impacts. When the total emissions from the proposed power plant are considered, the increased loadings of sulfuric and nitric acids, fly ash, and mercury as an addition over and above other regional sources will, with high probability, have significant consequences for the sensitive receptors in the BWCA-VNP region, especially for the future of sport fisheries and other aquatic resources.

CONTENTS

## FIGURES

TABLES

ACKNOWLEDGMENTS

Air Quality and Modeling

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# SECTION 1

# INTRODUCTION

The Boundary Waters Canoe Area Wilderness (BWCA), a wilderness unit within the Superior National Forest (Minnesota) and located along 176 km (110 miles) of the Minnesota-Ontario border, occupies 439,093 ha (1,085,000 acres) of characteristic northwoods terrain. The area varies from 16 to 48 km (10 to 30 miles) in width. Over 1,900 km (1,200 miles) of streams, portages, and foot trails connect the hundreds of pristine, island-studded lakes that make up approximately one-third of the total area. Few wilderness areas have been the focus of as much persistent concern for protection from human impacts as has the BWCA.

The 1976 proposal by Ontario Hydro to build and operate a major coal-fired power plant north of the Quetico-BWCA wilderness complex has led to concern that air quality and ecosystems in the area could be inadvertently degraded, in spite of the years of effort and the legislation designed to protect them. Because of the important natural resources represented by the waters, forests, and air of the BWCA, many individuals, legislators, and environmental organizations have been concerned with possible deficiencies in the available data, methodology, and scope of the assessments carried out since the plant was first proposed. These concerns have led to the decision by the U.S. Environmental Protection Agency, in cooperation with State agencies, universities, and other Federal agencies, to proceed with the present comprehensive study of potential impacts on the biota, air, and water. Additional data and new analytical tools, including a grid model that computes pollutant transformation and deposition, were available and appropriate for a second-level analysis.

## BACKGROUND

Ontario Hydro, a crown corporation established by the Ontario government, requested in 1976 and received in 1977 Provincial approval to build an 800-MW, coal-fired electric generating station near Atikokan, Ontario. The site is approximately 20 km (12 miles) from the northern boundary of Quetico Provincial Park and about 55 km (38 miles) from that portion of the U.S.-Canadian border which forms the northern edge of the BWCA in Minnesota.

Criticism of the project from Canadian and U.S. environmental organizations and individual scientists has centered on the proposed plant's proximity to the Quetico-BWCA wilderness complex, and on the omission from the structure of any scrubber technology. Concern also has been addressed to the Ontario Hydro environmental analysis document, which, critics said, failed either to give substantial evidence for its claim that no vegetation damage would result from $SO_2$ emissions or to treat adequately the problems of acid precipitation and deposition of pollutants in the Quetico-BWCA environment.

The Atikokan facility is to be staged in four 200-MW units, one of which is to be in service during 1984. The boilers for these units would burn either low sulfur subbituminous coal from Alberta or lignite from Saskatchewan. The proposed facility would feature electrostatic precipitators to control particulate emissions, but no scrubbers would be used to minimize $SO_2$ emissions. Planning for the Atikokan generating station began in 1974; in 1976 Ontario Hydro published an environmental analysis and supplementary report dealing with the project. The regulations of the recent Environmental Assessment Act of Ontario were not applied retroactively to the Atikokan generating station.

United States-Canadian international negotiations on the Atikokan plant began in August 1977. At that time the Canadian participants agreed to provide the U.S. Department of State with additional information for a more precise evaluation of the project's potential transboundary effects. Technical studies were undertaken in each country of the $SO_2$ concentrations expected to originate from this plant. The results were exchanged in late December 1977. With the additional Canadian information and in consultation with the Department of State, the U.S. Environmental Protection Agency proceeded with its initial review of the Atikokan proposal.

During this period Minnesota congressional representatives and several environmental organizations urged the Department of State to ask Canadian officials (1) to refer the matter to the International Joint Commission (IJC), with a moratorium on plant construction (to allow a comprehensive study of the plant and its impacts), or (2) to ask for installation of the best available scrubbers (90% efficient) similar to those already used extensively in Minnesota for new sources.

The Department of State presented the results of the EPA initial review at a second international negotiations meeting held on January 11, 1978. The EPA review included a literature survey on acid rain problems and projections of $SO_2$ dispersal based on the standard Gaussian plume dispersion model.

At this January meeting the U.S. team noted that results of both Canadian and U.S. modeling studies indicated that the concentrations of $SO_2$ entering the BWCA from the Atikokan plant occasionally may be in excess of the Class I air quality standards permitted under the U.S. Prevention of Significant Deterioration Criteria. (Covering classified wilderness, Class I is the most stringent standard.) Also using the studies from both countries, the Canadians concluded at the January meeting that the predicted transboundary impact of $SO_2$ emissions from the Atikokan generating station was below the threshold at which injurious environmental effects are known to occur. Canadian officials confirmed that the plant would meet all Canadian environmental requirements.

The U.S. negotiating team initially requested the installation of 50-percent-efficient scrubbers. The Canadian representatives indicated that they could not, at that time, accept such a requirement. The negotiators then focused on discussing a referral to the IJC that would not include a construction moratorium, but would feature a program to monitor effects of the plant. The Department of State submitted proposed wording for such an IJC reference, and the Canadian Office of Foreign Affairs agreed to consider the proposal.

The U.S. team, lead by officials of the Department of State, included representatives from the State of Minnesota, the Environmental Protection Agency, and the USDA Forest Service, which manages the BWCA. The Canadian team, headed by officials from the Bureau of USA Affairs of the Department of External Affairs, included representatives of the Province of Ontario, Environment Canada, the Canadian Embassy in Washington, and the Canadian consulate in Minneapolis.

On February 22, 1978, some members of the U.S. negotiating team met in Chicago to discuss additional potential air quality impacts such as acid fallout. Also present were staff of the EPA Office of International Activities, EPA Region 5; scientists from the EPA Environmental Research Laboratory-Duluth (Minnesota), and Environmental Research Laboratory-Corvallis (Oregon), and several universities; and representatives from conservation organizations (National Parks and Conservation Association, Friends of the Boundary Waters Wilderness, and National Clean Air Coalition). At this meeting the data, methodology, and scope of the initial EPA study were reviewed in detail, especially the following: (1) the lack of realistic simulation of meteorological and chemical transport and deposition processes by a Gaussian plume model over the distance involved in the Quetico-BWCA study; (2) the omission of data on existing conditions covering sensitive water quality, water-flow direction, and high mercury levels in fish; and (3) the necessity that contributions made by the Atikokan plant be assessed against present background levels and all planned future sources in the area. The consensus of those attending was that the Atikokan generating station had the potential to be a significant addition to the pollutants in the BWCA area for both air and water and that a much more comprehensive study to assess its significance should be undertaken.

On March 20 the Canadian Embassy issued a diplomatic note rejecting any International Joint Commission reference, citing as its reason "the lack of indiction of any potential injury" to the U.S. side, such injury potential being "the traditional basis for considering transboundary pollution questions" by the IJC. The Canadian team also concluded that since the existing studies predicted that concentrations of the pollutant of major concern in the United States, sulphur dioxide, would be far below injurious levels, there was no basis for considering the installation of scrubbers.

Subsequently, the U.S. Environmental Protection Agency agreed to support a limited additional study of potential impacts of the proposed Atikokan power plant, for which this report details results. This latest study was to be supported also in part by the Department of State; the USDA Forest Service; and the Minnesota Pollution Control Agency; and was to be coordinated by the EPA Environmental Research Laboratory-Duluth.

## UNIQUENESS OF THE BWCA

The Boundary Waters Canoe Area has been recognized as a unique resource for many decades. In 1930 the Shipstead-Newton-Newland Act was passed to protect its shorelines and water levels from dam building and drainage. In 1948 passage of the Thye-Blatnik Act allowed condemnation and purchase by the Federal government of private lands in the "roadless area," as it was then called. President Truman issued an air ban in 1950, stopping the floatplane flights into the "roadless area" which had allowed over-fishing of many lakes. The 1964 Wilderness Act designated the Boundary Waters Canoe Area as part of the National Wilderness Preservation System, thus recognizing it as a national resource of outstanding quality that should be preserved in an unimpaired condition so that the forces of nature rather than those of man could predominate. The act contained specific provisions allowing certain logging and motorized activity within portions of the BWCA, but otherwise mandated specific wilderness protection. Recently passed legislation in the 1977-78 Congress now further limits nonwilderness uses of the BWCA.

It is difficult to describe adequately the BWCA's significance to the American public as a conservation, scientific, and recreation resource for the present and future. It is the only lakeland canoe unit of the U.S. wilderness system and one of the system's largest units of any kind. Embracing the largest remaining virgin forest in the east, it attracts more recreationists than any other wilderness area in the nation and lies within 2 days' travel of nearly 50 million people. As the last large, unmodified northern coniferous forest ecosystem in the eastern United States, it has become the focus of much education and demonstration management in wilderness ecology, animal behavior, vegetation history, nutrient cycling, and aquatic ecosystems.

The attraction of the area appears to be not any single factor, but a combination of related ones: fishing and camping in a sought-for atmosphere of wild, unpolluted landscape. However, the evergreen forests, clear water and air, rock outcrops, and shallow soils that are the conspicuous ingredients of the BWCA landscape are all also unusually sensitive to regionally transported pollutants. The expansive and relatively unspoiled terrestrial and aquatic ecosystems in the BWCA are the major reasons for its recognition as a unique resource in the United States. This recognition and uniqueness have led to a protective degree of legislative and citizen vigilence, and, indirectly, to recent monitoring of air quality in northeastern Minnesota. Since August 8, 1977, the BWCA has been protected by U.S. Clean Air Act amendments that guarantee maximum "Class I" protection for parks and wilderness areas. The intent of a Class I status is to assure long-term maintenance of air quality over an area at essentially the 1974-75 levels. Class I applies to areas such as the BWCA in which practically any change in air quality would be regarded as signficant.

Complementing the BWCA is Ontario's adjacent Quetico Provincial Park, 453,258 ha (1,120,000 acres) where logging, snowmobiles, and motorboats are banned. In 1973 the Ontario Provincial Government determined that Quetico did not fit into any of the usual classifications for provincial parks and declared it a "primitive wilderness." The importance of the BWCA to the United States has been greatly augmented by the forward-looking decisions made by Canadians in regard to the Quetico Park, established simultaneously in 1909 with the Superior National Forest to create an international sanctuary. Approximately 90% of the people who visit and enjoy the resources of Quetico are U.S. citizens, and over the years the Quetico-Superior (BWCA) area has come to be viewed as a single air, water, biological, and recreational resource.

## STRUCTURE OF THE STUDY

This study has been structured to capitalize on, rather than duplicate, any of the previous assessments of the Atikokan power plant. New data and modeling approaches were available from two major energy-impact studies sponsored by the EPA, and results of an intensive study in the northern Minnesota area by the State of Minnesota also were becoming available. These results, together with the previously available literature, could be used in conjunction with the issues identified during reviews of the previous assessments to set a new standard of analysis and evaluation.

Thus, the analysis and assessment process incorporated in this report is divided into three areas: (1) air-quality modeling (with multiple modeling approaches for predicting air-pollutant concentrations and deposition); (2) terrestrial effects (emphasizing transformation products of the $SO_2$ and the receptors within the BWCA); and (3) aquatic effects (considering acid inputs, due to all substances leaving the stacks at Atikokan, as well as existing conditions including high levels of mercury in fish and water flow to the border from both countries). Each area involved participants from the two principal research sites, Madison (Wisconsin), and Colstrip (Montana), and other technical consultants and required the assessment data from sources throughout the region.

The task of the air-quality modeling group was (1) to determine what can be predicted regarding the route and deposition of the proposed emissions in the region, by using a regional grid model with provisions for chemical transformations and deposition; (2) to draw together information on current background levels of air pollutants and all of the emission sources in the northwestern Minnesota region and adjacent Canada; and (3) to model all current and proposed emissions so that the contribution of all regional inputs could be analyzed in relation to the total loadings in the region.

The goals of the groups studying terrestrial and aquatic effects were (1) to characterize the sensitivity of the components of the terrestrial and aquatic ecosystems to the gaseous and particulate pollutants; and (2) to summarize research results available on the responses of sensitive species as well as to summarize the overall sensitivity of these associated ecosystems to the current and expected levels of pollutants reaching the BWCA.

The assessment by these groups proceeded around two principal workshops and the preparations and follow-up for each workshop. Materials were prepared for study prior to a problem-definition workshop on each of the three tasks (held in April 1978). Detailed data summaries and first drafts of the final reports were prepared during the spring and early summer, leading to an assessment workshop (August 1978) where the findings of the model output, assessment of existing conditions, and a review of existing literature were evaluated by participants from all groups.

## SECTION 2

## SUMMARY OF RESULTS AND CONCLUSIONS

The goal of this study was to use the most relevant data and analytical methods to examine previously unanswered questions of potential effects from the Atikokan power plant on ecosystems in the Boundary Waters Canoe Area (BWCA) and Voyageurs National Park (VNP) of Minnesota. The approach has been to focus on the ultimate deposition of emissions from the plant (rather than only on pollutant concentrations), to use a time-varying grid model with provision for atmospheric transformations, and to review in detail all available data from the region on atmospheric deposition of pollutants and on water quality. The results are considered in relation to a review of responses by terrestrial and aquatic organisms to changes in the chemistry of this environment.

The study supports, in part, the conclusions reached previously concerning the predicted air concentrations of sulfur dioxide, but differs significantly with the conclusions concerning the significance of future impacts. When the total emissions from the proposed power plant are considered, the increased loadings of sulfuric and nitric acids, fly ash, and mercury as an addition over and above other regional sources will, with high probability, have significant consequences for the sensitive receptors in the BWCA-VNP region, especially for the future of sport fisheries and other aquatic resources. Additional research will be required to specify these and other possible impacts in detail.

### AIR-QUALITY IMPACTS

A time-varying grid model has been developed and applied to the plume from the proposed Atikokan generating station. Preliminary validation steps on the model have been carried out, and a number of outside reviewers have examined the model assumptions and output. Within the limits of the available data and the design specifications available to the study, the model performance provides a basis for reasonable confidence in the projected concentrations and deposition fluxes.

#### Conclusions of Fact

1. By using the coal type (western Canadian), sulfur content (0.8%), ash content (12%), and operating conditions agreed upon by previous assessment studies, the emissions from the 800-MW Atikokan generating station were computed to be 70,307 metric tons/yr (77,500 tons/yr) of sulfur dioxide, 2,358 metric tons/yr (2,600 tons/yr) of fly ash, 41,630 metric tons/yr (45,900 tons/yr) of nitrogen oxides, and 0.9 metric tons/yr (1 ton/yr) of mercury. Other volatile components of coal, such

as fluoride, arsenic, selenium, etc., will be emitted, and the amounts will vary depending on the source of coal.

2. The plume from the proposed Atikokan generating station will be carried over the BWCA by NW to NE winds persisting for 3-6 h. For the base study-year, 1964, such conditions occurred during 49 time-periods, which totaled 910 h or 10.3% of the year.

Probable Consequences

1. Model computations indicate that emissions from the proposed Atikokan stack reaching the 80-120 km BWCA region contained in the 35° south sector will increase atmospheric deposition of sulfate by about 0.9-1.4 kg/hectare-year (ha-yr), fly ash by 18 g/ha-yr, and mercury by 0.0016 g/ha-yr. These values will be added to the present 7-yr average atmospheric loading of 11 kg/ha-yr for sulfates. Fly ash deposition in the region has not been measured, and mercury deposition based on snow cores is at most 0.013 g/ha per snow season.

2. The planned operation of the Atikokan facility represents a potential 30 percent increase over probable unbuffered acid deposition even after the prospective closing of the Steep Rock iron ore processing facility. If the iron mining operation is closed, and only half of the Atikokan generating station is constructed (400-MW), unbuffered acid deposition in the BWCA is expected to increase by 15 percent.

3. The grid-model computations indicate that the 3-h $SO_2$ concentration would exceed the U.S. air-quality Class I regulations for protection of a wilderness area two times per year; the 24-h standard would be exceeded three times per year. The annual average $SO_2$ standard would not be exceeded.

4. Two-thirds of the particulate matter reaching the BWCA from the Atikokan plume will be as $SO_4^=$ rather than fly ash; and most of the sulfate deposition in the region will have been deposited initially as $SO_2$, followed by transformation *in situ*.

5. Approximately half of the $SO_2$-plus-$SO_4^=$ and fly ash and two-thirds of the mercury deposition will occur during the snow season.

6. The amount of sulfur leaving the 100-x 100-km region by atmospheric transport would be as much as 70% of the total emitted from the proposed Atikokan power plant.

TERRESTRIAL IMPACTS

Conclusions of Fact

1. The terrestrial ecosystems of the BWCA and VNP are dominated by short-season species, two of which, white pine (*Pinus strobus*) and trembling aspen (*Populus tremuloides*), are known to be particularly sensitive to the gaseous emissions of coal-fired generating stations.

The white pine is the largest and most long-lived of species in the BWCA (a lifespan often over 250 yr), and is essential to the lake-edge and skyline features.

2. Soils of the BWCA-VNP region are mostly shallow (0-46 cm), of glacial origin, coarse textured, derived from granites and other acid bedrock types, low in cations and available nitrogen, and low in percentage base saturation.

3. Geochemical weathering of rocks and soils has, throughout the earth's history, been dominated by the weak carbonic acid formed from carbon dioxide and water. The nitric and sulfuric acid components of atmospheric deposition now being measured in the BWCA-VNP are sufficient to modify the normal carbonic acid weathering of these soils and create a geochemical cycle in which dilute nitric and sulfuric acid are important.

4. A number of lichen species are among the plants that are most sensitive to gaseous coal-combustion emissions and acid particulates. Lichens are an important part of the BWCA-VNP biota and make up the principal plant cover on 5% of the land area. Lichen species also have been shown to be an important source of nitrogen (through N fixation) in a number of nitrogen-limited coniferous forest areas.

5. A number of insect groups with strong sensory systems, particularly saprophagous and predaceous beetles, social bees (pollinators), and parasitic wasps, have been shown to be reduced in abundance at very low concentrations of air pollutants, apparently because of pollutant avoidance or disorientation. Several plant-feeding insect groups have been shown to increase rapidly when the activity of parasites or predatory control insects is reduced, or the vigor of host-plant species is reduced, both of which have been shown to occur from gaseous pollutant emissions.

Probable Impacts

1. Given what is presently known on mobilization of toxic elements by acid fallout, the increase in fallout of sulfuric and nitric acid deposition from operation of the Atikokan generating station must be viewed with considerable concern. Some of the mobilized elements are toxic to terrestrial vegetation after relatively small changes in concentration are induced by additional acid fallout. The projected additions of $H^+$ through nitrate and sulfate represent an increase of more than 25% over the presently unbuffered atmospheric acid deposition and appear likely to exceed soil buffering capacities. These mechanisms lead to effects, as well, on small lakes that could begin to receive increasing amounts of nutrient and toxic elements within a few years. Detailed watershed geochemistry and mass balance studies will be required to document such a response.

2. Small additions of acidity to the thin, rocky soils common in the BWCA, coupled with the geochemical weathering changes that are probable, can be expected to have relatively rapid and irreversible effects on outputs

from the nutrient cycles of these ecosystems. These changes will affect groundwater quality and produce soil-mediated changes in cycling rates within the ecosystems. Although the net changes in cation leaching due to lowered soil pH are difficult to predict, $H^+$ additions to some soils will facilitate leaching of essential plant nutrients.

## Possible Impacts

1. The projected ambient concentrations of total suspended particulates, $SO_2$, ozone, and acid particulates from the proposed Atikokan plant may directly affect the growth and reproductive rates of sensitive pine species. The presence of phytotoxic elements by leaching of cations could produce similar effects. The possibility of such effects increases as other major point sources of gaseous emissions are developed in the region. Over periods of 100-200 yr (the lifespan of much of the vegetation) even small effects on growth rates affect survival of the dominant species and could have important consequences on the composition of the region's vegetation. Such plant responses could be assessed as part of long-term watershed monitoring.

2. Although visible effects on lichens that would be measurable within 5 yr are not anticipated at the projected pollutant levels, slowing of growth rates for a number of species is probable and could change the species composition over a period of a few decades, leading to detrimental effects on nitrogen fixation.

3. The lower pH of the forest soils could amplify trace-element effects by making these elements more available in the food chain, and hence in small herbivores, fish, and birds at the top of the food chain. Long-term monitoring will be needed to assess these effects.

4. Effects on insects at the proposed concentrations have not yet been documented because work on the insect groups is sparse and has not focused on the threshold for response. Additional emissions and higher concentrations can be expected in the area in the next few years, and effects are known for the concentrations expected in the future. Mobilization of toxic elements through insect food chains to small mammals and birds is possible. Since pollutant injury to sensitive pine species also is possible, increased insect damage may occur. Additional studies of the effects of low concentrations of $SO_2$ on the olfactory systems of pollinating and parasitic Hymenoptera, predatory beetles, and decomposer insects are urgently needed.

## AQUATIC IMPACTS

## Conclusions of Fact

1. The BWCA and VNP are in a region comparable in vulnerability to others that have already been severely affected by acid precipitation in Europe and North America. Most BWCA-VNP surface waters have a poor buffering capacity, and many have a low pH (below 6.5) as well.

2. Precipitation in the near vicinity of the BWCA-VNP is strongly acid on occasion, and the mean annual pH of precipitation is near the level where damage begins.

3. Atmospheric acid sulfate loadings in the near vicinity of the BWCA-VNP are at levels associated with the onset of severe lake acidification in Scandinavian countries.

4. Mercury levels in fish, which increase as lakes acidify, are already high in some lakes in and near the BWCA-VNP.

5. Most of the area within a 100-km (62-mile) radius of Atikokan is in the Rainy Lake watershed and drains into the international waters of the BWCA, VNP, and Quetico lakes.

6. The varied, valuable fishery resource of the BWCA-VNP includes many species that have been reduced or eliminated by acid precipitation elsewhere in the United States and Canada.

7. Increased metal concentrations, sufficient themselves to cause problems, often accompany reduced pH. As the pH is lowered, the forms of metals present also become more toxic in most cases.

Probable Impacts

1. It is likely that vulnerable lakes in the BWCA-VNP and Quetico areas (poorly buffered headwater lakes with small watersheds and shallow soils of low buffering capacity) are already being affected by acidity from atmospheric sources.

2. Although present atmospheric loadings of acid-producing material are probably affecting some BWCA-VNP-Quetico lakes, additional loadings from Atikokan will accelerate the rate of acidification in vulnerable lakes and endanger other lakes not presently being acidified. Long-term studies of lake-water and stream-water chemistry in the BWCA are needed. Special attention should be given to accurate hydrological and chemical budgets of inputs, outputs, and storage in ecosystems susceptible to damage by acidification to define the timing and magnitude of the effects.

3. Given the probable changes in the existing pH levels of lake water, we can project likely responses in the aquatic biota: reduction in decomposition of organic matter; undesirable accumulation of certain nuisance algae; decreases in phytoplankton species numbers, diversity, biomass, and production per unit volume; elimination of some species and simplification of zooplankton communities; alterations in benthic plant and animal communities; and the loss of fish species preceded by reproductive failure. These changes will occur over different time spans: for some lakes, several years; for others, several decades.

4. Likely increases in the acidity of the water will increase the severity of seasonal events such as acid flushing in the spring due to snow melt. Even moderately buffered lakes may form a shallow, but highly acid layer

of water from acid meltwater. This condition will result in a reduction in the variety of insect species emerging in the spring and cause death of exposed fish embryos.

A reconnaissance survey of the biota and productivity at all trophic levels should be carried out. It would be followed by detailed, long-term monitoring of population dynamics and lake metabolism, with special attention to organisms and processes sensitive to acidification, in a series of lakes of differing sensitivity to acid precipitation. Studies currently going on in Scandinavia and the Adirondacks can serve as models.

5. Increased acidity is likely to result in detrimental levels of aluminum and of other trace elements in the lake water by increasing leaching and creating more toxic forms of these elements. Detailed studies of precipitation chemistry in the BWCA-VNP are needed on a long-term basis (10-20 yr). Special attention should be given to loadings of acid, sulfate, nitrate, and heavy metals to define these changes.

6. The projected additions of mercury and of acid to the Rainy River watershed are very likely to aggravate an existing problem of mercury levels in fish tissues. Additional data will be required to define the precise changes and sources.

Possible Impacts

1. Fish populations in the most susceptible lakes of the BWCA-VNP and Quetico could be eliminated by acid precipitation. Some populations may be lost within a few years, and in many other lakes within a few decades.

2. The productivity and biotic diversity of the aquatic communities in these lakes is likely to be severely reduced over a period of one to several decades. Some of the most vulnerable lakes may already have experienced reductions in pH levels and undergone corresponding biological changes. The paucity of historical base-line data makes such an analysis very difficult to perform at this time.

3. It is possible that these changes and others (e.g. ground-water quality), will not be reversible within the foreseeable future, even if the acidity of precipitation is substantially reduced.

## SECTION 3

## AIR QUALITY IN THE BOUNDARY WATERS CANOE AREA (BWCA)

### INTRODUCTION

Air quality in the BWCA of Minnesota can be degraded by a combination of large emission sources within 80-160 km (50-100 miles) of the area and long-distance transport of pollutants which are accumulated during certain periods in the Midwestern United States and Canada. Degradation may occur by increasing ambient air concentrations of air pollutants and by the resulting flux of these pollutants to the ground either by dry deposition or by removal via rain or snow.

The air-pollutant concentrations or deposition, or both, may cause damage to vegetation and animal groups such as insects and degrade visibility. The deposition fluxes potentially may cause damage to fish and animals via the water and soil. If the concentrations and deposition rates are low enough (i.e., within some theoretical assimilative capacity for the region), no significant damage will occur. Since the BWCA is a U.S. wilderness area, the most sensitive effects must be considered. To assess the effects of future increased pollutant loadings and concentrations, careful estimates of the emissions near the BWCA, the transport, and the deposition are needed.

The objective of this section on air quality, therefore, is to develop and utilize a grid-type model of air pollution dispersion to assess the ambient air concentrations and deposition fluxes in the BWCA due to emissions from the proposed Atikokan generating station. Attention will be focused on sulfur dioxide, sulfate aerosol, total fly ash particulates, and mercury.

The study area contains the BWCA and the Quetico Provincial Park (Figure 1). The Atikokan generating station will lie 80-120 km north of the BWCA. Sources of pollutant emissions due to present electric power generation, mining activity, and industrial and municipal sources that may have an impact on the BWCA are considered as regional contributors to the current air quality and atmospheric loadings. Most of these sources are outside the grid considered in this report.

The BWCA-Quetico area has a cool continental climate characterized by short, warm summers and long, cold winters: mean annual temperature 2°C (36°F); mean July temperature, 17°C (63°F); mean January temperature, -15°C (6°F). The average annual precipitation is 71 cm (28 in.), 64% of which occurs as rain from May through September, the growing season. Annual mean snowfall is about 152 cm (60 in.), and the ground is usually snow covered from mid-November to mid-April.

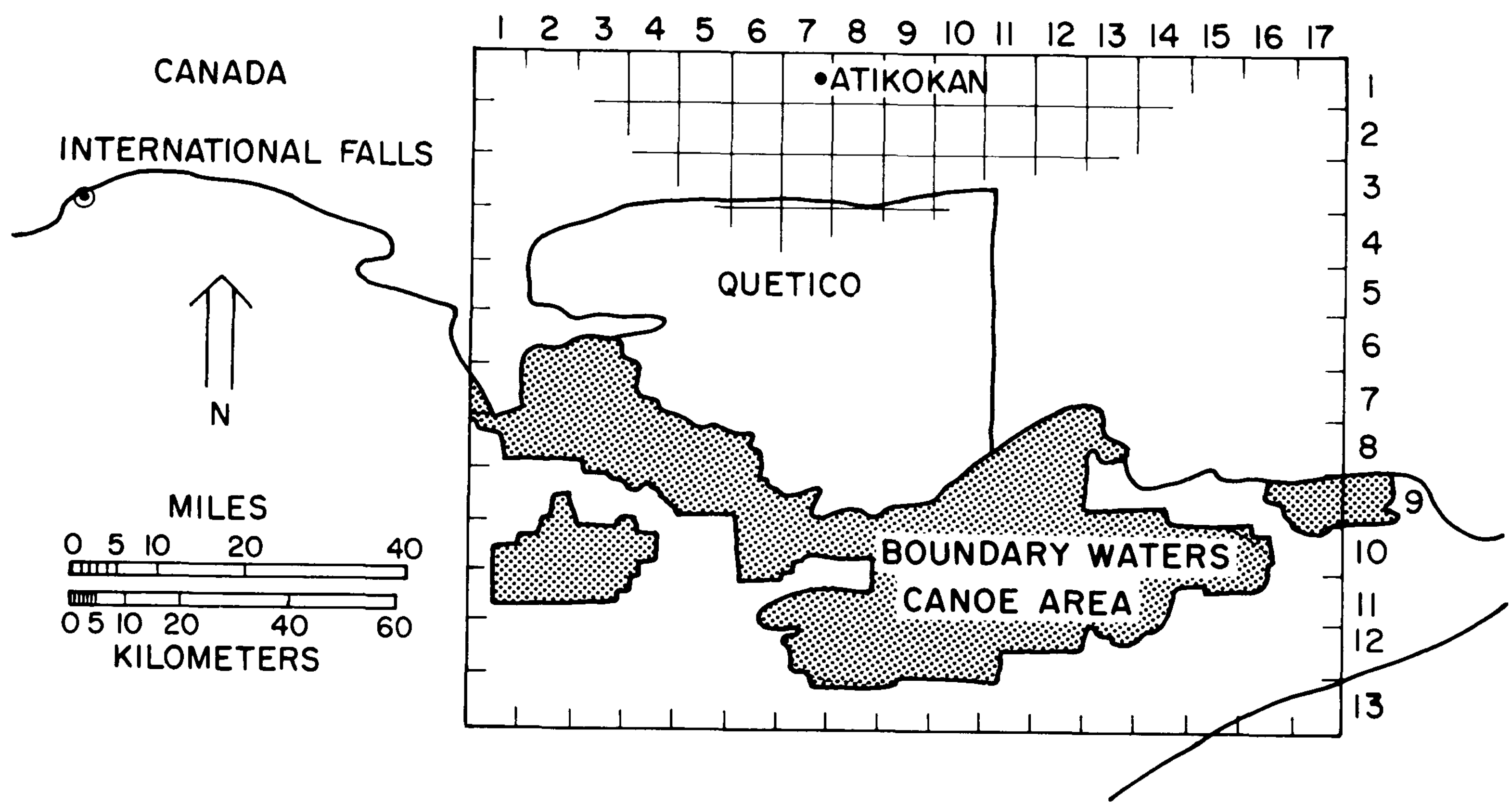



Figure 1. Map of the study area showing grid for computer model.

The BWCA's landscape has a generally slight but locally rugged relief left by preglacial erosion of the Canadian Shield. Elevations above sea level range from 341 m (1,119 ft) at Crane Lake to 680 m (2,232 ft) in the Misquah Hills; local differences in elevation range from 30 to 150 m. The land is heavily wooded, and 16.7% of the BWCA consists of lakes and streams.

## BACKGROUND AIR-QUALITY DATA NEAR THE BWCA

The BWCA currently has especially clean air. The available monitoring data near the BWCA are summarized in Table 1. The Fernberg Road site, presented in the table, is a remote site at the edge of the BWCA that has been monitored by the Minnesota copper-nickel study. Monitoring data for sulfur dioxide, suspended particulates, and bulk deposition are available from February to December 1977 and ozone from May to December (Valentine, Minnesota Pollution Control Agency, personal communication, 1978).

The sulfur dioxide levels at Fernberg during 1977 never exceeded the threshold level of the instrument, which was 10 $\mu g/m^3$ (4 ppb), and only once exceeded this level during 1978.

The suspended particulate matter, as measured by a high volume sampler, yielded an annual arithmetic average of 15 $\mu g/m^3$ and an annual geometric average of 11 $\mu g/m^3$. There were 53 days of data, taken approximately once per week. The maximum 24-h reading was 66 $\mu g/m^3$, which occurred on May 1, 1977.

The ozone data were recorded at Fernberg for 5,384 h from May to December 1977. The arithmetic average of all hourly values was 0.030 ppm, and the geometric average was 0.027 ppm. The maximum hourly readings were 0.100 ppm and 0.101 ppm, which occurred during the afternoons of May 28 and July 19, 1977.

Since the ozone concentrations are due to long-distance transport, it is instructive to compare the Fernberg site with another site at Cloquet, Minn., west of Duluth. At Cloquet the ozone readings followed a pattern similar to that at the Fernberg site, but were slightly lower. The peak reading on July 19 was 0.070 ppm rather than 0.10 ppm, for example. The highest reading was 0.097 ppm on August 20. The Cloquet site probably records lower ozone readings than Fernberg because of scavenging of the ozone by local sources of nitric oxide from automobiles.

The ozone measurements indicate that the Fernberg site is probably representative of the region. It is assured that the $SO_2$ and particulate readings are representative. These data indicate that the ambient $SO_2$ from regional sources is converted to sulfates, or the $SO_2$ is deposited out before it reaches the Fernberg site instrument. The total deposition of sulfate (wet plus dry) measured by the Minnesota copper-nickel study south of the BWCA was 10-15 kg/ha-yr during the 2-yr period 1976-78.

In addition, Ontario Hydro has monitored air and precipitation quality at five sites near Atikokan. Continuous monitoring of $SO_2$, $O_3$, and NOX started in July 1975 (Ontario Hydro 1976). The Nym Lake site, which is

TABLE 1. SUMMARY OF AVAILABLE DATA ON AIR POLLUTANTS IN THE BOUNDARY WATERS CANOE AREA AND ADJACENT ONTARIO

| Pollutant | Location | Level recorded | Averaging period |
|---|---|---|---|
| | MINNESOTA (near BWCA) | | |
| $SO_2$ | Fernberg Road[a] Superior Nat'l Forest | $\leq$ 10 $\mu g/m^3$ (4 ppb) | Individual hourly readings Feb.-Dec. 1977 |
| $O_3$ | Fernberg Road[a] Superior Nat'l Forest | 0.10 ppm | Hourly maximum May-Dec. 1977 |
| | | 0.03 ppm | Average May-Dec. 1977 |
| $O_3$ | Cloquet, Minn.[a] | 0.097 ppm | Hourly maximum May-Dec. 1977 |
| Suspended particulates | Fernberg Road[a] Superior Nat'l Forest | 66 $\mu g/m^3$ | 24-hr maximum Feb.-Dec. 1977 |
| | | 15 $\mu g/m^3$ | Annual arithmatic average Feb.-Dec. 1977 |
| | | 11 $\mu g/m^3$ | Annual geometric average Feb.-Dec. 1977 |
| Bulk $SO_4^=$ deposition | BWCA[b] | 1.5 kg/ha | Average $SO_4^=$ snow loading, 65 sites, March 1978 |
| Bulk $SO_4^=$ deposition | Minnesota Copper-Nickel[a] Project Area | 10-15 kg/ha-yr | Range 1976-78 |
| | ONTARIO (near Atikokan) | | |
| $SO_2$ | Nym Lake[c] | 0.02 ppm (50 $\mu g/m^3$) | Hourly maximum 1975-76 |
| $O_3$ | Nym Lake[c] | 0.10 ppm | Hourly maximum 1975-76 |
| NOX | Nym Lake[c] | 0.01 ppm | Summer average 1975 |
| NOX | Nym Lake[c] | 0.03 ppm | 24-h maximum 1975 |
| NOX | Nym Lake[c] | 0.10 ppm | Hourly maximum |
| Bulk $SO_4^=$ deposition | Atikokan Region[c] | 4 and 7 kg/ha-yr | 6/75-4/76 |
| Bulk $SO_4^=$ deposition | Experimental Lakes[d] Region (Kenora) | 7-14 kg/ha-yr (10.9 kg/ha-yr) | 1971-77 Average |

[a] Minnesota Pollution Control Agency (1978).

[b] Glass, G. E., L. J. Heinis, L. Anderson, C. Sandberg, and F. Boettcher, unpublished data (1979).

[c] Ontario Hydro (1976).

[d] Schindler, D. W., unpublished data, ELA Research Station (1978).

located 17 km SSW of the generating station site near the Quetico boundary, is the most remote site from the Steep Rock mines and will be briefly reviewed (see Table 1). The total deposition of sulfate measured at two sites was 4 and 7 kg/ha-yr.

The minimum detectable $SO_2$ level of 10 ppb was observed for short times on 25 different days, and the levels never exceeded 25 ppb (50 $\mu g/m^3$) during the 10-month period reported. Ozone levels reached maximum levels of 0.100 ppm on 2 consecutive days during July 1975 and were generally similar to those at the Fernberg site. When the ozone was high, the sulfur dioxide was usually not above threshold level of the instrument. The NOX levels typically averaged 5 ppb during June and 10 ppb during July, August, and September. On occasion the concentration reached an hourly value of 0.100 ppm; however, these high values did not correspond to either high $O_3$ or high $SO_2$ levels. It appears that the $SO_2$ is due primarily to local mining activities, and that the $O_3$ levels are due to long-distance transport. The elevated NOX levels may be due to local sources.

Measurements of bulk deposition of sulfate, wet-plus-dry fall, have been carried out at three locations in the vicinity of the BWCA (Table 1). The longest record, at the Experimental Lakes Area (ELA) lakes 180 km northwest of Atikokan, shows an average recent sulfate deposition of 10.9 kg/ha-yr. The average pH of the rainfall here during 1974-77 is 4.86. The presettlement pH for rainfall in this area appears to have been 5.7 (cf. carbonic acid equilibrium and data for 1955-56 shown by Galloway and Cowling (1978). Data from the ELA show that 70% of the nitrate and sulfate in the current rainfall is in a neutralized form. Thirty percent is in the acid form, and the $H^+$ ions were assumed to divide between $SO_4^=$ and $NO_3$ on a 2:1 ratio. This information yields an estimate of 7.6 kg/ha-yr of neutralized sulfate and 3.1 kg/ha-yr of acid sulfate producing the net depression in pH. Thus, depending on the historic potential of atmospheric constituents to neutralize anthropogenic acid, presettlement loadings of sulfate must lie between 0 and 7.6 kg/ha-yr. For purposes of further comparison a value of 4 kg/ha-yr will be used.

## ATIKOKAN EMISSIONS

The proposed Atikokan generating station consists of four 200-MW units burning sub-bituminous or lignite coal from Saskatchewan with a sulfur content not to exceed 0.8% and a maximum ash content of 12%[1]. Electrostatic precipitators for fly ash removal are to be employed. The potential emissions were calculated with the assumption of an overall thermal efficiency of 36% and a full load (Table 2). The emission factors were obtained as follows. For sulfur dioxide 38S is the current EPA handbook (EPA-AP-42) value for pulverized coal boilers. The sulfate emission factor of 1.2 corresponds to the assumption that 2% of the sulfur is emitted directly as sulfate. Mercury is assumed to go entirely up the stack (Billings et al. 1973). The nitrogen oxide emission factor is based on the

[1] Fry, R.J. (Manager of Air Pollution and Environmental Contaminants Division, Environmental Protection Service, Ontario). Letter I.M. Goklany, U.S. Environ. Prot. Agency, Region V, Chicago, Oct. 14, 1977.

TABLE 2. ATIKOKAN POWER PLANT EMISSIONS[a]

| Item | High | Low |
|---|---|---|
| Heating value (BTU/lb) | 7,500 | 6,500 |
| Sulfur content (% weight) | 0.8 | 0.4 |
| Ash content (% weight) | 12.0 | 6.5 |
| Mercury content (% weight) | $2 \times 10^{-5}$ | $2 \times 10^{-5}$ |
| Sulfur dioxide emission factor (lb/ton) | 38S[b] | 38S |
| Sulfate emission factor (lb/ton) | 1.2S | 1.2S |
| Total particulate emission factor[c] (lb/ton) | 0.085A | 0.085A |
| Mercury emission factor (lb/ton) | 20Hg | 20Hg |
| Coal rate (full load) (tons/h) | 583 | 506 |
| Sulfur dioxide emissions (g/s) | 2,230 | 969 |
| Sulfur dioxide emissions (tons/yr) | 77,500 | 33,700 |
| Sulfate emissions (g/s) | 67 | 29 |
| Sulfate emissions (tons/yr) | 2,325 | 1,010 |
| Total particulate emissions (g/s) | 75 | 35 |
| Total particulate emissions (tons/yr) | 2,600 | 1,226 |
| Mercury emissions (g/s) | 0.029 | 0.025 |
| Mercury emissions (tons/yr) | 1.01 | 0.89 |
| NOX emission factor ($lb/lb^6$ BTU) | 1.2 | 1.2 |
| NOX emissions (g/s) | 1,323 | 955 |
| NOX emissions (tons/yr) | 45,900 | 34,500 |

[a] If 36% thermal efficient and a full load at 800-MW are assumed, the heat input rate is $7.59 \times 10^9$ BTU/h.

[b] S, A, and Hg are percentage by weight, e.g., S = 0.8.

[c] Assuming 99.5% removal in precipitator.

current U.S. emission standard, which reflects current boiler technology. There are to be four stacks each 198 m high with a 3.8-m exit diameter. The stack gas-flow rate is 288 $m^3/s$ and the exhaust temperature is 408°K. Representative coal analysis is given in Appendix C.

In addition, the Steep Rock Iron Mines at Atikokan currently emit an estimated 14-27,000 metric tons/yr (15-30,000 tons/yr) sulfur dioxide and 10-18,000 metric tons/yr (10-20,000 tons/yr) particulates. The Caland Ore Company at Atikokan emits an estimated 254 metric tons/yr (280 tons/yr) sulfur dioxide and 1,490 tons/year particulates. Only the main stack of the Steep Rock Iron Mine facility, which is 91 m high, will possibly influence the BWCA directly, since the other stacks are short. These emission sources are reportedly being closed in the near future and hence are not considered in this modeling effort.

## ATMOSPHERIC DISPERSION, TRANSFORMATION, AND DEPOSITION

A realistic air-quality model to meet the objective of this study must consider a number of physical and chemical processes. Consider a parcel of air emitted from a tall stack. The advection caused by the wind diffuses laterally and vertically at a rate that depends on the amount of turbulence in the air. The turbulence depends on the wind speed and net heat flux. The vertical spread is constrained by an inversion layer which moves up or down depending on the net heat flux and overall pressure patterns in the atmosphere. If the inversion is low, the plume will rise above the inversion, and pollutants will not reach the ground unless there is precipitation. The wind speed, wind direction, and heat flux are continually changing as the parcel of air is dispersing within the region, and hence a time-dependent model is more appropriate than a steady-state model.

Certain pollutants within the plume can undergo chemical reaction as they are being transported, such as the conversion of sulfur dioxide into sulfate aerosol. The reaction rate depends on the concentration of the reacting species as well as other species in the air and on the intensity of the sunlight. As part of the parcel diffuses to the ground, it is partially removed by dry deposition at the surface depending on the type of surface and type of pollutant. When precipitation occurs, pollutants are scavenged at a rate related to the amount and type of precipitation. The precipitation, which is usually more acidic because of the pollutants, is deposited on the ground.

Plume modeling is often done with a so-called Gaussian plume model, such as the EPA CRSTER (Guldberg 1977) model. Since this type of model is not time dependent and does not include pollutant transformation, or wet and dry deposition processes, the Gaussian plume models are more appropriate to smaller regions. For a study such as this a grid-type model based on numerical solution of the general, time-dependent diffusion equation is more appropriate because the meteorological, chemical, and deposition processes can be more realistically simulated.

Before describing the modeling work, a general discussion of chemical reactions in the plume and dry deposition processes is presented.

## Plume Chemistry

The primary gases emitted from the stack of a power-plant plume are nitrogen, carbon dioxide, and water vapor. The release of these gases from the regional sources will not have a direct known effect on the BWCA. Carbon monoxide and low molecular weight hydrocarbon emissions are considered to be small and thus will not be considered. Sulfur oxides, nitrogen oxides, total particulate matter, halogens, and mercury will be discussed below.

Most of the sulfur in the combustion chamber is oxidized to $SO_2$ although a small percentage is oxidized to $SO_3$ in the combustion chamber and reacts with water vapor in the stack to form sulfuric acid. Approximately 2% of the sulfur is in sulfate form in the plume close to the stack (Forrest and Newman 1977a, b). There is general agreement that $SO_2$ continues to react in the plume and form sulfate aerosol as the plume diffuses (Gillani et al. 1978, Schwartz and Newman 1978). Recent studies by Husar et al. (1978) found that during noon hours the $SO_2$ conversion rate was 1-4% per hour, whereas at night the conversion rate was below 0.5% per hour in the Labadie plume, which is from a 2,400-MW coal-fired power plant near St. Louis. The sulfate aerosol which is formed is primarily in the light-scattering size range (0.1-1 μm) so that visibility is reduced by sulfate formation. The mechanism for sulfate conversion can be photochemical or heterogeneous reactions in combination with particulate matter in the plume. Although theories exist for rapid conversion of $SO_2$ to sulfates in the plume, the exact mechanisms have not been established.

Nitrogen oxide (NO) is formed in the combustion chamber from nitrogen in the supply air and nitrogen bound in the coal. Nitrogen oxide is generally converted to nitrogen dioxide ($NO_2^-$) in the plume as ambient ozone diffuses into the plume.

The $NO/NO_2^-$ ratio in a plume is difficult to model, and hence it is customary to model NOX, which is NO plus $NO_2^-$ weighted as $NO_2^-$.

Particulate matter in the form of fly ash is emitted from the stack in mostly submicron size. The fly ash serves as condensation nuclei for aerosol formation. The particulate matter can also serve as a catalyst for sulfur dioxide reactions. In our modeling work we assume that the particulate matter represents the fly ash only; the sulfate aerosol is modeled separately.

Mercury in coal is believed to be vaporized in the combustion chamber and emitted as a vapor. It is possible that part of the mercury may condense on the fly ash as the plume cools. For modeling purposes, however, mercury should be considered in the vapor phase. Coal also contains trace amounts of chlorine, fluorine, and bromine, which can form the acids HCl, HF, and HBr and particulates containing these elements. These components were not considered in detail because of lack of information concerning their environmental behavior.

## Dry Deposition

Dry deposition of gases occurs by absorption and adsorption on vegetation, soil, and surface water. Dry deposition of particulates occurs by impaction onto the surface material. The dry deposition flux of any species can be determined by multiplying the concentration of that species near the ground by the effective deposition velocity. The deposition velocities have been determined experimentally and have been shown to depend on the rate of diffusion and the characteristics of the underlying surface. Frequently a deposition resistance is used, which is the inverse of the deposition velocity. The total resistance is the sum of the aerodynamic resistance and the surface resistance.

Calculation of the aerodynamic resistance will be discussed later. For $SO_2$ the surface resistance of tall forest lands, which is the majority of the surface in the BWCA during summer, is generally agreed to be about 0.5 s/cm (Chamberlain 1966, Shepherd 1974). The surface resistance of snow to $SO_2$ is about 3 s/cm (Whelpdale and Shaw 1974, Dovland and Eliassen 1976). Also, the atmosphere tends to be more stable over snow, and hence the deposition velocity of $SO_2$ to snow is considerably lower than to summer vegetation.

The dry deposition velocity of particles is strongly dependent on particle size. Most of the sulfate mass lies in the 0.1- to 1-μm-diameter range for which the deposition velocity is not expected to exceed 0.1 cm/s (Anon. 1978). Hence we have used a surface resistance of 5 s/cm for both winter and summer for sulfate aerosol. Fly ash emitted from the stack is also predominantly in this size range, and hence a deposition velocity of 0.1 cm/s has been used.

## Wet Deposition

The concentration of sulfate in precipitation is a consequence of several cumulative processes occurring within and beneath the clouds. Brownian motion, phoretic attachment, inertial impaction, and nucleation all serve to remove the sulfate aerosol from the air and attach it to the cloud and precipitation elements. However, Brownian and phoretic attachment mechanisms cannot place sufficient $SO_4^=$ mass into the cloud water to account for observed concentrations, and inertial impaction of subcloud sulfate is of second-order importance when compared to other removal mechanisms (Scott and Laulainen 1979).

Since sulfate particles are generally soluble and are quite small, and the majority of mass is distributed over particles with diameters less than 1.0 μm (Harrison et al. 1976), they should be effective as cloud condensation nuclei. Indeed, if as Weiss et al. (1977) claim, the major portion of the aerosol with diameters between 0.1 and 1.0 μm is sulfate, then the airborne sulfate aerosol could be responsible for nearly all of the cloud droplets appearing in continental clouds.

Sulfate may be generated within the cloud and precipitation water through the oxidation of absorbed $SO_2$. The oxidation processes appear to be temperature dependent and often appear to rely on the presence of metal catalysts. Laboratory and theoretical work also suggests that oxidants such as $O_2$, $O_3$, and $H_2O_2$ are capable of producing substantial quantities of sulfate in cloud water (see e.g., Levy et al. 1976 for an extensive literature survey).

Both the oxygen and ozone transformation mechanisms are pH dependent and begin to decrease substantially in importance as the pH decreases to less than 6 for $O_2$ reactions and 4.5 for $O_3$ reactions. The hydrogen peroxide mechanism is relatively insensitive to acidity, but few measurements of tropospheric $H_2O_2$ exist to determine the contribution to $SO_4^=$ by this oxidant. Ammonia can also play an important role in aqueous phase $SO_2$ oxidation by neutralizing some of the $H_2SO_4$ that is formed and reducing the acidity. However, recent solubility measurements by Drewes and Hales (1979) imply that oxidation mechanisms based upon the presence of ammonia proceed more slowly than previously thought.

Fortunately some evidence is beginning to accumulate suggesting that it is not necessary to consider in-cloud conversion of $SO_2$ to $SO_4^=$ in order to predict the sulfate concentration in precipitation. Recent observations by Scott and Laulainen (1979), and modeling efforts by Scott (1978) have suggested that for certain precipitation events, the sulfate concentration in precipitation is determined largely by the sulfate concentration in the air flowing into the storm system. Scott suggests that the sulfate concentration in precipitation is inversely proportional to the precipitation rate and strongly dependent upon the type of storm system producing the precipitation.

The removal of soluble, submicron, pollutant aerosol from clouds appears to be accomplished primarily by large collector particles, such as snowflakes or raindrops, sweeping downward through the cloud and capturing the small cloud droplets containing high concentrations of the aerosol. The final concentration in the precipitation reaching the ground is dependent upon two features; first, the initial concentration in the collector particles as they start their descent through the region of the cloud where accretion of cloud droplets is the primary growth mechanism, and secondly, the concentration of pollutant in the cloud water accreted by the collector particles.

The solubility of sulfate particles makes them extremely effective as cloud condensation nuclei. The sulfate concentration in the collected cloud droplets depends upon the amount of cloud water condensed about each activated sulfate particle which, in turn, depends upon the number of available aerosol, their size, and the intensity of the updraft velocity within the cloud.

The model of sulfate removal by Scott (1978), considers the three basic precipitation systems illustrated in Figure 2. In the first case (Figure 2a), the Bergeron or ice growth process is primarily responsible for precipitation development. Ice crystals nucleate in the upper portions of the cloud, grow rapidly to precipitation sized particles, aggregate with each other, and accrete tiny cloud droplets. Even if melting should occur before the ice particles reach cloud base, the hydrometeors are large enough so that accretion of small cloud droplets continues to be the primary growth

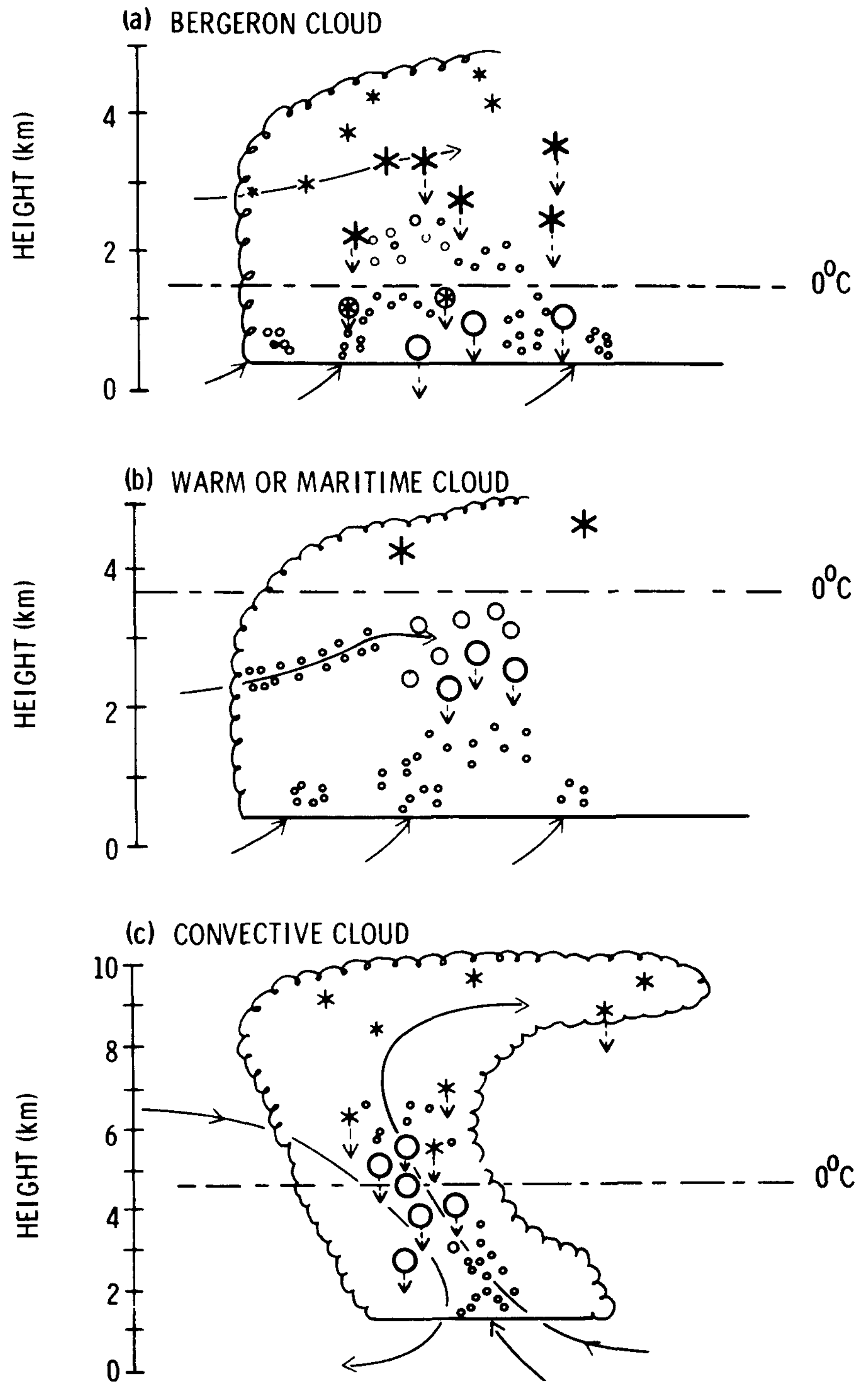



Figure 2. Qualitative description of synoptic situations envisioned for the model. The symbols represent: large stars, ice particles; small stars, melting ice particles; large circles, liquid drops; small circles, cloud droplets; →, trajectory of air flowing into the storm (solid lines); -- →, motion of hydrometeors relative to the storm (dashed lines). The vertical scale represents typical cloud depths.

mechanism*. The sulfate incorporated into the precipitation is assumed to be predominantly that advected through the cloud base. This first case represents a situation where the collector particle (snow) is relatively pollutant free when it begins to accumulate liquid water. The ice nucleation is in an environment subsaturated with respect to water and upon nuclei with lattice structures similar to ice, such as silicas and clays (McDonald 1964). Sulfate aerosol are not activated as cloud condensation nuclei in the upper portions of the cloud and are not initially incorporated into the hydrometeor water. Sulfate pickup comes primarily through incorporation of the dirty cloud water in the lower portions of the cloud. Surface precipitation from this type of cloud may be snow or rain.

The Bergeron or cold cloud is felt to be responsible for the majority of precipitation falling from layer-type clouds over the continents (Mason 1971). The precipitation from continuous rain or snow storms over northern Minnesota almost certainly relies upon a Bergeron process for its development.

In the second situation (Figure 2b) the ice-growth process is assumed to be ineffective in initiating precipitation. Rain develops entirely through warm phase mechanisms. Gentle uplift (0.1-0.5 m/s) is implied, and long times are available for precipitation-sized drops to develop by condensation and coalescence. A major fraction of the moisture and pollutants is assumed to be transported through the sides of the storm. For this second case, sulfate aerosol flowing into the storm at the higher levels are activated in environs saturated with respect to water. The collector particles therefore have an initial sulfate concentration when they begin their descent through the lower portions of the cloud. Net sulfate pickup is equal to the sum of the sulfate material activated in the collector particles at their formation altitude and the sulfate accumulated by accretion of the dirty cloud droplets near cloud base. Thus, this warm cloud is capable of removing more sulfate than the cold cloud.

The third case (Figure 2c) considers precipitation development in convective storms. Here strong updrafts produce large supersaturations and large liquid water contents which enable combined condensation and coalescence to produce precipitation-sized drops faster than they can be removed by hydrometeors falling from above. The mass flux of moisture and pollutants is assumed to be largely through the cloud base. In the convective cloud both the ice-capture mechanism of the cold cloud and the condensation, coalescence growth of the warm cloud are effective in removing sulfate from the atmosphere. The removal potential exceeds that of either the individual warm or cold clouds primarily because those droplets that grow into collector particles have grown by coalescence in the lower portions of the cloud where the cloud water contains high concentrations of sulfate. Showery, summertime precipitation in Minnesota should exhibit removal characteristics of the convective cloud; that is, extremely high concentrations of sulfate should be associated with convective showers affecting a small (approximately 1-10% of the total area) area at any one time.

* Hydrometeors refer to ice or water particles large enough to fall from the cloud to the land surface

These qualitative results can be expressed explicitly in terms of a washout ratio, E, defined as the ratio of sulfate concentration in the precipitation water ($g_{sulfate}/g_{water}$) to the sulfate concentration in air below the cloud base ($g_{sulfate}/g_{air}$). Figure 3 (from Scott and Laulainen 1979) illustrates the predicted variation in washout ratio as a function of precipitation rate, J, for the cold cloud (curve 3), the warm cloud (curve 2), and the convective cloud (curve 1). For a fixed concentration of airborne sulfate and for a given precipitation rate, Figure 3 predicts the lowest sulfate concentrations in precipitation originating as snow. Factor 2 and 3 increases are predicted when precipitation develops by warm phase mechanisms in stratiform clouds. The greatest sulfate concentrations are predicted to occur in precipitation from convective clouds. The convective and warm cloud mechanisms would be most prevalent during the summer months whereas the ice-growth mechanism would naturally occur during the winter.

If the precipitation is in the form of snow or originated as snow in the upper portions of the clouds (curve 3), then the surface sulfate concentration in precipitation is roughly proportional to $J^{-0.3}$ over the interval from J = 0.2 to 2.0 mm $h^{-1}$. If the precipitation-sized drops develop independently of an ice stage, then the surface sulfate concentration becomes more strongly dependent upon rainfall rate and upon the airborne sulfate concentration at the inflow levels of the storm. If the precipitation forms without the benefit of an initial ice-growth stage, then for light precipitation rates ($J \cong 0.2$ mm $h^{-1}$) the sulfate concentrations in precipitation water can increase by a factor of 70 or more over the ice-dependent predictions. At more moderate precipitation rates ($J < 1$ mm $h^{-1}$) the precipitation originating as snow is predicted to have about one-third to one-half the sulfate concentration of that originating on water droplets. At heavy precipitation rates ($J > 7$ mm $h^{-1}$), the sulfate concentration is nearly independent of the precipitation-formation mechanisms.

The curve of Figure 4 provides a clue that might help to explain natural seasonal variations in sulfate concentration detected in the northeast United States. Figure 4 illustrates the variability observed in the Multistate Atmospheric Power Production Pollution Study (MAP3S 1977) precipitation chemistry network. Although the scatter is considerable in these precipitation-chemistry data, there seems to be a definite decline in winter concentrations of sulfate followed by an increase during the warmer seasons. High concentrations in the summer may be related to removal by convective storms, whereas winter-time removal of sulfate is probably associated with cold rain and snowstorms. Similar seasonal variations in sulfate removal are also expected in northern Minnesota.

In summary, both experimental and theoretical data are beginning to accumulate that suggest that sulfate deposition is seasonally dependent and related to such features as storm type, precipitation rate, and concentration of pollutant being drawn into the storms. Of the three storm situations discussed above, the sulfate concentration in the precipitation falling on the BWCA should be best predicted by using the cold cloud model, except for situations when the precipitation is clearly from convective clouds.

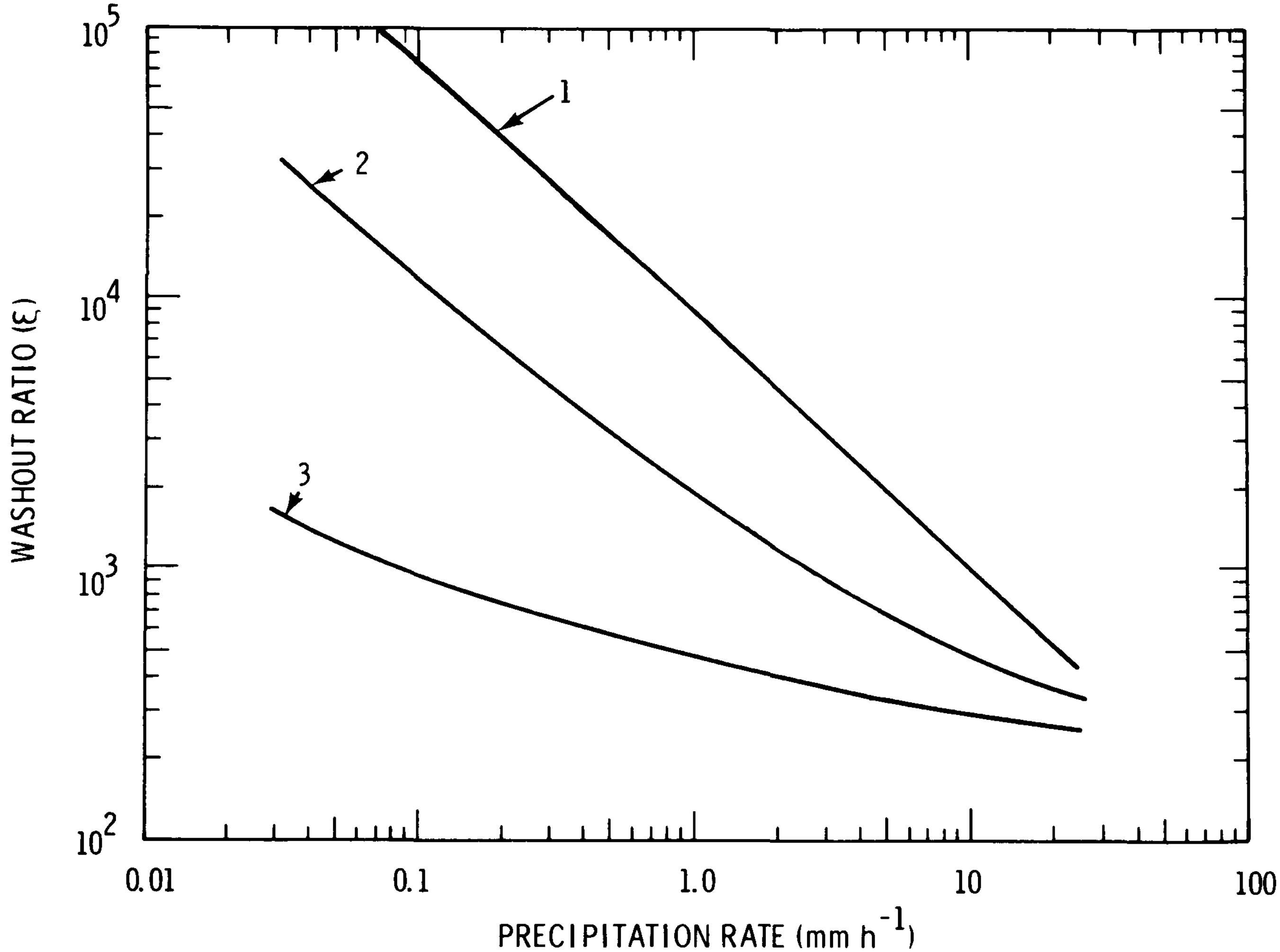



Figure 3. Washout ratio as a function of precipitation rate. Curve 1 represents predictions for intense convective storms or from clouds where tops are warmer than 0°C; curve 2 represents predictions for storms where rain develops without the assistance of an ice-growth stage; curve 3 is for storms where the ice-growth process is necessary for initiating precipitation.

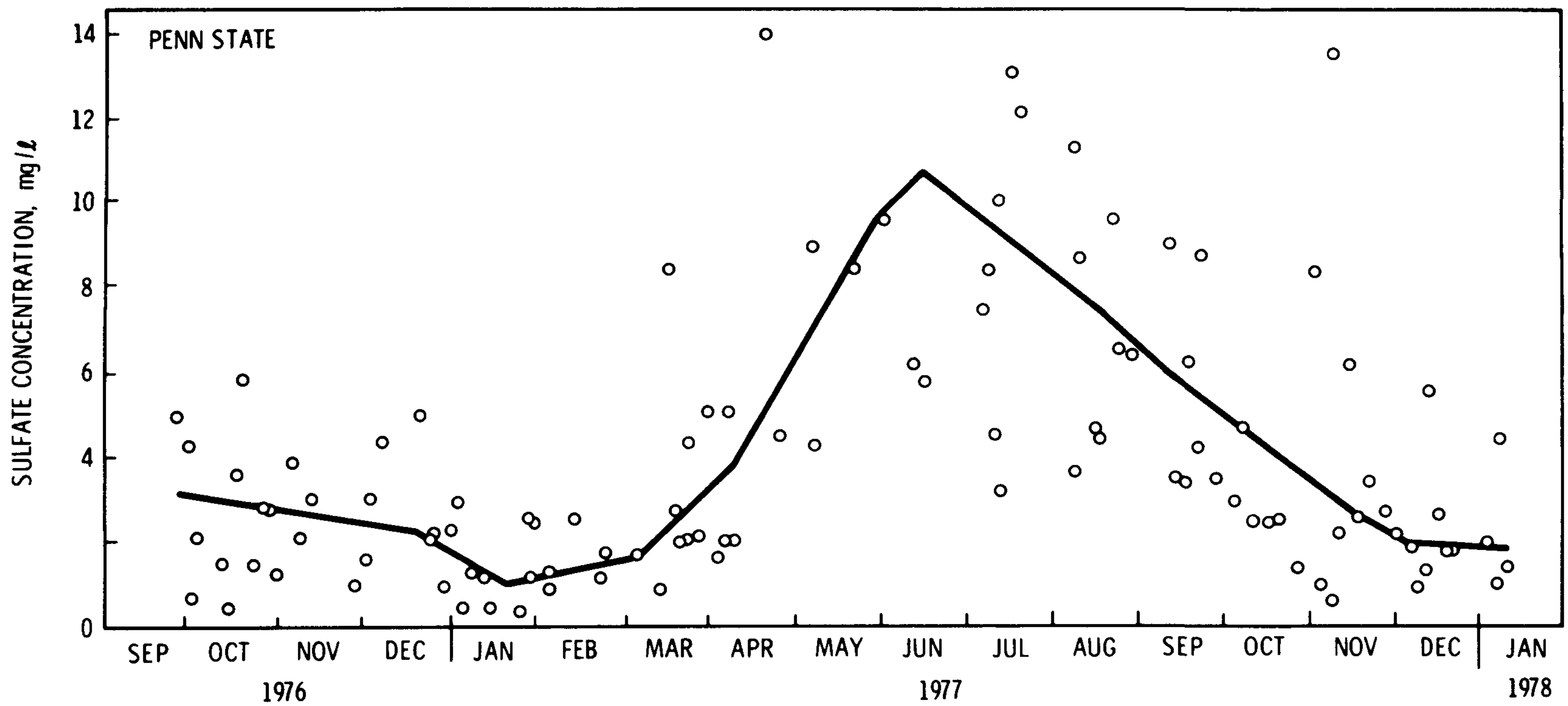



Figure 4. Sulfate concentrations in surface precipitation at Pennsylvania State University, September 1976 through January 1978. The curve is an eyeball fit to individual data points.

The BWCA faces an additional impact due to the washout of $SO_2$, which once in the surface waters is likely to convert to $SO_4^=$. This conversion of $SO_2$ in surface waters may or may not present problems for the environment, depending upon its concentration and acidity.

DESCRIPTION OF THE THREE-DIMENSIONAL DISPERSION MODEL

The model may be characterized as a grid-type model of atmospheric dispersion which numerically integrates the species continuity equation. Chemical reaction between two species, horizontal advection, vertical diffusion, and wet and dry deposition processes are simulated. The model computes temporal and three-dimensional spatial concentration distributions due to single or multiple point and area sources. A fully implicit finite difference scheme is utilized so that numerical errors are minimal. A single station is used to characterize the meteorological conditions throughout the grid. Three-h, 24-h, and annual average concentrations and deposition fluxes are computed.

The model formulation, the numerical solution procedure, and the meteorological data used are described in the remainder of this section. The modeling scheme and treatment of meterological parameters follows that reported by Ragland (1973), and Ragland and Dennis (1975).

Model Formulation

Consider first a two-component mixture undergoing a first-order chemical reaction. The pollutant species are affected by advection of the wind, diffusion in the lateral and vertical direction, and removal by dry and wet deposition. The wind speed and diffusivity vary with height, surface roughness, and net heat flux (Figure 5). The plume is trapped by an elevated inversion layer.

If we align the x-axes with the wind vector and use the fact that the diffusion term in the x-direction is small compared to transport by the wind, then the set of equations to be solved for two species C and S is:

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} - K_y\frac{\partial^2 C}{\partial y^2} - \frac{\partial}{\partial z}\left(K_z\frac{\partial C}{\partial z}\right) = -kC - W_c + Q_c \qquad (1)$$

$$\frac{\partial S}{\partial t} + u\frac{\partial S}{\partial x} - K_y\frac{\partial^2 S}{\partial y^2} - \frac{\partial}{\partial z}\left(K_z\frac{\partial S}{\partial z}\right) = kC\frac{m_s}{m_c} - W_s + Q_s \qquad (2)$$

at $z = 0$

$$K_z\frac{\partial C}{\partial z} = -V_{DC}C \qquad (3)$$

$$K_z\frac{\partial S}{\partial z} = -V_{DS}C \qquad (4)$$

for the reaction

$$C \xrightarrow{k} S. \qquad (5)$$

The upper boundary condition is zero species flux into the inversion layer at $z=z_m$. For example, C represents the concentration of sulfur dioxide and S represents the concentration of sulfate aerosol. If, for example, mercury is to be simulated, C represents mercury and S is zero. Equation (5) defines

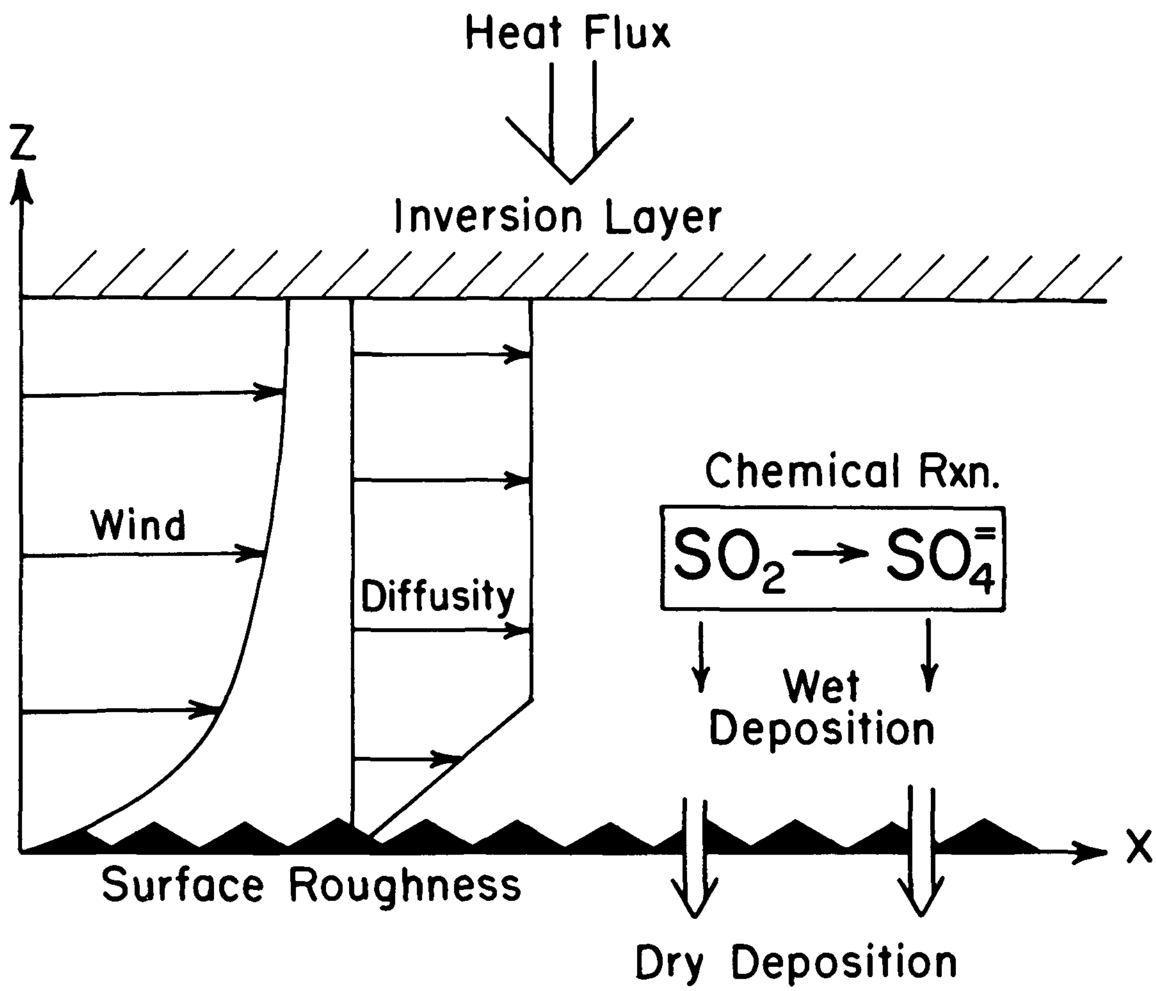



Figure 5. Schematic diagram of the parameters used in the grid model.

the rate constant, k. The letter W is the wet deposition removal rate per unit volume, Q is the mass flow rate of emissions, $V_D$ is the dry deposition velocity, and m is the molecular weight.

The wind speed (u) and vertical eddy diffusivity ($K_z$) are calculated as a function of height (z) within the surface layer which extends up to $z_{sL}$ and from the top of the surface layer to the inversion layer $z_m$. According to the scheme outlined in Table 3 the parameter L is defined as

$$L = \frac{-u_*^3 \rho c_p T}{0.4gH} , \tag{6}$$

and

$$u_* = \frac{0.16 u_g}{\log_{10} \frac{u_g}{z_o f} - 1.8} . \tag{7}$$

It should be noted that the geostrophic wind ($\mu_g$), the net heat flux (H), and the surface roughness ($z_o$) are required inputs. Since only the surface wind at 10 m is available hourly, the program internally computes the geostrophic wind.

The net heat flux is obtained from data for cloud cover and cloud ceiling height by first computing a radiation index according to the scheme used for STAR data (Turner 1964). The radiation index is then converted by the following procedure:

| Radiation Index | 4 | 3 | 2 | 1 | 0 | -1 | -2 |
|---|---|---|---|---|---|---|---|
| H(cal/cm$^2$ - min) | 0.24 | 0.18 | 0.12 | 0.06 | 0 | -0.03 | -0.06 |

The lateral diffusivity is an important parameter that is not well-known for the time and distance scales of this study. The available data have led us to the assumption that $K_y = 100 K_z$. This accounts for gusts that veer and back and also accounts for a certain amount of wind vector shift with height due to the Coriolis force.

Changes in the wind direction from hour to hour are handled by a coordinate rotation transformation. In this way any arbitrary wind direction can be simulated.

The deposition velocities ($V_D$) that appear in Eq. (3) and (4) depend on an aerodynamic resistance ($r_a$) and a surface resistance ($r_s$),

$$V_D = \frac{1}{r_a + r_s} . \tag{8}$$

The aerodynamic resistance is represented by

$$r_a = \frac{u(1)}{(u_*)^2} . \tag{9}$$

TABLE 3. WIND AND DIFFUSIVITY PROFILES

| | Stability | Vertical distance | Wind speed $u$ | Eddy diffusivity $K_z$ |
|---|---|---|---|---|
| Within Surface Layer | Neutral | $0<z-z_{SL}$ | $\frac{u_*}{.4} \ln\left(\frac{z+z_0}{z_0}\right)$ | $.4u_* z$ |
| | Stable | $0<z\leq z_{SL}$ AND $0<z\leq L$ | $\frac{u_*}{.4}\left[\ln\left(\frac{z+z_0}{z_0}\right) + \frac{5.2z}{L}\right]$ | $.4u_* z/(1+\frac{5.2}{L}z)$ |
| | | $L<z\leq z_{SL}$ | $\frac{u_*}{.4}\left[\ln\left(\frac{z+z_0}{z_0}\right) + 5.2\right]$ | $.4u_*/6.2$ |
| | Unstable | $0<z\leq z_{SL}$ OR $0<z\leq \lvert 2L \rvert$ | $\frac{u_*}{.4}\left[2(\tan^{-1}x-\tan^{-1}x_0) +\ln\left(\frac{x-1}{x_0-1}\right)-\ln\left(\frac{x+1}{x_0+1}\right)\right]$ <br> $x = [1-15(z+z_0)/L]^{1/4}$ <br> $x_0 = [1-15z_0/L]^{1/4}$ | $.4u_* z(1-\frac{15z}{L})^{.25}$ |
| Above Surface Layer | Neutral | $z_{SL}<z\leq z_m$ | $(u_g-u_{SL})\left(\frac{z-z_{S0}}{z_m-z_{SL}}\right) + u_{SL}$ | $.4u_* z_{SL}$ |
| | Stable | $z_{SL}<z\leq z_m$ | $(u_g-u_{SL})\left(\frac{z-z_{SL}}{z_m-z_{SL}}\right) + u_{SL}$ | $.4u_* L$ |
| | Unstable | $z_{SL}<z\leq z_m$ OR $\lvert 2L \rvert<z\leq z_m$ | $(u_g-u_{SL})\left(\frac{z-z_{SL}}{z_m-z_{SL}}\right) + u_{SL}$ | $160u_*^2(1-\frac{6000u_*}{L})^{.25}$ |

and hence may change hourly. The surface resistance depends on the particular pollutant and surface such as snow, water, vegetation, etc.

The reaction rate constant (k) can also vary hourly and is a function of the solar radiation index and other pollutants present in the plume. In very clean air, such as is typical of the BWCA, the conversion rate constant is smaller than in urban air. Following the work of Husar et al. (1978) we have used 2% per hour during the day time and 0.5% at night.

The wet deposition removal rate is calculated according to the procedures outlined in Appendix A. By using Eq. (A-22) we have

$$W_c(\text{rain}) = 0.96\ \beta\ \bar{C}\ J^{0.9}, \tag{10}$$

$$W_c(\text{snow}) = 0.48\ \beta\ \bar{C}\ J^{0.9}\ (1-\exp(-2\bar{m})),$$

and

$$W_s(\text{rain or snow}) = 0.44\ \bar{S}\ J^{0.625}. \tag{12}$$

The symbols $\bar{C}$ and $\bar{S}$ are the average sulfur dioxide and sulfate concentrations ($\mu g/m^3$) and J is the rate of precipitation (water equivalent) in millimeters per hour. From Eq. (A-15) $\bar{m}$ is given by

$$\bar{m} = 1.56 + 0.44 \ln J. \tag{13}$$

The parameter $\beta$ depends on the pH of the rain according to Figure A-2, which for this study has been simplified to the following equation:

$$\log_{10} \beta = -2 + 0.75\ (\text{pH}-3.9) \tag{14}$$

for pH less than 5.1; otherwise $\beta = 0.067$.

As explained in Appendix A,

$$\text{pH} = -\log_{10}(2{,}000\ S_W/96), \tag{15}$$

where $S_W$ is the sulfate concentration in the cloud drops from Eq. (A-10):

$$S_W = 0.45\ S\ J^{-0.27}. \tag{16}$$

The wet deposition fluxes are determined by multiplying Eqs. (10), (11), and (12) by the height of the layer being scavenged, which is given by Eq. (A-9). For this study we have used a height of 2,000 m as an approximation to Eq. (A-9).

## Numerical Solution of the Plume Model

The solution of the diffusion equation with the various terms as described above can only be accomplished by numerical techniques. Equation (1) with boundary and initial conditions is solved numerically by means of a first-order fully implicit finite difference technique. This method is numerically stable for any step size. Consider a volume of fluid with sides $\Delta x$, $\Delta y$, $\Delta z$ located at a point i+1, j, k. Properties at the point i, j, k at the time t are known, but in the i+1 plane at time t and the i plane at the time t + $\Delta t$ are unknown. Conservation of mass for a particular species in an element of fluid not adjacent to a boundary may be written as:

$$
\begin{aligned}
& C'_{i+1,j,k}(dxdydz/dt) \\
&+ U_k C'_{i+1,j,k}(dydz) \\
&+ (K_y)_k(C'_{i+1,j,k} - C'_{i+1,j+1,k})(dxdz/dy) \\
&+ (K_y)_k(C'_{i+1,j,k} - C'_{i+1,j-1,k})(dxdz/dy) \\
&+ (K_z)_{k+1/2}(C'_{i+1,j,k} - C'_{i+1,j,k+1})(dxdy/dz) \\
&+ (K_z)_{k-1/2}(C'_{i+1,j,k} - C'_{i+1,j,k-1})(dxdy/dz) \\
&+ k\ C'_{i+1,j,k}(dxdydz) + W_c C'_{i+1,j,k}(Z_m\ dxdy) \\
&= C_{i+1,j,k}(dxdydz/dt) + U_k C'_{i,j,k}(dydz) + Q_c \qquad (17)
\end{aligned}
$$

Here C' denotes the unknown concentration at time t + $\Delta t$, and C denotes the known concentration at time t. At a boundary one or more terms on the left hand side is zero. A similar equation is written for each cell of fluid in the i+1 plane, and the set of equations is solved simultaneously stepping forward along x and then stepping through t. A similar equation is written for species S from Eq. (2) and solved along with Eq. (1). The source emission rate Qc is added in only one cell at the point of effective release.

For an individual step it is seen that Eq. (17) can be written as

$$[\underline{A}]\ [C]_{x + \Delta x,\ t \text{ or } x,\ t + \Delta t} = u\ [C]_{x,t}, \qquad (18)$$

where $[\underline{A}]$ is determined as a dispersion matrix $(NUMY \cdot NUMZ)^2$ large containing only known meteorological parameters and step size, and

[C] is the concentration vector NUMY times NUMZ long. The right-hand side contains only known terms, and NUMY and NUMZ are the number of cells in the cross-wind and vertical directions, respectively.

The set of equations (18) is solved by factoring A such that $A = LL^T$, where L is a lower triangular matrix and $L^T$ is the transpose of L. This may be readily done since A is a positive-definite, symmetric band matrix. The solution of the system of linear equations is determined by lettering Y $L^TC$ and computing Y by back substitution in the equations LY = D. When Y = is known, C may be determined by back substitution in $L^TC = Y$.

Changes in wind direction were handled by means of a rotation of the coordinate axes. Hence two grid systems are used: a rotating grid in which the computations are done and a fixed system in which the results are stored. The x and y coordinates of a grid point are transformed as follows:

$$X_F = X_r \cos(\theta) - Y_r \sin(\theta)$$

$$Y_F = X_r \sin(\theta) + Y_r \cos(\theta)$$

where $\theta$ is the wind direction.

A major difficulty in the procedure is that the grid rectangles don't overlap in a uniform way, so the question arises of how to apportion the concentrations for one grid to the grids for the other system. This difficulty was overcome by subdividing a grid into a number of smaller grids and assigning to each small grid the concentration of the larger divided by the number of subgrids. The subdivision can be as fine as desired, but more subgrids means greater computing time and cost. In this model there are nine subgrids. The final concentration is the sum of all the smaller grids of the rotation system which overlap it. The concentrations originally calculated in the rotating system have now been stored in the fixed system, so we can rotate the grid to the new wind direction. Then we simply reverse the process and subdivide the grids in the fixed system, use the above fixed-to-rotating equations to transform the coordinates, arrive at the "already present" concentrations in each larger grid in the rotating system, and begin the model's numerical calculations for the next hour. This procedure of going back and forth between the rotating and fixed grid systems for wind-direction changes continues for as long as there is a continuous set of meteorological data. The errors created by the coordinate transformation are generally less than 5%.

For the model runs reported here a box system of 13 x 17 x 6 high was used with $\Delta X$, $\Delta Y$ = 9,655 m (6 mi) and $\Delta Z$ = 50 m for the lower three boxes and $\Delta Z$ = (ZM-150)/3 for the upper three boxes, where ZM is the height of the inversion layer. The time step used in the model's numerical scheme was 10 min. The meteorological input, as previously noted, varies every hour. The model can therefore simulate on a continuous basis and is limited only by computer core space and time.

The required computer core space for a single non-reacting species was 28 K and for the $SO_2/SO_4^=$ reacting species was 40 K. The computing time per hour of simulated time was approximately 9.7 s for a single species and 20.1 s for $SO_2/SO_4^=$. The computer used was a UNIVAC 1110, and the code for the model is on file at the Madison Academic Computing Center.

The parameters in the model, which are dependent on the type of pollutant to be simulated, are summarized in Table 4, and the values that we have used are shown.

## Meteorological Data Used in the Model

International Falls, Minn., was selected as the site for the meteorological data. It is reasonably close to the BWCA and is the nearest site with a consistent set of surface and upper air data. International Falls is considered to be representative of the BWCA.

TABLE 4. MODEL PARAMETERS THAT ARE SPECIES DEPENDENT

| Parameter | $SO_2$ | $SO_4^=$ | Fly ash | Hg |
|---|---|---|---|---|
| Chemical reaction rate (%/h) | 0.5 (nighttime) 2.0 (daytime) | | 0 | 0 |
| Dry deposition surface resistance | | | | |
| (summer s/cm | 0.5 | 5.0 | 5.0 | a |
| (winter s/cm) | 3.0 | 5.0 | 5.0 | a |
| Wet deposition coefficient (%/h) | b | b | 36 | 0.5 |

[a] For Hg a dry deposition velocity of 0.001 m/s was used rather than specifying the surface resistance, which is not known.

[b] The washout of $SO_2$ and $SO_4^=$ was handled in a more complex manner than the fly ash and mercury. See text for a detailed description of the precipitation washout formulation.

The year 1964 was chosen for the model runs because this was the last year when hourly surface data were recorded. After 1964 the surface data are available only every 3 h. The total precipitation was about 10% greater than average during 1964. Upper air data, which are taken twice daily, are used to obtain the height of the inversion layer. Hourly values of the inversion height were obtained from a National Climatic Center data tape. All other necessary data are generated from the surface observation data tape.

The cloud cover, cloud ceiling height, day of the year, and time of day are used to calculate a radiation index, which is used to define the net heat flux, H, as indicated earlier. The wind speed at the inversion height, $U_g$, is calculated from the wind speed at 10 m. In summary, the following meteorological data are needed as input to the model:

1) Surface wind speed
2) Surface wind direction
3) Net heat flux
4) Surface air temperature
5) Height of the inversion
6) Precipitation type and amount

The Atikokan generating station subtends an arc of about 90° across the BWCA. The model was run for those periods when the wind persisted from the NW to NE direction for at least 6 h. A duration of 6 h or more implies that the plume will be over the BWCA for 3 h or more. Forty-nine different periods covering 901 h, or 10.3% of the year 1964, met this criterion and hence were used. Only winds from the NW to NE were considered to reduce the amount of computing time without seriously influencing the results in the BWCA.

The total precipitation during the year was 68 cm (26.63 in.) of water, and with winds from NE-NW sector the total precipitation was 4.9 cm (1.92 in.) or 7.2%. The total rain for the region was 55.8 cm (21.96 in.) of water, and the total snow was 11.9 cm (4.67 in.) of water. With the winds out of the NE-NW sector, total rain was 3.1 cm (1.22 in.) of water or 5.5%, and the total snow was 2.0 cm (0.77 in.) of water or 16.4%.

Although the model is run from hourly data, it is instructive to consider some seasonal and annual average meterological data from International Falls (Table 5). The wind is northerly 20% of the time, the annual mean wind through the mixed layer is 7.2 m/s, the annual nighttime inversion height is 400 m, and the annual daytime inversion height is 1,300 m. Frequently at night and also sometimes during the day in winter the plume rise from a tall stack such as Atikokan is in or above the inversion layer and hence isolated from the ground.

PLUME MODEL RESULTS FOR ATIKOKAN

The model was run for every hour in the year when the wind was from the NW to NE sector causing the Atikokan plume to flow over the BWCA. Three separate runs were made: one for sulfur dioxide and sulfates, one for particulate matter, and one for mercury. Ambient air concentrations, dry deposition fluxes, and wet deposition fluxes for each cell in the region and for each hour were computed and stored on tape. Annual, seasonal, 24-h, and

TABLE 5. AVERAGE METEROLOGICAL DATA, INTERNATIONAL FALLS, MINN., 1970-74

| Season | Wind direction[a] | | | | Mean wind speed (m/s) | Inversion height (m) | | Precipitation (in.) | Snow[b] (in.) |
|---|---|---|---|---|---|---|---|---|---|
| | N | E | S | W | | Night | Day | | |
| December - February | 18 | 17 | 25 | 40 | 7.0 | 347 | 656 | 2.08 | 30.26 |
| March - May | 21 | 29 | 21 | 29 | 7.5 | 411 | 1,646 | 4.86 | 14.34 |
| June - August | 18 | 18 | 31 | 33 | 6.9 | 337 | 1,747 | 9.53 | 0 |
| September - November | 17 | 18 | 31 | 34 | 7.4 | 511 | 1,146 | 7.41 | 10.20 |

[a]Percentage of time in direction indicated.

[b]The water equivalent of snow is approximately 1/10 the snow depth.

3-h average ground-level concentrations were obtained, and frequency distributions of 1-h, 3-h, and 24-h averages were tabulated by means of a separate tape-processor program. The seasonal and annual wet and dry deposition fluxes were obtained. The total mass of the particular pollutant that is transported out of the region by the wind during the year was also computed.

The ambient air concentrations and deposition fluxes were computed for each grid point indicated in Figure 1. Since only winds from the NW to NE were used, it is appropriate to consider a traverse across the region in the N-S direction starting with the grid containing the source at Atikokan. Figures 6-10 present the model output as a function of distance due south of Atikokan for sulfur dioxide, sulfates, fly ash, and mercury.

The annual arithmetic average ambient ground-level concentrations due to the Atikokan generating station are presented in Figure 6. In the BWCA the levels were computed to be 0.25 $\mu g/m^3$ for $SO_2$, 0.025 $\mu g/m^3$ for $SO_4^=$, 0.01 $\mu g/m^3$ for fly ash, and $4 \times 10^{-6}$ $\mu g/m^3$ for mercury. The 24-h average worst-case concentrations, which is a composite of the worst-case days for each grid point, is shown in Figure 7. The worst-case day occurred on February 23 along the N-S line. In the BWCA the highest 24-h concentrations were computed to be 10 $\mu g/m^3$ $SO_2$, 0.75 $\mu g/m^3$ $SO_4^=$, 0.4 $\mu g/m^3$ fly ash, and 0.0015 $\mu g/m^3$ Hg. The 3-h worst-case concentrations, which also occurred in the BWCA on February 23, are shown in Figure 8. In the BWCA the levels were 30-35 $\mu g/m^3$ $SO_2$, 1.8 $\mu g/m^3$ $SO_4^=$, 1 $\mu g/m^3$ fly ash, and 0.0004 $\mu g/m^3$ Hg.

The frequency of occurrence of 1-h, 3-h, and 24-h average $SO_2$ concentrations at a grid point due south of Atikokan just across the U.S. border in the BWCA is presented in Table 6. The results for the non-snow season from April 15 to November 15, defined here as "summer," are also shown. The summer season experiences significantly lower concentrations than the winter (snow) season because the inversion height is generally higher in the summer, and the thermal turbulence that disperses the plume is greater.

The computed levels for sulfur dioxide and particulate matter may be compared to the U.S. standards for wilderness areas. According to the Clean Air Act Amendments of 1977 for any class I area, the maximum allowable increase in concentrations of sulfur dioxide and particulate matter over the baseline concentration of such pollutants shall not exceed the following amounts:

| | |
|---|---|
| Particulate matter | |
| Annual geometric mean | 5 $\mu g/m^3$ |
| 24-h maximum | 10 |
| Sulfur dioxide | |
| Annual arithmetic mean | 2 $\mu g/m^3$ |
| 24-h maximum | 5 |
| 3-h maximum | 25 |

The modeling results show that the 24-h and the 3-h $SO_2$ standards would be exceeded a few times during the year during the snow season. The annual average $SO_2$ standard would not be exceeded. The particulate matter standards may be addressed by adding the fly ash and the sulfate concentration levels. The results indicate that the particulate matter standards would not be exceeded.

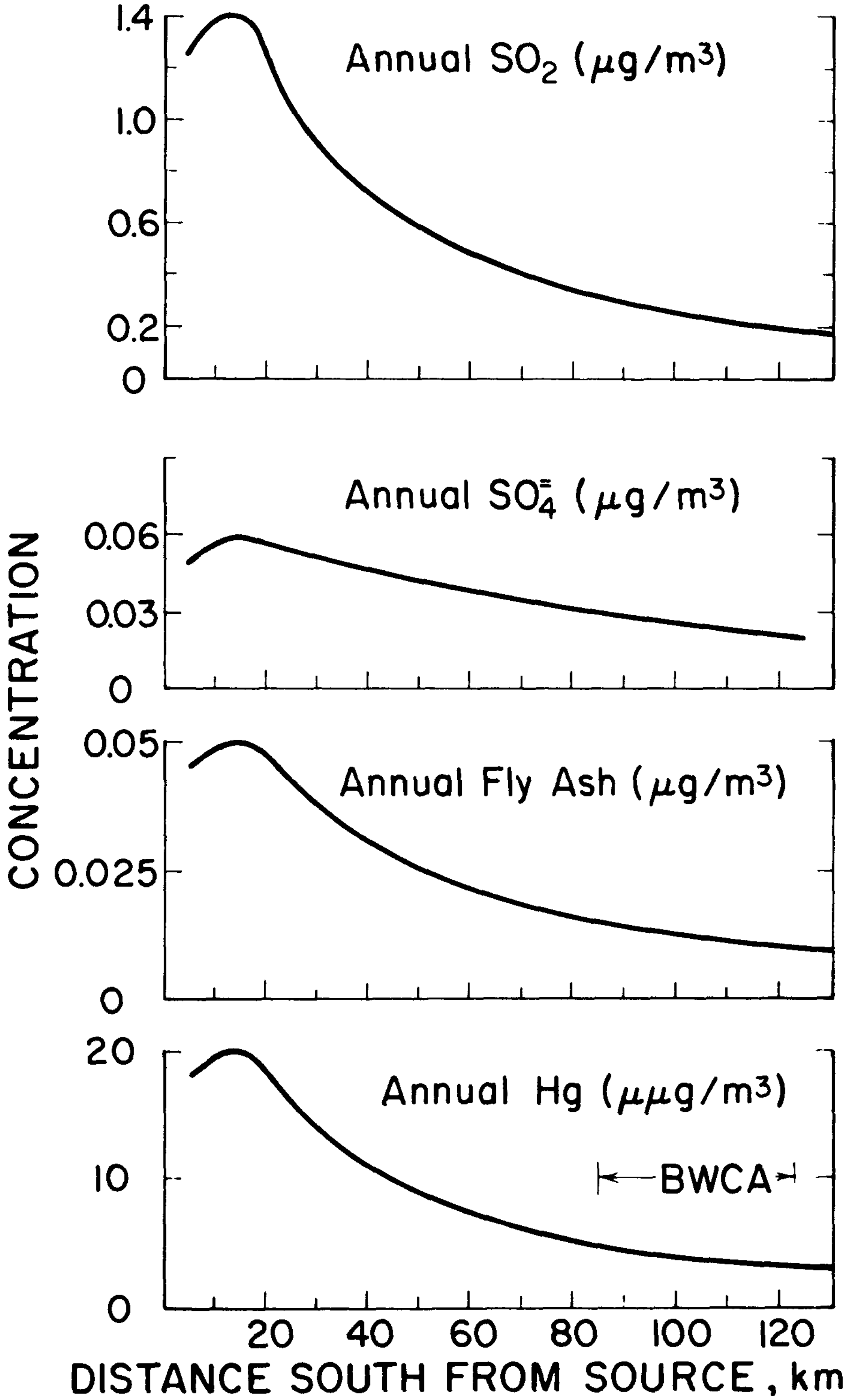



Figure 6. Computed annual average concentrations due south of Atikokan for $SO_2$, $SO_4^=$, fly ash, and mercury.

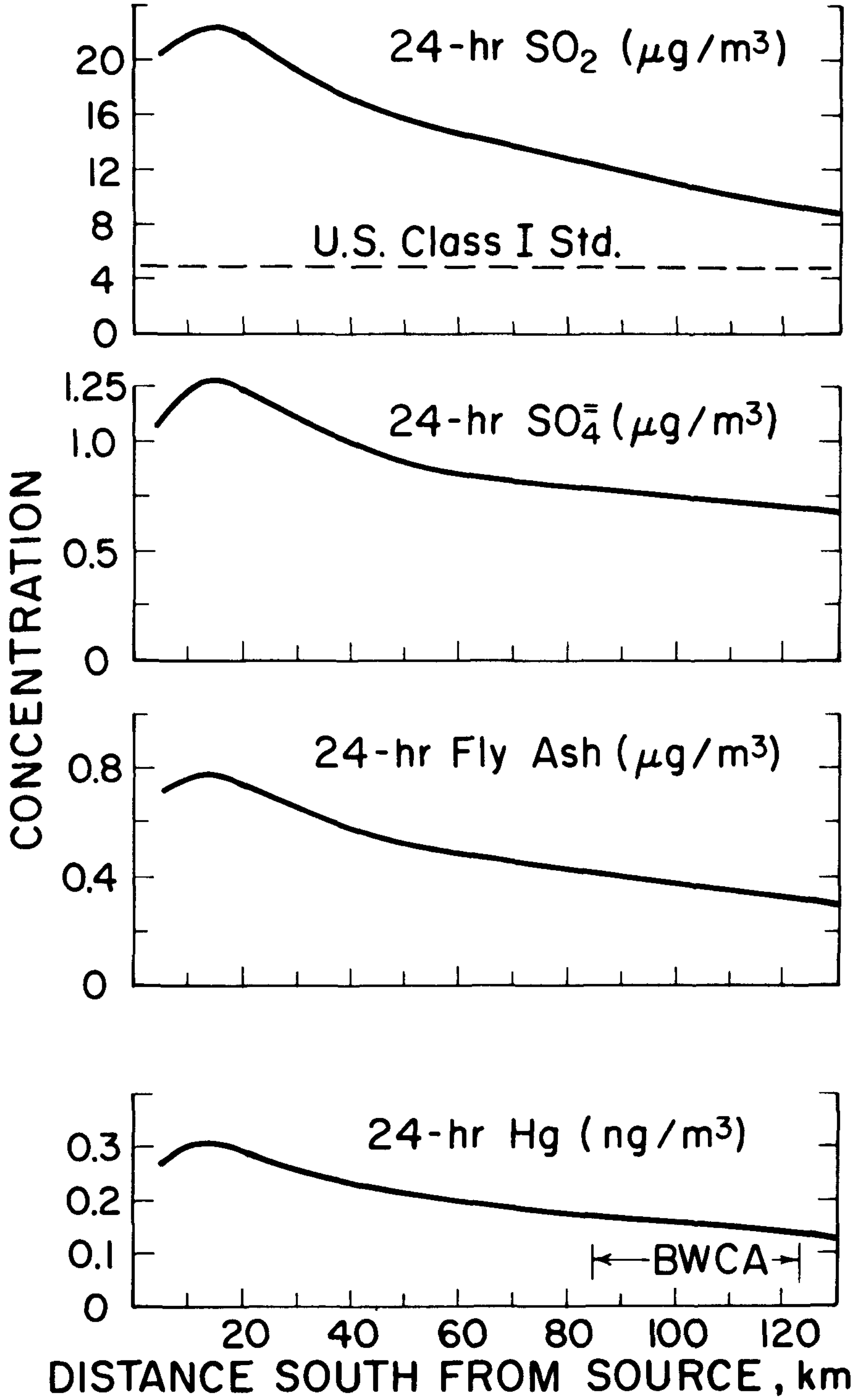



Figure 7. Computed 24-h worst-case concentrations due south of Atikokan for $SO_2$, $SO_4^=$, fly ash, and mercury.

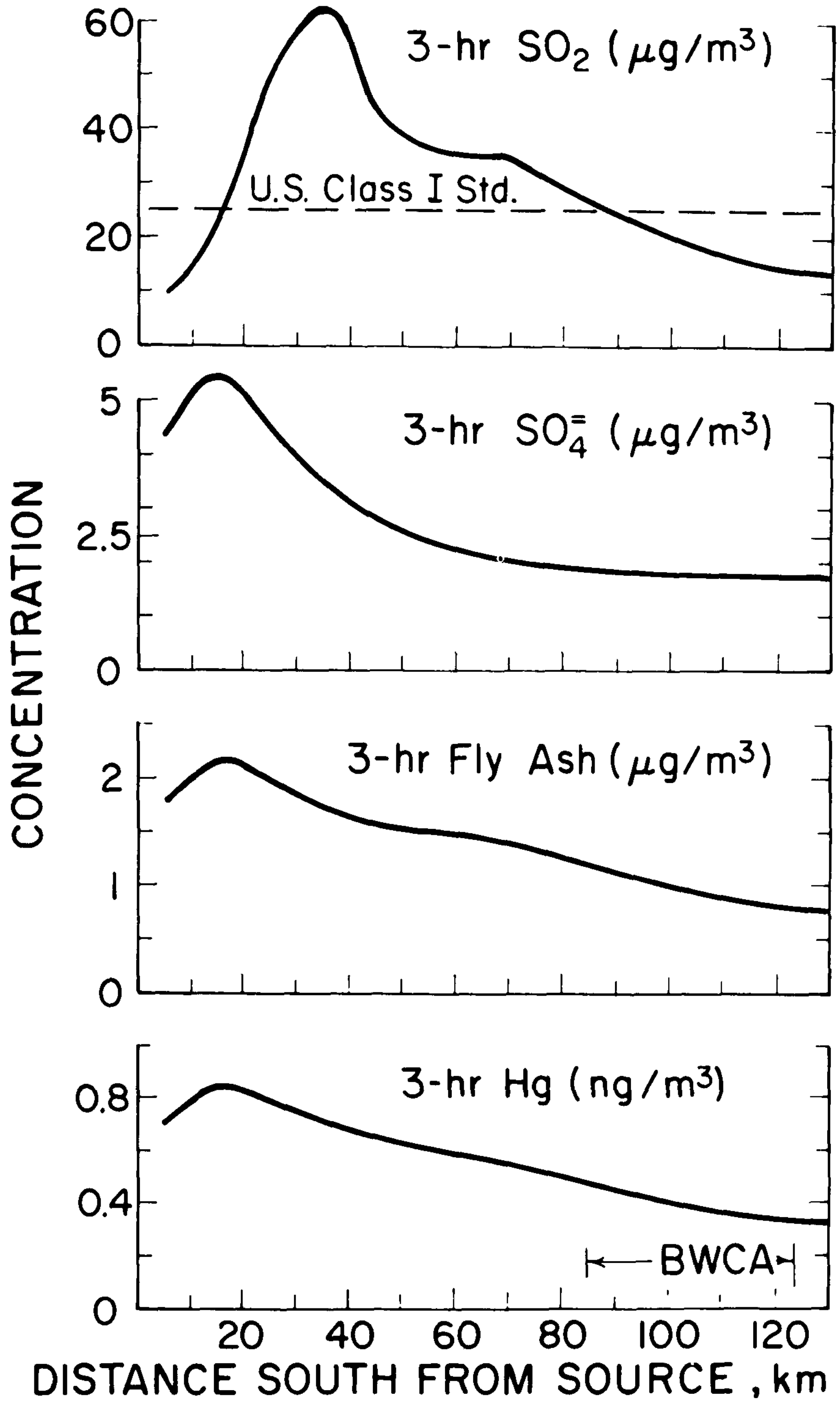



Figure 8. Computed 3-h worst-case concentrations due south of Atikokan for $SO_2$, $SO_4^=$, fly ash, and mercury.

TABLE 6. NUMBER OF PERIODS PER YEAR WHEN THE $SO_2$ CONCENTRATION IN THE BWCA IS CALCULATED TO BE IN A GIVEN RANGE DUE TO THE ATIKOKAN PLUME

| | $SO_2$ Concentration range ($\mu g/m^3$) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | >0,<1 | 1-5 | 5-10 | 10-15 | 15-20 | 20-25 | 25-30 | 30-35 | 35-40 | 40-45 | >45 |
| 1-h average | 397 | 343 | 90 | 36 | 17 | 8 | 6 | 1 | 1 | 1 | 0 |
| (Summer only) | (243) | (201) | (18) | (5) | (1) | (0) | (0) | (0) | (0) | (0) | (0) |
| 3-h average | 132 | 131 | 34 | 16 | 2 | 2 | 1 | 1 | 0 | 0 | 0 |
| (Summer only) | (80) | (6) | (1) | (0) | (0) | (0) | (0) | (0) | (0) | (0) | (0) |

| | $SO_2$ Concentration Range ($\mu g/m^3$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | >0,<1 | 1-2 | 2-3 | 3-4 | 4-5 | 5-6 | 6-9 | 9-10 | >10 |
| 24-h average | 50 | 4 | 3 | 1 | 1 | 2 | 0 | 1 | 0 |
| (Summer only) | (27) | (2) | (2) | (0) | (0) | (0) | (0) | (0) | (0) |

The deposition fluxes from the model runs are shown in Figures 9 and 10. These annual and seasonal values were obtained by summing the hourly values. The deposition fluxes due to the Atikokan generating station may be summarized as follows for a location due south of the source in the BWCA:

| $SO_2$ | Dry deposition | Wet deposition |
|---|---|---|
| Winter | 0.3 | 0.01 kg/ha |
| Summer | 0.25 | 0.02 |
| Annual | 0.55 | 0.03 |

| $SO_4^=$ | Dry deposition | Wet deposition |
|---|---|---|
| Winter | 0.010 | 0.01 kg/ha |
| Summer | 0.005 | 0.01 |
| Annual | 0.015 | 0.02 |

| Fly ash | Dry deposition | Wet deposition |
|---|---|---|
| Winter | 4 | 6 g/ha |
| Summer | 2 | 6 |
| Annual | 6 | 12 |

| Mercury | Dry deposition | Wet deposition |
|---|---|---|
| Winter | 1 | 0.05 mg/ha |
| Summer | 0.5 | 0.05 |
| Annual | 1.5 | 0.10 |

The dry and wet deposition may be added to obtain the total deposition. If we assume that the $SO_2$ deposition is converted to sulfate at the surface (multiply by 1.5 for additional $O_2$), then the total sulfate deposition at this location in the BWCA is 0.9 kg/ha-yr. The fly ash total deposition is 18 g/ha-yr, and the mercury deposition is 0.0016 g/ha-yr. These deposition values are, of course, an addition to the regional background deposition fluxes of 11 kg/ha-yr for sulfates (see Table 1), indicating an absolute increase of about 10 percent in sulfate loadings over present background at the BWCA.

Two other comparisons are also worth making. Earlier (Section III) it was noted that the sulfate in the precipitation of the Quetico-BWCA area is about two-thirds neutralized (7.6 kg/ha-yr) by other atmospheric constituents, while 3.1 kg/ha-yr of sulfate (and a contribution of nitrate) are producing the net depression in pH. The projected addition of 0.9 kg/ha-yr of sulfate

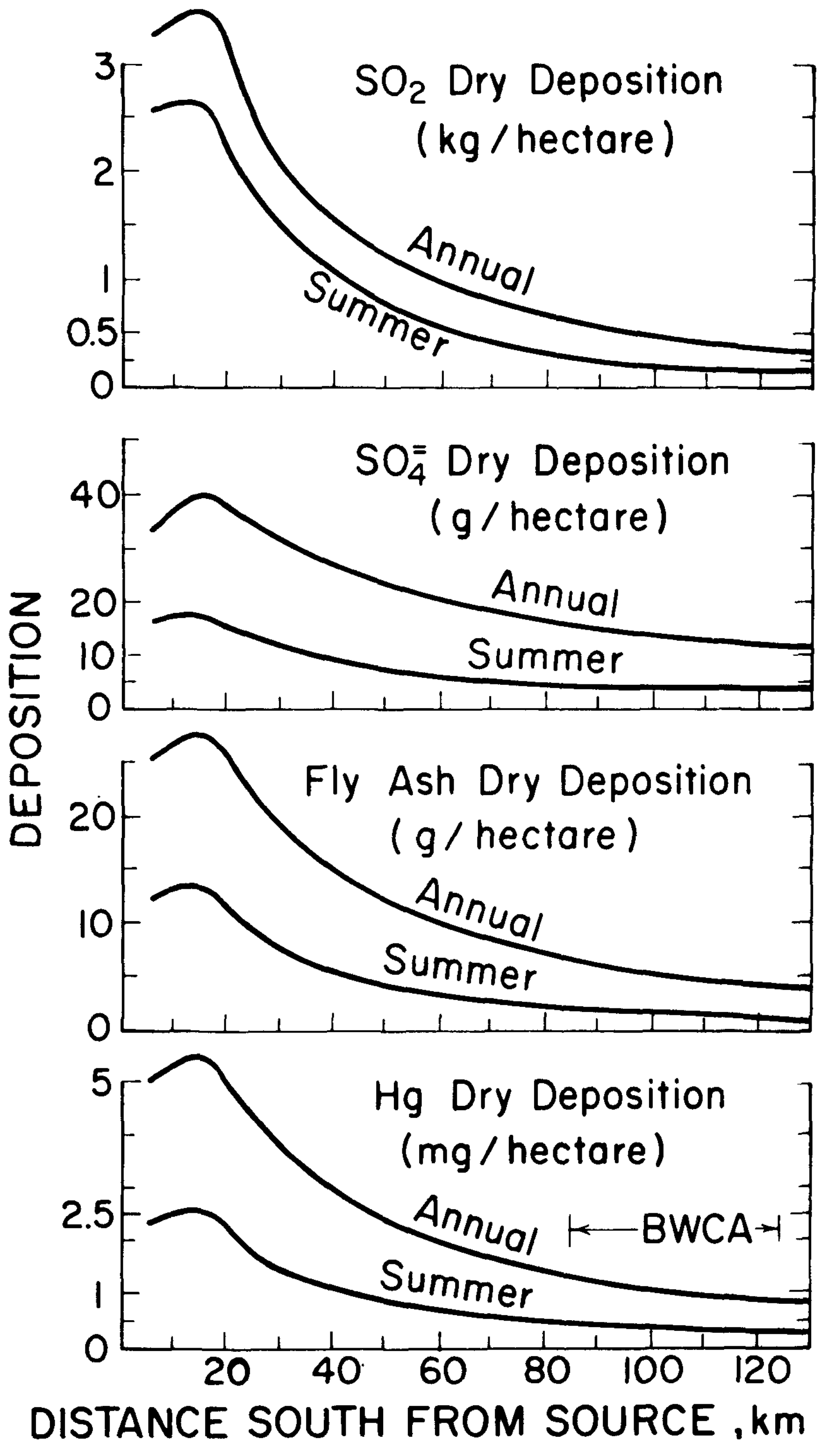



Figure 9. Computed annual and seasonal dry deposition flux due south of Atikokan for $SO_2$, $SO_4^=$, fly ash, and mercury. There are only two seasons: summer and winter. Summer is defined as the time when the snow is not on the ground.

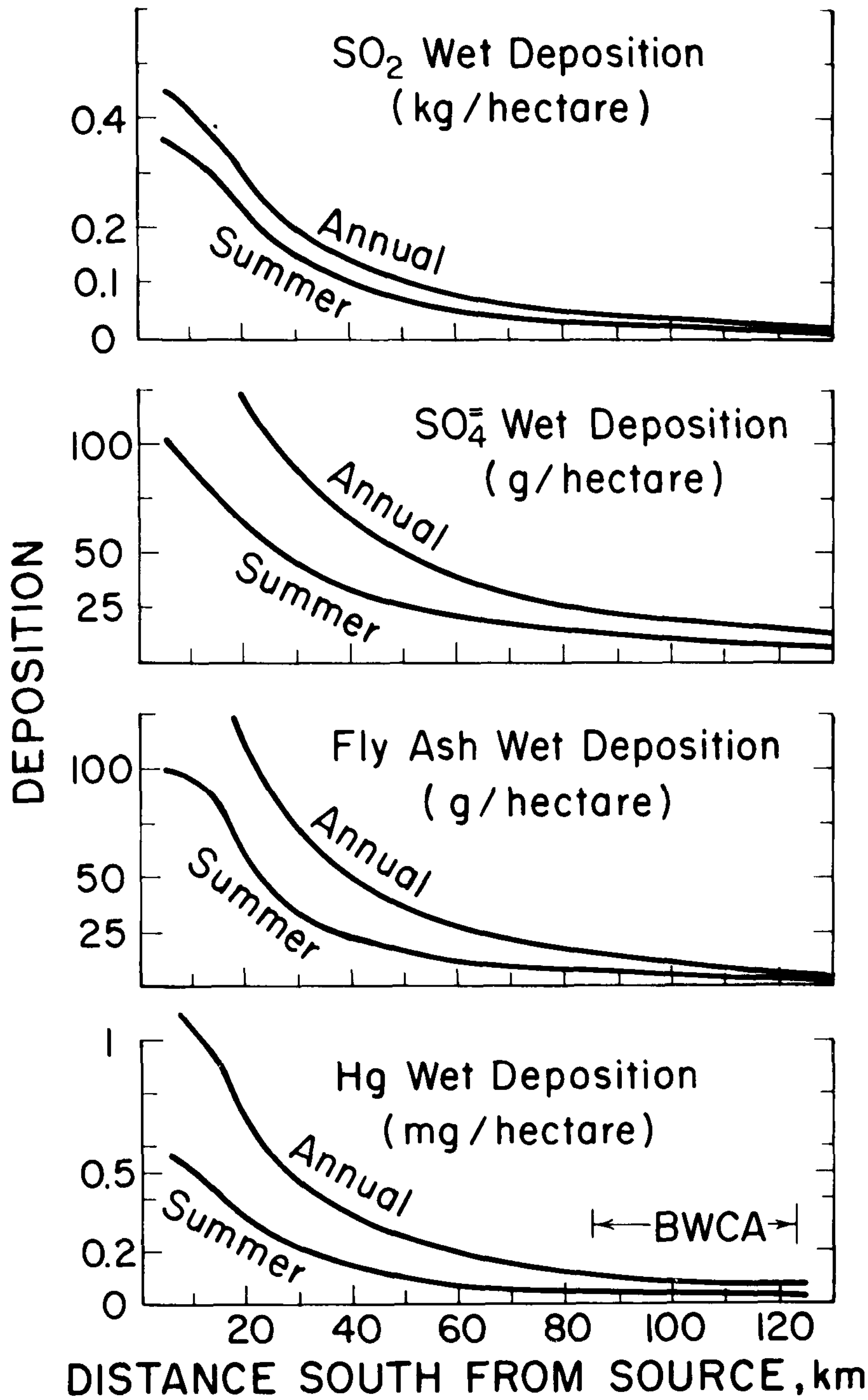



Figure 10. Computed annual and seasonal wet deposition flux due south of Atikokan for $SO_2$, $SO_4^=$, fly ash, and mercury. There are two seasons: summer is rain, and winter is snow.

(and nitrogenous compounds) from operation of the Atikokan generating station at full capacity thus represents a potential increase of 25 percent in the unbuffered atmospheric acidity.

These estimates of total acid deposition also can be evaluated from the viewpoint of mitigative needs. The present Steep Rock iron mine operations, which release 15 to 30,000 tons of $SO_2$ annually, may be terminated before the Atikokan power facility is completed. Thus, the present deposition rates for sulfate could be expected to decrease somewhat at that time. The Steep Rock emissions are about 40 percent of those expected from the 800-MW generating station, but the reduction in sulfate deposition in the BWCA would be less than half of this proportion of the projected power plant increase because doubling the stack height of the power plant effectively transmits twice the amount of $SO_2$ to the BWCA compared to the shorter stack height of the iron sintering operations. These data, however, allow the contribution of the Atikokan generating facility to be judged as a percent addition to the background acid deposition levels after the proposed closing of iron ore operations. Taking half of the 40 percent of the generating station transport to the BWCA as the improvement from closing of the iron mines gives a net decrease of 0.2 kg/ha-yr in total sulfate deposition and unbuffered acidity. These considerations indicate little change in the projected 10 percent total increase in sulfate loadings and 30 percent increase in unbuffered acidity (0.9 kg deposition in relation to 2.9 kg/ha-yr of unbuffered acidity) following the closing of the iron mine. Even if the mine closed, and only one-half of the Atikokan plant was constructed (400-MW), the unbuffered acid sulfate contributed by the new source represents a 15 percent deterioration in precipitation quality. Thus, the absolute levels of acid loadings in the region will significantly increase by operating the Atikokan facility at 400-MW, even assuming the iron ore facility closes.

## Atmospheric Loadings in the Quetico Area

As indicated in Figures 9 and 10, the deposition loadings are much higher in the northern Quetico than in the BWCA for the 10.3% of the time the winds are from the NE to NW for a duration of more than 6 h. The watersheds of the Maligne River and other rivers in the Quetico south of Atikokan drain to international waters along the BWCA boundary. Hence deposition from the Atikokan plume within these watersheds must be considered in the total BWCA-VNP impacts evaluation. Model estimates of deposition 35 km south of Atikokan in the area of Sturgeon Lake are as follows:

| | |
|---|---|
| Annual sulfate deposition | 3.4 kg/ha-yr |
| Annual fly-ash deposition | 88 g/ha-yr |
| Annual mercury deposition | 4 mg/ha-yr |

These results for the proposed Atikokan source are for only the long duration windfield; three to five times these values will be the probable minimum total deposition at the Sturgeon Lake location. These estimates represent a 100% or more increase over the current sulfate deposition in this area, and a much larger increase over the expected background deposition following closing of the Steep Rock Iron mine operations.

VALIDATION OF THE MODEL

In a brief study such as this it is not possible to complete direct validation of the model in the field. A number of approaches can be used, however, to determine the present level of confidence appropriate for the model.

First of all, a version of this model which does not include deposition or chemical transformation has been used successfully in a seven-county region in southeastern Wisconsin. A detailed emission inventory was developed by State and local agencies. Computed annual average particulate concentrations were compared with 25 high-volume particulate monitors, and a correlation coefficient of 0.87 was obtained. Computed annual average sulfur dioxide concentrations were validated with six monitoring stations, and a correlation coefficient of 0.78 was obtained (Southeastern Wisconsin Regional Planning Commission 1978). The modeling work is being used to develop the Wisconsin Implementation Plan as required by the U.S. Clean Air Act.

The validity of the model depends in part on the value of the parameters selected for the execution of the model. The key parameters which are dependent on the particular pollutant species to be modeled were summarized in Table 4. These values were selected from experimental values in the literature and are felt to be known within a factor of 2 except for the values for mercury, which are probably known only to a factor of 10. In addition, the surface roughness and the horizontal eddy diffusivity are important parameters. One surface roughness must be selected for the entire region, and the selected value of 1 m represents typically wooded terrain. The horizontal eddy diffusivity is not well known for this scale model, and more research is needed on this parameter (see Liu and Durran 1977). The model used a value of 100 times the vertical diffusivity.

A sensitivity analysis was performed on the key parameters in the model. A worst-case day was selected, and the model was run for 24 h. The sensitivity of the ground-level concentration of $SO_2$ to a factor of 2 change in each of the key parameters was determined as shown in Figure 11. The most sensitive parameter was the height of the inversion. This parameter was measured at International Falls and hence is well known. The horizontal eddy diffusivity was the next most sensitive parameter: a doubling decreased the $SO_2$ concentration by 10-15%. The other three parameters --the chemical reaction rate, the surface resistance, and the surface roughness-- when doubled, changed the concentration by less than 10%.

The accuracy of the input data is another factor that influences the validity of the results. Assumptions have been made on the type of coal used and the reliability of the electrostatic precipitator. The meteorological data-- the wind speed, wind direction, solar intensity, inversion height, and precipitation amount and type --will all influence the resultant output. Nevertheless, it is felt that the input data are rather well known.

When any complex model is used, the results should be compared with those from other models, and especially from less complex models. Examination

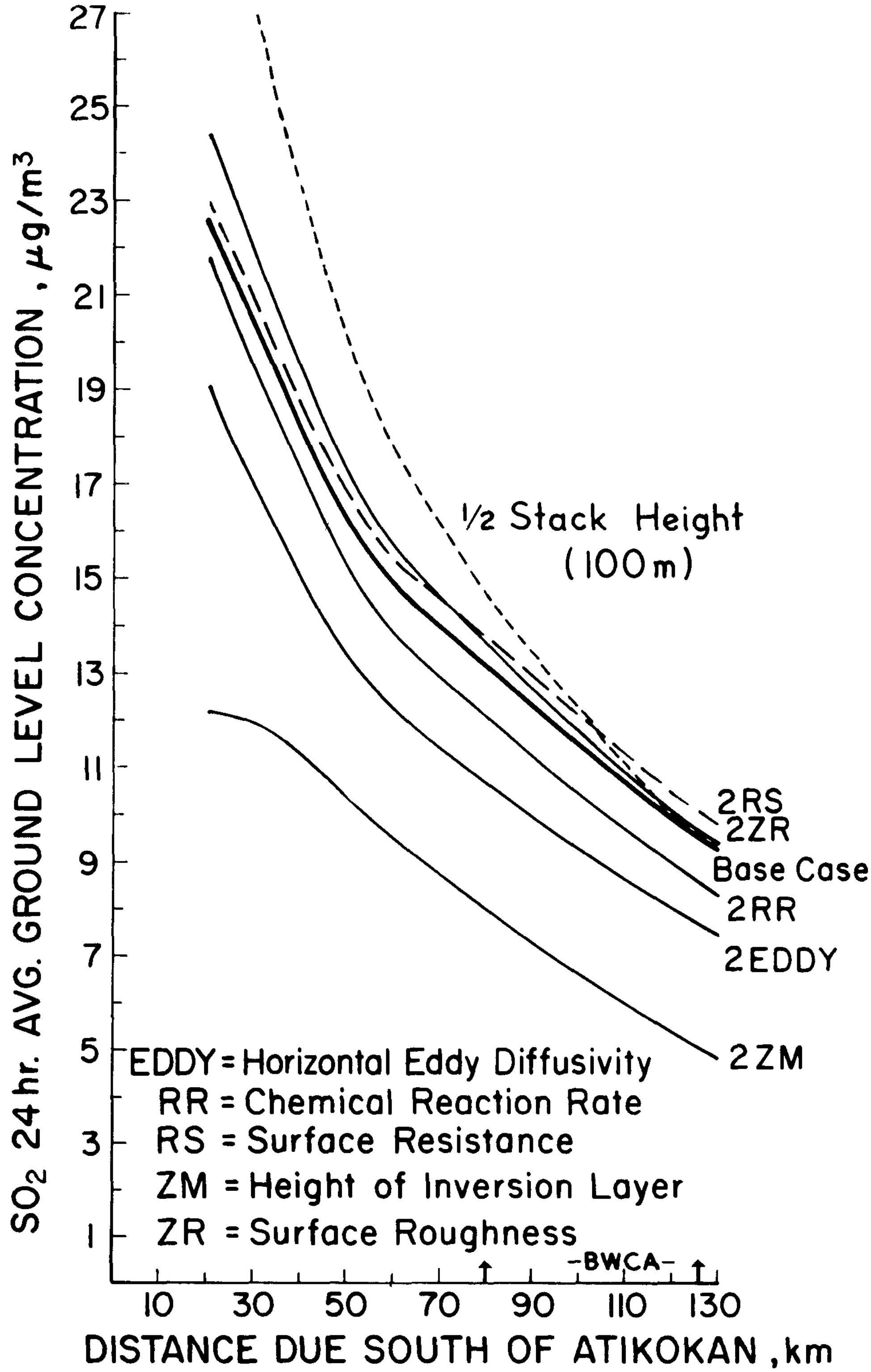



Figure 11. Results of the sensitivity tests of the grid model showing the influence on $SO_2$ concentration for a worst-case day.

of the similarities and differences between different modeling results can yield confidence in the final results. Modeling results from a simple box model approach, from Gaussian plume concepts, and from the EPA CRSTER model are summarized in Appendix B. These results lend support to the findings of the numerical grid model.

## SUMMARY DISCUSSION OF THE ATIKOKAN MODELING RESULTS

A time-dependent plume model that includes transport, diffusion coupled chemical transformation, and wet and dry deposition has been developed and applied to Atikokan. A grid was set up that included Atikokan, Quetico Provincial Park, and the Boundary Waters Canoe Area. The model was run hour by hour for an entire year for those hours when the wind was from the NW to NE. Separate model runs were made for sulfur dioxide and sulfates, fly ash, and mercury. The sensitivity of key model parameters was analyzed, and the validity of the results was examined.

The following conclusions are drawn from the modeling effort with respect to the Atikokan plume on the BWCA:

1. The 3-h and 24-h worst-case sulfur dioxide concentrations exceed the U.S. allowable incremental standards of 25 and 5 $\mu g/m^3$, respectively, for protection of a Class I wilderness area. The frequency with which these values are exceeded is low, however. The annual average $SO_2$ concentration was 0.25 $\mu g/m^3$, which is eight times less than the U.S. standard.

2. The increase in particulate matter is not expected to approach the U.S. allowable incremental standards for a Class I wilderness area. The annual particulate (fly ash plus sulfate) concentration was 0.03 $\mu g/m^3$, and the worst-case 24-h concentration was 1.1 $\mu g/m^3$. The particulate matter contains twice as much sulfate as fly ash.

3. The total potential sulfate deposition was 0.9-1.4 kg/ha-yr in the BWCA, which is significant compared to the existing regional background deposition of 11 kg/ha-yr.

4. The total deposition of fly ash was 0.018 kg/ha-yr for the BWCA.

5. Annual mercury ambient air concentrations were $4 \times 10^{-12}$ $g/m^3$, and the total deposition flux was $1.6 \times 10^{-3}$ g/ha-yr for the BWCA.

## SECTION 4

## POTENTIAL EFFECTS OF COAL-COMBUSTION EMISSIONS ON THE TERRESTRIAL BIOTA OF THE BWCA

### INTRODUCTION AND GOALS

The expanse of relatively pristine terrestrial ecosystems in Minnesota's Boundary Waters Canoe Area Wilderness is a major reason for its recognition as a unique recreational resource in the United States. The flora and fauna growing in the BWCA have not previously been subjected to elevated concentrations of toxic air emissions or the deposition of chemically transformed products of these emissions (Section 3). However, the emissions inventory presented earlier indicates a gradual increase in toxicant concentrations and deposition over previous very low levels (Section 3). A careful assessment of the consequences of continued increases for terrestrial species in these ecosystems now seems warranted.

In this section we will:

1) Characterize the components of terrestrial ecosystems in the BWCA that could be affected by elevated concentrations or increased deposition, as a consequence of coal-burning emissions;

2) summarize the research results available for evaluating the responses of sensitive species to changes in air, water, and soil characteristics, and the overall sensitivity of the ecosystems to these changes; and

3) define potential effects on plants, animals, and ecosystems where sufficient information is available to cause concern, but is insufficient to quantify the magnitude or timing of responses.

Sensitivities of the regional biota to the emissions and deposition products from coal-fired generating facilities have been reviewed in several previous forms (N. R. Glass 1978). Because of measurable differences in terrain, meteorology, vegetation density, rainfall, and soil moisture from one location to the next within the BWCA, absolute comparisons are not possible for short- or long-term biological responses at specific sites. Thus, responses to air pollutants and dry fall that hold for several locations already studied must be used to evaluate potential impacts on other locations, such as the BWCA.

Under relatively extreme emission loads, many effects on ecosystems such as the BWCA are well documented. Some responses are evident on a short-term (less than a decade) time scale, and others are apparent on a long-term (decades) time scale. Studies of other influences on the vegetation of the

BWCA, particularly the effects of intermittent fire in the past, require the use of time scales of hundreds of years. Although the studies presented here focus on relatively immediate, often subtle impacts on species, it is apparent that these impacts also should be viewed in a time frame of 100 or 200 yr if their ultimate effect upon the entire ecosystem is to be assessed fully.

## BIOLOGICAL AND TEMPORAL CHARACTERISTICS OF THE BOUNDARY WATERS CANOE AREA

Approximately 70,000 ha (172,000 acres) of the total 439,000 ha (1,085,000 acres) of the BWCA are taken up by lakes and streams over 4 ha (10 acres) in size. Some 215,000 ha (532,000 acres) support remnants of the natural ecosystems of Minnesota's Laurentian shield country, virgin areas with the flora and fauna nearly intact. These virgin areas are those which have never been directly altered by human activities such as logging, clearing, tree planting, farming, mining, road building, etc. Almost all these areas, however, have been burned in the past 400 yr, and many virgin forests are postfire successional communities less than 110 yr old (Heinselman 1973). It is these virgin areas of natural vegetation patterns upon which this discussion will focus.

Part of the Superior Upland Physiographic Region, the BWCA's landscape has a generally slight but locally rugged relief left by preglacial erosion. Elevations above sea level range from 341 m (1,119 ft) at Crane Lake to 680 m (2,232 ft) in the Misquah Hills (Ohmann and Ream 1971); local differences in elevation range from 30 to 150 m (Heinselman 1973). Most of the relief of this area, glaciated repeatedly during the Pleistocene and deglaciated some 16,000 yr ago, is related to the contours of its exclusively pre-Cambrian bedrock: metamorphosed sedimentary rock leading to quartzite, metagraywacke, and slate. In contiguous Quetico Provincial Park (Ontario) the bedrock types are principally associated with a granite batholith exposed as part of the Laurentian Shield.

A network of more than 1,000 interconnected lakes and streams occupies the bedrock troughs and basins of the BWCA, some lying in granite (Saganaga Lake and Lac La Croix) and some in ancient greenstones and slates (Knife Lake). The landforms are determined by the configurations of the bedrock: slates typically form long, narrow, steep ridges, and granites the low, irregular round-topped hills (Ohmann and Ream 1971).

Deposition was offset by glacial scouring, which left bedrock exposed on many ridgetops, cliffs, and lakeshores, and a thin covering of till, outwash, and lacustrine deposits varying considerably within short distances. Glacial boulders are common within the soils derived from this sandy and gravelly loam glacial deposition.

### Plant Community Types

The plant communities of the virgin upland forests have been quantitatively described by Ohmann and Ream (1971). Even after 60 yr of fire control the jack pine (Pinus banksiana) communities remain the most common of the virgin upland forest, followed closely by the broadleaf group, which is largely dominated by aspen (Populus tremuloides) and paper birch (Betula papyrifera) (Table 7). White pine (Pinus strobus) and red pine (P. resinosa) communities made up 10% of the 106 virgin stands randomly sampled by Ohmann and Ream (1971). The distribution of the vegetation types in the BWCA area is shown in Figure 12.

Transitional between the Great Lakes-St. Lawrence and boreal forest regions, biotic communities in the area have an abundance of boreal trees: jack pine, black and white spruce (Picea mariana, P. glauca), balsam fir (Abies balsamea), tamarack (Larix laricina), northern white cedar (Thuja occidentalis), and paper birch. The two pines characteristic of the Great Lakes forest, eastern white pine and red pine, are also plentiful (Heinselman 1973). Citing Dean's preliminary 1971 study of the area wetland communities, Heinselman (1973) indicates that they are closely related to the glacial Lake Agassiz peatland communities, a region some 160 km (100 miles) to the west.

Of the 12 community types described by Ohmann and Ream (1971), only the lichen community type is nonforest. Characterized by the lack of many woody plants and by the importance of lichens and mosses, this type comprises slightly less than 5.7% of the stands in their random sample of 106 sites. Ohmann and Ream grouped lichens other than the reindeer mosses, and mosses other than the feather mosses, Dicranum, and the hairycap moss. Together they make up 40% of the ground cover within the community. Another 30% of the ground surface is bare rock. The reindeer mosses (actually lichens) are also important in this essentially two-layered community.

Lichens and mosses are also an important component of the ground cover in four other communities designated by Ohmann and Ream: jack pine (fir), 19% of the ground cover; red pine, 26%; black spruce-jack pine, 59%; and budworm-disturbed balsam fir, 46%, including herbs. As computed by Ohmann and Ream, these communities make up 32% of the upland virgin vegetation area in the BWCA. They view the lichen community as an early stage of succession after some major disturbance, such as fire, as primary succession on rock outcrop.

In the BWCA today tree lichens are found largely on the lower limbs of old fir and spruce and on dead balsam fir killed by the spruce budworm. Ground lichens are most abundant on open bedrock ridges and upper slopes, which become well covered by lichens 60-100 yr after fire (Heinselman 1973).

Stands including the white and red pine community types are slightly older than those in most of the other communities and make up 9.5% of total stands sampled by Ohmann and Ream in 1971 (5.7% white pine; 3.8% red pine). As described by these researchers the white pine community is really a two-layer forest: an upper canopy of large, old white pines with scattered red pines, and a lower layer of balsam fir trees and saplings. The attractiveness of the red pine community stems from the presence of open stands of old, majestic red and white pines that survived fires along the lakeshore and are prominent along the ridgetops forming the skyline. The understory is short on saplings and seedlings, and shrubs and lichens characteristic of dry conditions are dominant.

TABLE 7. VIRGIN UPLAND COMMUNITIES IN THE BWCA AND THE IMPORTANCE OF STANDS, TYPES, SPECIES, AND FAMILIES[a]

| Community type | Stands | | Number of species | Number of families |
|---|---|---|---|---|
| | Number | Percentage of total | | |
| Lichen | 6 | 5.7 | 32 | 19 |
| Jack pine (oak) | 11 | 10.4 | 81 | 25 |
| Jack pine (fir) | 7 | 6.6 | 95 | 30 |
| Jack pine-black spruce | 7 | 6.6 | 83 | 26 |
| Black spruce-jack pine | 10 | 9.4 | 75 | 23 |
| Aspen-birch | 13 | 12.3 | 112 | 30 |
| Maple-aspen-birch | 15 | 14.2 | 104 | 34 |
| White pine | 6 | 5.7 | 80 | 23 |
| Red pine | 4 | 3.8 | 67 | 25 |
| Budworm-disturbed balsam fir | 10 | 9.4 | 102 | 31 |
| Fir-birch | 8 | 7.5 | 86 | 30 |
| White cedar | 9 | 8.5 | 85 | 28 |

[a]Adapted from Ohmann, L. F., and R. R. Ream (1971).

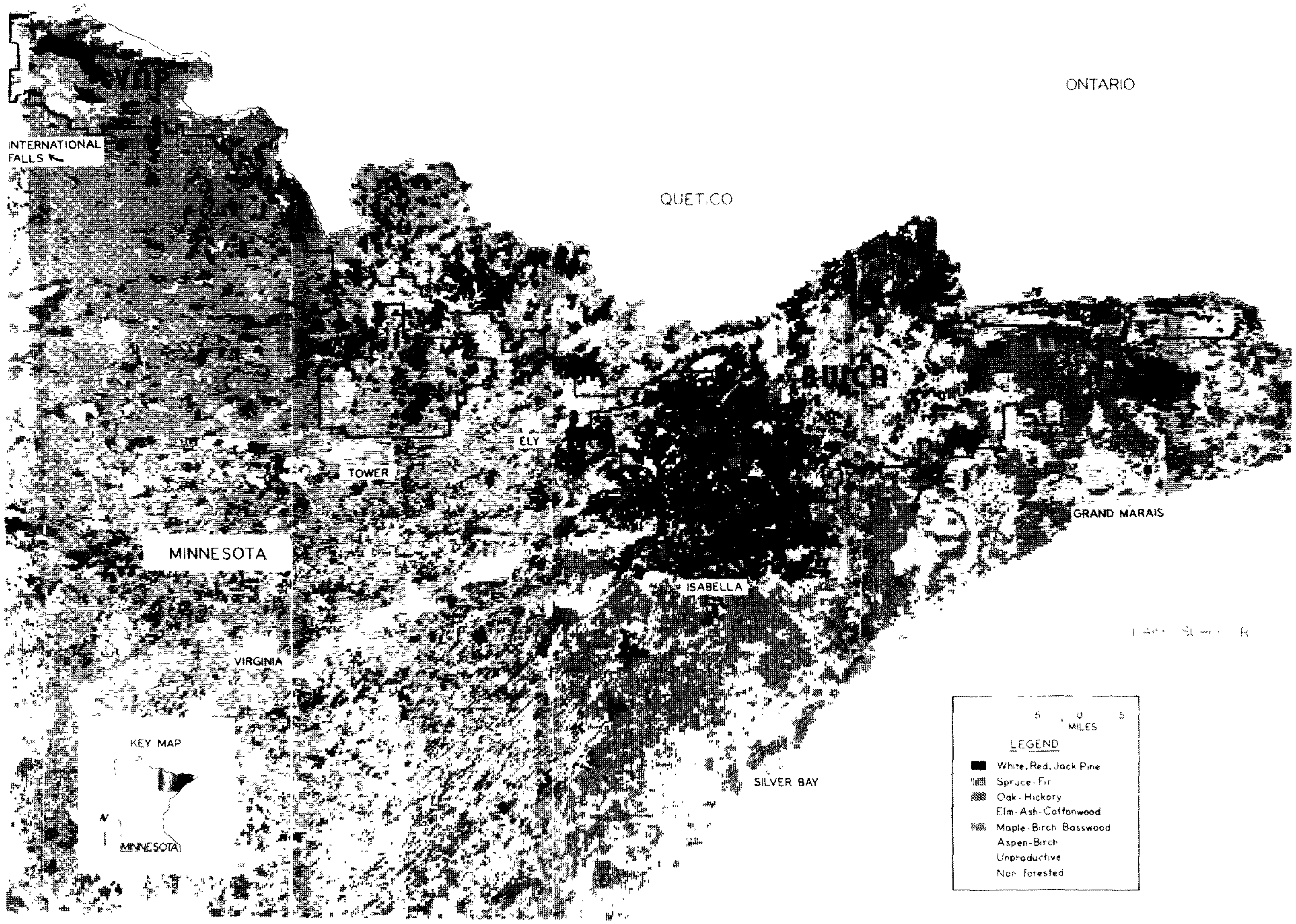



Figure 12. Distribution of vegetation types in the BWCA-VNP area and vicinity. From the Minnesota State Planning Agency 1978.

The mammals and birds of the area are also representative of a transition between the Great Lakes and boreal forest ecotones. The moose (Alces alces), Canada lynx (Lynx canadensis), fisher (Martes pennati), pine marten (Martes americana), snowshoe hare (Lypus americana), spruce grouse (Canachites canadensis), Canada jay (Perisoneus canadensis), and (formerly) the woodland caribou (Rangifer caribou) are all species with boreal affinities. The northern white-tailed deer (Odocoileus virginianus) and bobcat (Lynx rufus) are species more typical of the Great Lakes forests. The eastern timber wolf (Canis lupus), red squirrel (Tamiasciurus hudsonicus), red fox (Vulpes fulva), beaver (Castor canadensis), otter (Lutra canadensis), mink (Mustella vison), black bear (Ursus americanus), ruffed grouse (Bonasa umbellus), bald eagle (Haliaeetus leucocephalus), etc., are all species more typical of the Great Lakes forests. Most of the native animals and birds also have habitat requirements that correspond with niches in various post-fire successional stages (Heinselman 1973).

## Long-Term Stability of the BWCA Landscape

Ohmann and Ream (1971) conclude from their studies that the structure and composition of each stand in today's virgin forests are more closely related to the length of time since the last fire, and probably to the character of the fire and the age of composition of the former stand, than to all of the other environmental factors studied, such as soils, aspect, slope, or elevation.

The stand origin and fire year maps developed by Heinselman (1973) indicate that from 1595 to 1973 nearly all of the one-million-acre virgin forest study area burned at least once, 1910 being the last year of major burns. At least 44% of the million-acre virgin study area was involved in the drought year burns of 1893 and 1894. Many even-aged stands also date from a similar drought-fire sequence 220 yr ago in 1755-59. Those large upland ridges and ridge complexes distant from or west of natural firebreaks were the areas most frequently or intensely burned. Such areas are today often dominated by jack pine, black spruce, birch, and other sprout hardwoods. White pine, red pine, white spruce, northern white cedar, black ash, elm, and fir are relatively more abundant on those sites burned least frequently or intensely: swamps, valleys, ravines, the lower slopes of high ridges, islands, and the east, north, northwest, or southeast sides of large lakes or streams. Very fire-sensitive northern white cedar has retreated to the lakeshores where it forms a typical narrow fringe (Heinselman 1973).

Heinselman (1973) cites Ayres' 1899 observation that by 1855, because of its long history of fire, only 20% of the region supported the mature pines desired for lumber. Thus, Heinselman indicates, just a small fraction of the BWCA was affected by the early logging, and the young stands, recent burns, and scattered areas of older forest that covered three-fourths of the region were little touched. As of 1973, he notes, the net land area undisturbed by cutting exceeded 167,950 ha (415,000 acres), most within the lands set aside for national forest between 1902 and 1913. The Anderson bill, recently passed by the U.S. Congress, eliminates logging as a management alternative from the entire BWCA.

As indicated by H. E. Wright Jr. (1974), the same 370 years covered by Heinselman's tree-ring/fire studies in the BWCA represent only a portion of the total lifespan of the forest. Although humans may have modified the natural frequency of fire during those years, pollen curves and charcoal profiles from the sediment of Lake of the Clouds (in the heart of the BWCA) show that major fires occurred about every 80 yr for the last 1,000 yr.

What H. E. Wright Jr. (1974) has called the "time factor in landscape evolution" must be applied to environmental influences other than fire control. If we look ahead 50, 100, or 200 yr to how succession in the absence of a natural constituent, fire, may significantly change the BWCA forest communities, then it is equally appropriate to consider a similar time frame for assessing what effects rising levels of pollutant deposition may eventually have on these same communities. Such a long-range view provides an important perspective on the possible significance of relatively immediate, if subtle, effects now manifested in individual indicator species in other ecosystems, where effects of exposure to increased doses of $SO_2$, $NO_x$, TSP, $H_2SO_4$, HF, and Hg are already known.

The vegetation resource that presently covers the BWCA was initiated 300 to 100 yr ago. Today's land managers and policy decision-makers are stewards of whatever the landscape of this area is to be 200 years from now.

## BIOTIC RESPONSES TO COAL-FIRED POWER-PLANT EMISSIONS

The following considerations have been summarized from various current research projects on the impact of coal-fired generating stations and from the literature on the BWCA ecosystem components and their response to known levels and durations of exposure to point-source pollutants from coal-fired power plants.

Various types of terrestrial ecological effects may be anticipated from exposure to generating station emissions and associated deposition (Figure 13). Direct effects may be anticipated from both dry and wet deposition of air pollutants on ecosystem components (see Section III). In addition to direct effects, a number of indirect effects may be manifested through changes in ecosystem processes, such as bioaccumulation of toxic compounds, alterations in mineralization or rates of nutrient flow, and changes in host-parasite relationships.

The discussion that follows considers such major emission products (residuals) from the viewpoint of the plant, animal, and soil components of the terrestrial ecosystem on which they could have important potential effects. The material presented reflects data or information already available. New data needs are identified by the inadequacy or lack of results from long-term, low-level exposures. The emission residuals considered are those for which sufficient information is available to anticipate some effect on an ecosystem component at some concentration, and for which the air-quality modeling work has provided estimated concentrations and loadings in the BWCA.

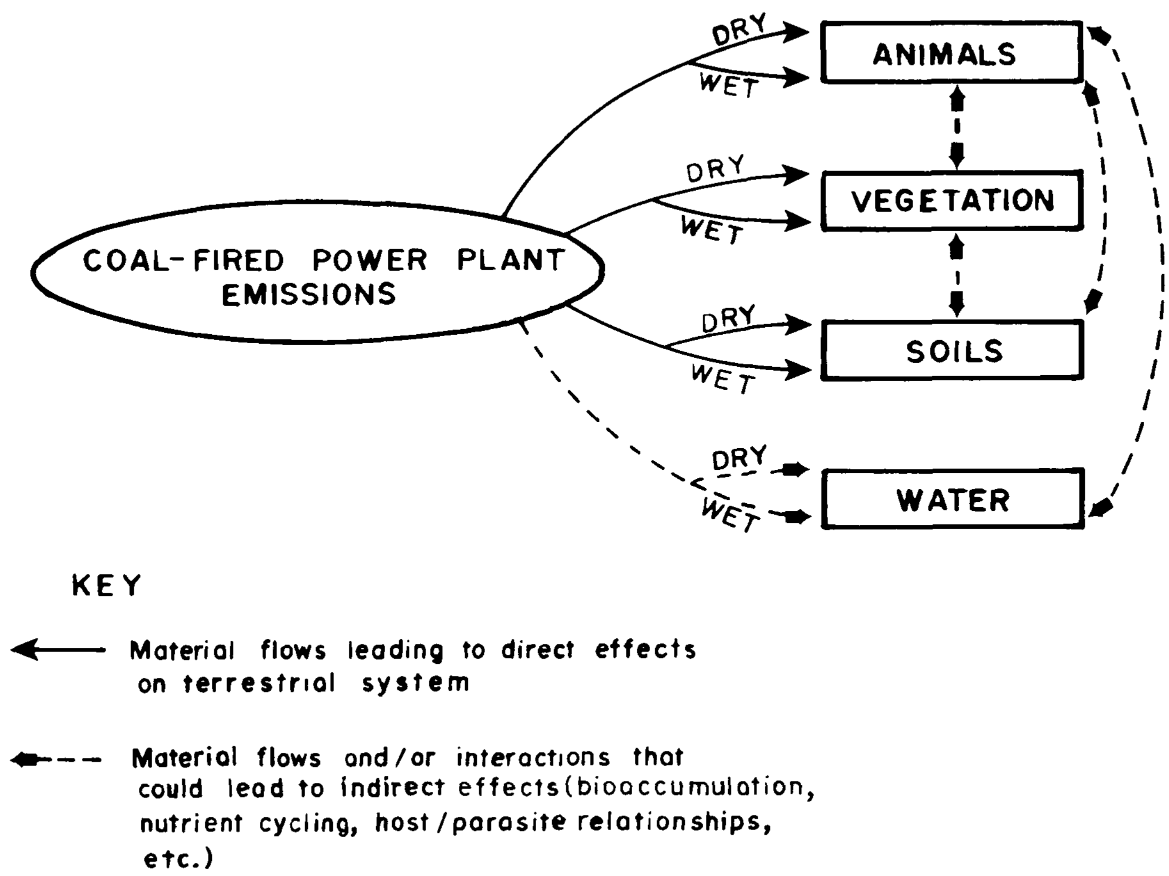



Figure 13. Schematic diagram of regional material exchange system and biological response processes that may be anticipated in response to coal-fired power-plant emissions.

Residuals of Concern

$SO_2$--

Sulfur dioxide and the effects of exposure to it have been studied more than any other pollutant (Benedict et al. 1971, Guderian 1977, Rennie and Halstead 1977). A wide variety of organisms are sensitive to damage from exposure to elevated $SO_2$ concentrations (Tibbitts et al. 1977, Electric Power Research Institute 1976, Van Haut and Stratman 1970). Many organisms also exhibit synergistic reactions to combinations of $SO_2$ with other coal-fired power plant emissions such as $O_3$ or $NO_x$ (Dochinger et al. 1970, Kress and Skelly 1977, Houston 1974).

Numerous extensive reviews of $SO_2$ and its effects are available (Braunstein et al. 1977, N. R. Glass 1978). A reading of these and other references in relation to the principal vegetation types reviewed supports focusing on responses of pines, lichens, and soils in the BWCA.

$NO_x$ $NO_2$--

Forest soil and insects are generally less sensitive to $NO_2^-$ than to other major pollutants (National Academy of Sciences 1977). Although organisms are more sensitive to $NO_2^-$ than to the other nitrous oxides, the usual measurement combines the forms as $NO_x$, and levels necessary to affect susceptible members of the terrestrial ecosystem (vegetation) are much greater than for sulfur dioxide and photochemical oxidants (MacLean 1975). Estimates of the economic impact of air pollutants on vegetation have not included $NO_x$ by itself; rather it has been combined with ozone and peroxyacetyl nitrate (PAN). However, emissions of $NO_x$ have been increasing substantially throughout the United States and Canada, and the synergistic effects on plants from low concentrations of $NO_2^-$ and sulfur dioxide (found in experimental exposures) and of $NO_x$ in the production of photochemical smog and acid precipitation pose the greatest threat (N. R. Glass 1978).

Ozone--

Photochemical oxidants, ozone ($O_3$), and, to a lesser extent, peroxyacetyl nitrates are the most damaging air pollutants affecting agriculture and forestry in the United States (Jacobson 1977). Peroxyacetyl nitrate is more phytotoxic than $O_3$, but the ambient concentration of PAN is much lower than $O_3$ in most areas of the United States (Taylor 1969). In the northern Minnesota area it may be almost negligible. Formation of ozone in the atmosphere has a complex dependence on the amounts of precursors (nitrogen dioxide and hydrocarbons), meteorological conditions, and time of day (National Academy of Sciences 1977), but moderately high levels are being observed in northern Minnesota given the area's relative isolation from the usual ozone sources (Table 1). Photochemical oxidants, including ozone, have been problems in southern California for more than 30 years. The severity of losses to agricultural crops, exclusive of forests and ornamental plantings, had reached more than $55 million by the 1970's (Millecan 1976).

Trace elements--

Trace elements have been defined as those elements present in the crust of the earth at less than 0.1% or 100,000 ppm. More than 63 of them are found in coal. Some are more concentrated than others in coal, and there is considerable variation in trace-element concentration from different coal sources. Most trace elements (including arsenic, beryllium, chromium, copper, lead, selenium) appear to occur at mean concentrations less than 7,000 ppm, notable exceptions being boron, zinc, and titanium (Ruch et al. 1974, Zubovic 1975). These trace components, however, are concentrated on the surface of the fly ash particles and are highly reactive (G. E. Glass 1978). Of the macro elements in coal (e.g., aluminum, calcium, iron, silicon, sulfur, and sometimes titanium) only sulfur is the element of concern here. Sulfur oxides represent the major pollutants of gaseous emissions and are mentioned here because of the known ability of some metallic trace elements to catalyze the further oxidation of sulfur oxides into more toxic substances capable of greater respiratory damage than sulfur dioxide alone (Amdur and Underhill 1970) or to interact and form metallic sulfates. Excessive deposition of trace elements upon a balanced ecosystem can cause problems because of the high toxicity of many trace elements and the potential for bioaccumulation.

Acidic fallout (acid rain)--

Although acidic fallout has long been studied by European researchers (Oden 1968), the phenomenon received only cursory attention by Canadian and United States scientists until the early 1970's. Since the beginning of the decade, however, scientists of both these North American countries have expanded their interest in the long-term effects of acidic precipitation and the precursors of this phenomenon. Canadian scientists have shown that acidic precipitation is a serious problem in both terrestrial and aquatic ecosystems of eastern Canada (Summers and Whelpdale 1976, Beamish 1976, Stokes and Hutchinson 1976).

In the United States a report to the Secretary of the Department of Health, Education, and Welfare by a special scientific advisory committee considered the long-term consequences of the United States National Energy Plan (NEP). This committee concluded that one of the most serious environmental consequences of the expanded use of coal-fired power plants will be increased acidic precipitation throughout the areas where the power plants are located (U.S. Federal Register 1978). Although this advisory committee supported the conversion from oil to a coal-based energy economy (NEP), they concluded that all converted and new facilities should install the best available abatement technology to reduce to a minimum the precursors of acidic precipitation.

Contributors reviewing the literature and current research for this report reached the consensus that, for the BWCA, the principal ecosystem components or organisms to be emphasized regarding the effects of acid rain were pines, lichens, insects, and amphibians (direct effects) and soils (indirect effects).

## Conifers (Pines) and Aspen

### Effects of $SO_2$ on pines--

The effect of the gaseous emissions of large coal-fired power plants initially becomes evident in the responses of the most sensitive of the species in any ecosystem. In the BWCA these sensitive species are lichens, conifers of the genus *Pinus*, and trembling aspen. The three dominant species of *Pinus* in the BWCA are *P. strobus*, *P. resinosa*, and *P. banksiana*. Of these three species eastern white pine is the most sensitive to $SO_2$. Red pine and jack pine are considered about equally sensitive to $SO_2$, but not as sensitive as eastern white pine. Trembling aspen is a dominant species over 20% of the BWCA (Table 7, Figure 12) and is recognized by Driesinger and McGovern (1970) as a very sensitive species.

The major manifestations of pollution damage in these three species of pine are foliar tip necrosis, mottling chlorosis, basal necrosis of the needle tissues beneath the fascicular sheaths, and premature needle casting. The premature loss of needles from the second-, third-, and fourth-year internodes causes a reduction in annual growth as well as the loss of normal health and vigor, which in turn predisposes these species to more severe effects of other abiotic (drought, frost, nutrient deficiencies) and biotic (insect infestations, root-attaching fungi) causal agents (Carlson 1978).

Several studies document the development of visible injury symptoms on eastern white pine by low level chamber fumigations. Costonis (1970) reported tissue damage on new needles of eastern white pine after a single 1-h treatment with 5 pphm $SO_2$. Houston (1974) observed necrosis in elongating needles of eastern white pine after 6 h of fumigation with 2.5 pphm $SO_2$. In a field study in the Sudbury, Ontario, region Linzon (1971a) observed damage to eastern white pine at a 7-yr fumigation average of 0.8 pphm, a level of $SO_2$ commensurate with the background levels already being recorded in areas of Ontario near Atikokan (Table 1).

After field observations Costonis (1972) reported that 6 pphm of $SO_2$ caused acute injury to the new needles of eastern white pine after 4 h of exposure. Ozone measurements in the field did not exceed 4 pphm. Preliminary laboratory tests conducted before these field studies indicated that sensitive white pines developed necrotic lesions after $SO_2$ exposure of 3 pphm for 1 h; if fumigation was continued for 3 h, severe necrosis on current needles occurred. Laboratory tests also revealed that $O_3$ fumigations of 15 pphm for 4 h produced equivalent injuries.

Houston and Dochinger (1977) reported a decrease both in the number of seeds produced per cone and in the percentage of pollen germination in white pines in a low level $SO_2$-polluted area. Effects on red pines included decreases in cone length, seed weight, percentage seed germination, percentage pollen germination, and pollen tube length. None of the trees displayed foliar injury patterns, indicating that low levels of air pollutants may be affecting the reproductive tissues of pines at concentrations lower than those required to produce visible injury. In the vicinity of a copper smelter at White Pine, Mich., low level $SO_2$ exposure has caused no plainly visible vegetation damage, but ring widths of balsam fir and white spruce suggest that growth has been substantially reduced in trees downwind from the smelter (Kotar 1978).

Driesinger and McGovern (1970) found trembling aspen to be the most sensitive forest species to air pollution in the Sudbury, Ontario, area. Visual injury to foliage was caused by $SO_2$ concentrations of 26 pphm for 4 h. Pollen-tube elongation is inhibited at $SO_2$ concentrations greater than 30 pphm for 4 h (Karnosky and Stairs 1974).

The U.S. Environmental Protection Agency (Davis and Wilhour 1976) attempted to classify the susceptibility of various woody plants to $SO_2$ and photochemical oxidants based on foliar injury, growth loss, etc. They observed that eastern white pine near the Sudbury, Ontario, region ($SO_2$ source) has a poorer regenerative capacity to repeated $SO_2$ exposures than various hardwoods (aspen, birch). They also documented that red pine was very sensitive to $SO_2$ emissions.

Effects of $NO_x$ on pines--

Skelly et al. (1972) carried out field observations of eastern white pines exposed to $SO_2$ and $NO_x$. The most severely affected trees were in areas where the highest readings were 8.5 pphm $NO_x$ (1-h average) and 69 pphm $SO_2$ (2-h average). They also found that oxides of nitrogen at moderate concentrations acting alone or in combination with low $SO_2$ concentrations caused acute to chronic damage in eastern white pine. Young seedlings were extremely susceptible to $NO_x$ fumigations. Van Haut and Strattman (1967) observed damage to plants exposed to 250 pphm $NO_x$ for 4-8 h.

Effects of ozone on pines and aspen--

In chamber studies conducted by the EPA, eastern white pine was classified in the intermediate sensitivity range to $O_3$ and red pine in the tolerant range. Davis and Wood (1972) used chamber experiments to determine the relative susceptibility of 18 conifers to ozone. They found jack pine to be the most susceptible, damaged by 4 h of 25 pphm $O_3$. Eastern white pine was also very sensitive, damaged by 8 h of 25 pphm $O_3$, but red pine was resistant (no injury manifestation) at these fumigation levels.

In a field study in West Virginia, Berry and Ripperton (1963) observed damage to eastern white pines 48 h after a 1-h fumigation of 5 pphm $O_3$. The damage observed was considered a "light attack" of emergence tipburn, but severe symptoms were noticed following ambient $O_3$ exposures of 6.5 pphm for a total of 4 h during a 48-h period. Using chamber experiments, they determined $O_3$ was the causal agent of the injury observed in the field. (The damaged area was remote from any major sources of air pollutants.) Ozone levels higher than these have already been observed in the BWCA (Table 1).

Botkin et al. (1971) observed that fumigations of $O_3$ (50 pphm for 4 h and 80 pphm for 3 h) suppressed photosynthesis of eastern white pines.

Further studies carried out by Botkin et al. in 1972 determined that photosynthetic depression occurs before visible $O_3$ damage becomes apparent. In a chamber experiment on 5-yr-old eastern white pine they determined that 50 pphm fumigations of $O_3$ for 4 h was the threshold level for photosynthetic suppression (Botkin et al. 1972).

Treshow and Stewart (1973) found visible injury to trembling aspen at 15 pphm $O_3$ for 2 h. Since this was the lowest concentration tested, it does not establish the injury threshold, but does indicate that trembling aspen is among the most sensitive species tested.

Effects of $SO_2$ and $O_3$ in combination on pines--

Eastern white pine is generally considered to be more susceptible than other pines to a pollutant mix. Several studies support the finding that greater than additive responses occur when eastern white pine is exposed to both $SO_2$ and $O_3$ (Jaeger and Banfield 1970, Berry 1971, Banfield 1972, Costonis 1973, Houston and Stairs 1973, Houston 1974) (Table 8). Menser and Heggestad (1966) support the findings that "tolerable levels of a single pollutant can damage plants (in general) when in association with another at an equally low level." These studies, however, are mainly chamber studies and deal only with $SO_2$ and $O_3$. They do not account for other pollutants and environmental stresses that occur in the field.

Berry (1971) conducted chamber studies to determine the relative sensitivities of red pine, jack pine, and eastern white pine seedlings to $O_3$ and $SO_2$ fumigations. The 3-, 5-, and 7-wk-old seedlings were exposed to 2-h fumigations of 25 pphm $O_3$, 50 pphm $O_3$, 25 pphm $SO_2$, or 50 pphm $SO_2$. Jack pine was the most sensitive to both $SO_2$ and $O_3$, but there was no significant difference in the sensitivities of the age groups of any of the trees. At 50 pphm $O_3$ red pine was less tolerant than eastern white pine. Fumigations with $SO_2$ at 25 pphm, however, were more injurious to eastern white pine than to red pine. Red pine injury was detected at 25 pphm $O_3$ for 2 h, but at 50 pphm $O_3$, 87% of the 468 seedlings observed were injured (banding, flecking, tip necrosis). Injury symptoms were detected from 24 to 48 h after fumigation.

Jaeger and Banfield (1970) studied responses of eastern white pine to prolonged exposures to $O_3$, $SO_2$, and a mixture of both pollutants. When eastern white pine was exposed to 50 pphm of $O_3$ and 50 pphm $SO_2$ for 10 days, profuse necrotic spotting occurred on new and 1-yr-old needles. The most significant finding was that at the above fumigation levels, with increasingly humid environments, severe necrotic spotting occurred after 3 days. That is, the synergistic effect was much more severe with high humidity. Banfield (1972) observed necrotic spotting and tipburn of eastern white pine when exposed to 10 pphm $O_3$ and 0.5 pphm $SO_2$ for 1-12 days in a chamber fumigation study.

Dochinger et al. (1970) observed injury to eastern white pines when they were exposed to 10 pphm $O_3$ for 10-20 days and 10 pphm $SO_2$ for 10-20 days. When exposed to 10 pphm of both $O_3$ and $SO_2$ for the same time intervals, injury to the pines quadrupled.

TABLE 8. EFFECTS OF $SO_2$ IN COMBINATION WITH OTHER POLLUTANTS ON NATIVE VEGETATION

| Time | Concentration | Response of vegetation | Plant species | Author |
|---|---|---|---|---|
| 6 h/day for 28 days | 14 pphm $SO_2$ +5 pphm $O_3$ +10 pphm $NO_2$ | Significant growth reduction (measured as height) compared to ozone and sulfur dioxide combined, or ozone alone. Needles were significantly narrower than for any other exposure. This study is an example of growth reduction with slight foliar symptoms. Foliar symptoms response most sensitive in early July. | Loblolly pine (*Pinus taeda*) (2 wk old)<br><br>Sycamore (*Datams occidentales*) (1 wk old) seedlings | Kress and Skelly 1977 |
| 6 h | 2.5 pphm $SO_2$ +5 pphm $O_3$ | 20-28-day-old white pine needles on ramets, exposed 9 am - 3 pm. All sensitive clones adversely affected. Response judged in terms of needle elongation (growth) and foliar lesion or tip necrosis. Author calls response synergistic. 0.025 ppm $SO_2$ or 0.05 ppm $O_3$ = threshold; 0.10 ppm $O_3$ = 20% necrosis. | Eastern white pine (*Pinus strobus*) | Houston 1974 |
| 4-8 h/day 5 days/wk, 4-8 wk | 10 pphm $SO_2$ + 10 pphm $O_3$ | 16% needle necrosis (chlorotic, yellow spots, current year needles thin and twisted), shedding of older needles far exceeded damage responses from single exposures. 0.1 ppm $SO_2$ injured 4% of needle area; 0.1 ppm $O_3$ injured 3% of area. | Eastern white pine (*Pinus strobus*) | Dochinger et al. 1970 |

Effects of trace elements on pines--

Accurate assessment of trace-element impact cannot be known without a thorough characterization of endogenous levels of soil trace elements and the processes ongoing within soil. Trace element input from weathering differs from that of fossil fuel combustion and, in some cases, may exceed that from fossil fuels. Trace-element input is attentuated by distance from the pollutant point source and by filtering action of the surrounding canopy. Since more than 80% of the BWCA is forested (about 75% of this in coniferous stands), most trace-element emissions may affect the tree canopy directly. Very little is known concerning the effects of most trace elements applied directly to foliage.

Fluoride is known to be directly phytotoxic, but very little work has been done on the susceptibility of either eastern white pine or red pine to ambient concentrations of fluoride pollutants. In 1970 the EPA carried out field studies on fluoride-affected vegetation in Glacier National Park, Montana, the closest boundary of which is 15 miles northeast of a large aluminum reduction facility (U.S. EPA 1973). They observed that tip necrosis due to fluorides was clearly visible on older needles of sensitive western white pine growing in areas deep within the interior of Glacier National Park. Western white pine (*Pinus monticola*) was classified by EPA in 1976 as being "less sensitive" to airborne pollutants than eastern white pine (*Pinus strobus*). In another report (Gordon 1974), the EPA observed tissue necrosis on western white pine occurring at fluoride levels only two or three times higher than background fluoride levels in healthy trees.

Linzon (1971b) carried out studies during the 1969 growing season in the Cornwall area of Ontario near three fluoride-emitting industries. Early in the growing season the current 1969 needles on eastern white pine had not emerged, but the 1968 foliage displayed severe brown terminal necrosis and many needles were prematurely lacking. Later the 1969 needles displayed severe orange-red terminal necrosis. Studies carried out in the summer of 1977 in the same area of Ontario by the University of Montana documented severe visible injury to both eastern white pine and red pine despite considerably lower fluoride concentrations in the needles than determined by Linzon in 1971 (Miles 1978).

Solberg and Adams (1956) state that, in general, fumigation of vegetation with HF or $SO_2$ may produce temporary decreases in photosynthesis in the absence of visible injury. They found that histological responses to $SO_2$ and HF were indistinguishable in ponderosa pine and apricot leaves.

Impacts of acidic precipitation on coniferous forests--

Effects on growth of fully mature coniferous species have been difficult to document with methods currently available. Several studies have failed to identify significant effects (Abrahamsen et al. 1977, Tamm et al. 1977), whereas other studies provide suggestive circumstantial evidence that acidic precipitation has adversely affected growth of trees in coniferous forests (Jonsson and Sundberg 1972, Jonsson 1977). Long-term growth effects are exceedingly difficult to demonstrate because their cause may be confounded by interaction with numerous variables. In addition, even if the long-term effects on growth are very significant, significant changes in growth do not usually occur within the timespan of typical research projects.

The quickest and most severe impact of acidic precipitation on soils is likely to occur in the 1-2-cm horizon. Deeply rooted plants (e.g., trees) are not likely to be directly affected very much by changes in this horizon, but plants rooting in this zone (understory vegetation and germinating plants of all types) may be affected considerably (Mayer and Ulrich 1977). Effects on understory vegetation may be very important because at certain stages of succession a greater weight of chemical elements circulates through the understory than through the trees. This relationship has been demonstrated in old spruce and pine forests in the U.S.S.R. (Ovington 1962).

Perpetuation of a coniferous forest depends upon the continued reproductive success of the conifers. Spruce (*Picea abies*) germination has a broad optimum around pH 4.8 and is adversely affected at soil pH of 4.0 or lower. Spruce seedling establishment has a narrow optimum at pH 4.9 and is quite sensitive to pH levels lower than this (Abrahamsen et al. 1977). In a 20-wk study of the effects of acid rain on growth of white pine (*Pinus strobus*) seedlings, best growth was found in seedlings exposed to rain of the lowest pH (pH 2.3) (Wood and Bormann 1977). This increased growth was presumed to be caused by the increased nitrogen impact from the acid rain. Apparently, once seedlings are established, they are relatively tolerant of acidic soil. Considerable mineral leaching occurred throughout the 20-wk experiment. Availability of basic cations would probably have become limiting to growth had the experiment been carried out over an extended period.

Impacts of acidic precipitation were also reported at the First International Symposium on Acid Precipitation and the Forest Ecosystem (Dochinger and Seliga 1976) when European, Canadian, and United States scientists presented the data obtained on both continents during the last 20 yr.

Summary of effects on pines--

Based on the above literature evidence and the projected ambient air levels of total suspended particulates (TSP), $SO_2$, $NO_x$, and trace elements, it is possible but unlikely that short-term, visible damage will be incurred by the pines in the BWCA. Acid rain damage to plant tissues seems possible in view of results suggesting that the pH of rain under worst conditions may become as low as 3.5-4.3, although the projected frequency of these rains is not immediately available (Section 3). Literature reports indicate that this range of pH could alter growth and reproductive success of conifers.

The long-term implications of small, subinjurious effects on processes such as photosynthesis rates, radial growth, nutrient uptake, germination success, and lifespan could be substantial. Whether the effect would be strong enough to affect community structure or the rate of secondary succession is open to debate. In view of recent data which indicate that impacts may occur at residual levels lower than previously reported (Gordon et al. 1978, Kotar 1978), the possibility of long-term effects must be seriously considered. Signficant new research programs focused on the most sensitive species and on subinjurious effects must be carried out if these problems are to be resolved.

## Lichens and Bryophytes (Sphagnum)

### Effects of $SO_2$ on lichens--

The adverse effects of gaseous $SO_2$ on lichens are well documented in field and laboratory observations. The laboratory observations have generally been made at $SO_2$ levels of above 50 pphm and will not be elaborated on here. The field observations have tended to concentrate on mapping lichen communities around pollution sources, documenting the disappearance of lichen species as one approaches the pollution source (LeBlanc and Rao 1975). This approach seems to be accurate in determining zones of air quality in urban and industrial areas where there has been a pollution source for a long period of time (e.g., Sudbury, Ontario; LeBlanc et al. 1972), where environmental conditions are such that no interruptions in adequate indicator lichen cover would be expected. The approach is also useful where one is close enough to the source that short-term acute effects can be easily observed (Clay Boswell plant, Cohasset, Minn.; Coffin 1978).

LeBlanc and Rao (1973) indicate that lichens in the Sudbury, Ontario, area were not injured if ambient $SO_2$ concentration for the 6-month growing season was less than 0.2 pphm; growing season average concentrations of 0.6-3 pphm were adequate to produce chronic injury. Average growing season concentrations above 3 pphm produced acute injury. Background levels in the BWCA have reached 10 $\mu g/m^3$, or 0.37 pphm (Table 1).

Significant decreases in respiration rates of lichen samples occurred in 100-200 days at median $SO_2$ concentrations of 1.8 pphm in southeastern Montana (Eversman 1978), a level that could be approached in the BWCA given projected effects from Atikokan (Section 3). Thalli of yellow-green lichens (*Parmelia chlorochroa*, *Usnea hirta*) bleached to a yellower color within 100 days, and the percentage of normally plasmolyzed[1] cells increased from a baseline of 5-8% to 25-30% in 30 days (Eversman 1978). *Usnea hirta* is an epiphyte on trunks and branches of ponderosa pine in southeastern Montana. It also grows in the BWCA (Hale 1969). This type of lichen (fruticose) is particularly sensitive to air pollutants. *Parmelia chlorochroa* lives on bare soil between grass clumps and shrubs in the grasslands. This foliose lichen intergrades with western forms of *P. taractica*, and is found on exposed rocks in the BWCA (Hale 1969).

At median $SO_2$ values above 2 pphm in southeastern Montana, bleaching and plasmolysis occurred faster, and *P. chlorochroa* and *U. hirta* exhibited symptoms of acute damage. Within 33 days of $SO_2$ exposure at median concentrations greater than 3.3 pphm, plasmolysis of algal cells approached 100%, and the respiration rate of these lichens dropped significantly below that of controls (Eversman 1978). Selected indicator species in Minnesota, such as

[1]Plasmolysis is the shrinking of the cytoplasm away from the wall of a living cell due to water loss by exosmosis.

*P. caperata* and *U. subfloridana*, could be expected to show effects of $SO_2$ at median concentrations of less than 2 pphm.

Recent studies of lichens in the vicinity of the Columbia generating station in Wisconsin (S. Wolf, *personal communication*, 1979) have shown more subtle responses. Here, maximum 1-h $SO_2$ exposures at only 3-5 pphm occur once or twice a month. Two of four species studied (*Parmelia caperata* and *P. bolliana*) showed significant increases in the number of plasmolysed cells at the "high" impact sites (1-h exposures at 3-5 pphm once or twice a month) compared with samples from more remote sites. In another part of the study, these results have been related to small changes in the abundance of these and other lichen species during a 4-yr field study of lichen species composition in a zone around the power plant impacted by the 1-h exposures at 3-5 pphm. A number of secondary effects, including nitrogen fixation (see later section) are influenced by the composition of lichens in conifer forests, and species changes over a period of a decade or more could be significant for forest growth.

Effects of $O_3$ on lichens--

The very few studies that have been made on the effects of $O_3$ on lichens indicate that at concentrations of about 25 pphm and below, $O_3$ has stimulatory effects. A study by Anderson (1963) cited in Rosentreter and Ahmadjian (1977) concluded that $O_3$ may have induced production of young reproductive structures in *Cladonia coniocraea*, a common ground species. They also cited a study by Sernander-du-Rietz (1957), that suggested lightning storms stimulate fruiting of lichens.

Rosentreter and Ahmadjian (1977) found that $O_3$ concentrations of 10, 30, 50, and 80 pphm for 1 wk did not appreciably change the chlorophyll *a* content of the algae, the thallus color, or morphology of the reproductive structures of *C. arbuscula*. Chlorophylls *a* and *b* increased slightly at 10 pphm. Rosentreter and Ahmadjian (1977) agreed with Anderson and Sernander-du-Rietz that $O_3$ may induce lichen fruiting. Lichens may thus respond physiologically to levels of $O_3$ already reached on occasion in the BWCA (Section 3, Table 1). Nash and Sigal (1979), however, documented significant reduction in gross photosynthesis in *Parmelia sulcata* and *Hypogymnia enteromorpha* when these lichens were fumigated with 0.5 and 0.8 ppm ozone.

Unpublished field data (Sigal, *personal communication*, 1978) from the San Bernadino Mountains in California show a marked reduction in percentage cover of *Letharia vulpina* and *Nypogymnia enteromorpha* on conifers in areas subjected to oxidants ($O_3$ and PAN), compared with those on control sites.

Effects of trace elements on lichens--

Work involving lichens has not usually dealt with any potential or possible effects of trace elements. One Michigan study conducted near Lake Superior established an inverse relationship between lichen cover on tree bark and the presence of chloride precipitate found in snow (Brown 1977). Lichen cover varied from 85% at 0.001 g/cm $H_2O$ of chloride precipitate to 0% at 0.012 g/cm $H_2O$ chloride. Among the lichens eliminated at the higher concentrations of chloride precipitate were P. caperata, P. exasperatula, and Physcia millegrana, all present in the BWCA flora (Hale 1969, Wetmore, personal communication, 1978).

Effects of total suspended particulates on lichens--

Relatively little information is currently available regarding potential or possible effects of TSP on lichens. In his study of snow as an accumulator of air pollutants, Brown (1977) recorded an inverse relationship between lichen cover on tree bark and the amount of total particulate matter present in the snow. At 0.045 g/cm $H_2O$ of total solid particulate, lichen cover was 85%; at 0.23 g/cm $H_2O$ it was 0%. He did not determine, however, if this decrease was due to the levels of TSP or to those of $SO_2$ and chloride also measured.

Impacts of acidic precipitation on lichens--

Lichens are sensitive first to the ambient $SO_2$ concentration, then to the pH of stem-flow water (Robitaille et al. 1977). The gaseous $SO_2$ and particulate $SO_4^=$ are adsorbed onto moist bark surfaces, as well as onto lichen surfaces, a process that decreases pH.

Lötschert and Köhm (1977) compared ambient $SO_2$ concentrations with bark sulfur content and pH of deciduous trees (which have a higher natural pH than conifers) in Frankfurt. Where the $SO_2$ concentration was less than 2.8 pphm (0.09 mg/m$^3$), the bark pH was greater than 3.5 and the "greatest number" of lichens occurred. As $SO_2$ concentration increased to 3.9 pphm (0.10-0.11 mg/m$^3$), bark pH dropped to 3.1-3.2, and the lichens disappeared.

The buffering capacities of both bark and lichens decrease with acidic precipitation according to Robitaille et al. (1977). From this 1977 study these researchers concluded that stem-flow pH determined bark pH, thus the proportions of sulfurous acid ($H_2SO_3$) and the very toxic $HSO_3^-$, which in turn determine the presence or absence of sensitive lichen species. Of the derivatives $SO_2$ forms with water, $HSO_3^-$ is the most toxic to lichens (Puckett et al. 1973, Robitaille et al. 1977). In addition, when the $HSO_3^-$ dissociates to $H^+$ and $SO_3^=$, the ratio of $SO_3^=$ to $HSO_3^-$ (which is 1:1 at pH 7) increases by a factor of 10 for each decrease of one unit in pH (i.e., 10:1 at pH 6, 100:1 at pH 4) (Turk and Wirth 1975).

The mapping studies of Gilbert (1970) showed that bark pH and lichen cover decrease as $SO_2$ increases and that lichens only survive on highly buffered substrates (e.g., limestone and calcareous soil). Conifer trees, the habitat of many epiphytic lichens in northern Minnesota, probably have bark pH of less than 5.00 (Gough 1975). Thus lichens on conifer trees have very little pH "maneuvering space" and could be expected to be adversely affected by increasing ambient $SO_2$ and resulting acid precipitation conditions before lichens on deciduous trees and calcareous substrates.

Denison et al. (1977) reported less nitrogen fixation by Lobaria pulmonaria at pH 2 than at pH 4, 6, or 8. As acid rain increases in Pacific northwest forests, they expect the nitrogen-fixing activities on L. pulmonaria and similar L. oregana to decrease.

Impacts of acidic precipitation on Sphagnum--

Although much is known of the distribution of swamp and bog organisms in relation to natural pH gradients, there is currently no complete study of the effects of acid deposition upon wetland ecosystems (Gorham 1978).

Gorham (1978) has observed completely "dead" peat bogs in the vicinity of Sudbury, Ontario, where both acid and heavy metal pollution are extreme. Apparently, a progressive decline in both biotic diversity and productivity occurs with increasing saturation of the peat exchange complexes by hydrogen ions. Direct and secondary effects upon invertebrate and vertebrate animals may be anticipated, but are essentially unknown as are effects upon bacteria and fungi--which must be presumed vital to the breakdown of organic detritus and the recycling of limiting nutrient elements such as nitrogen, phosphorus, etc. (Gorham 1978).

Ferguson et al. (1978) state that the disappearance of Sphagnum species from the bog vegetation of the southern Pennines in Great Britain is correlated with the Industrial Revolution of the past 200 yr. Peat profiles of the southern Pennines show that Sphagnum species were once a much larger component of the blanket bog vegetation than they are now.

The laboratory studies (artificial acid rain, immersion, fumigation) reported by Ferguson et al. (1978) suggest that the growth of a number of Sphagnum species is sensitive to sulfur pollutants ($HSO_3^-$, $SO_4^=$, $SO_2$) within the range of concentrations found in Great Britain today. The species differ in their response to the pollutants; 0.5 mM $HSO_3^-$ eventually proved lethal to the most sensitive species, but reduced the growth rate of the most resistant, S. recurvum, by only 35%.

Ferguson et al. (1978) also note that in 1973 Tallis determined S. recurvum to be a recent dominant in the mire communities of north Cheshire. The only Sphagnum to exist in considerable quantities in the southern Pennines today, it is confined to flush areas. The ability of S. recurvum to withstand relatively high concentrations of the sulfur pollutants may contribute to its ability to survive and achieve dominance.

Summary of effects on lichens and Sphagnum--

Lichens are among the most sensitive organisms to air pollution. Though response thresholds for $SO_2$ exposure have not been established for most species, available information suggests that effects are not to be expected at median $SO_2$ concentrations below 0.2 pphm. Lichens appear to be tolerant of short-term exposure to relatively high ozone concentrations (up to 80 pphm). Lichens on the trunks of conifers are probably those most susceptible to direct effects of acid rain and $SO_2$ because their substatum may have an inherently low pH and be poorly buffered.

Sphagnum has been shown to be sensitive to lowered pH due to acidic rainfall near industrial areas. Thresholds for effects have not been established.

Concentrations of those toxic emissions from Atikokan known to affect lichens and Sphagnum are not expected to affect lichen populations in any substantial manner quantitatively or qualitatively. Some worst-case rainfall events in the BWCA may have low enough pH to have some effect on some species. Effects (if they occur) will be subtle and insidious.

Arthropods (Insects)

Effects of $SO_2$ on insects--

The effects of air pollutants on insects and plants are complex. The effects of environmental contaminants on insect-plant interfaces may be reciprocal, acting on the insect through the plant or on the plant through the insect. Air pollutants reported to have significant effects on entomological systems include sulfur and nitrous oxides, ozone, hydrocarbons, fluorocarbons, smog, dusts, acid mists, major and trace elements, and radionuclides.

Air contaminants accumulate in the tissues of insects by ingestion, respiration, or penetration through the cuticle. These substances may act directly on an insect, be passed through food webs to the insect, or indirectly affect the insect through alterations in food and habitat resources. Toxic substances may be transferred through food chains to higher trophic levels and accumulate in the insect predators and parasites. Pollinators, particularly social insects such as bees, appear to be especially susceptible to poisoning from the zootoxins they accumulate during their foraging activities.

Known effects of air pollutants on insects include death of sensitive species, proliferation of pest insects in forests and croplands, loss of parasitic and predacious insects, loss of saprophagous insects, and loss of pollinators. Other effects include temporary or permanent changes in behavior, reduced hatchability and fecundity, teratologies, and genetic alterations such as chromosome disjunction. No one has attempted to establish the thresholds of dose responses. Reported relationships between pollutant concentrations and changes in insect systems represent, for the most part, historical incidents and not a reliable threshold of response. The response threshold probably occurs at lower concentrations than reported.

Investigations of $SO_2$ effects by Bromenshenk (1979, 1978b) and Bromenshenk and Gordon (1978) at the EPA Zonal Air Pollution Delivery System (ZAPS) in southeastern Montana have demonstrated significant reductions in decomposer beetles, particularly Canthon laevis, on the fumigated plots of ZAPS sites I and II. Data from 15 cm, the lowest fumigation level measured, indicated that the levels at which these beetles first responded did not exceed 2.1-2.6 pphm average for 30 days. Because $SO_2$ concentrations decreased closer to the ground, this level probably was higher than that to which the beetles were responding. The decreased abundance (sometimes termed activity abundance) occurred on the lowest $SO_2$ treatment plots at both ZAPS I and II during 1976 and 1977. Beetle captures demonstrated a significant inverse linear regression with increasing $SO_2$ expressed as the reciprocal of the sulfation concentrations.

Similarly, Leetham et al. (1979) noted population reductions with increasing $SO_2$ concentrations for the coleopteran families Curculionidae and Carabidae (predators), the lepidopteran family Pyralidae (larvae), and adult grasshoppers (Acrididae). Also population reductions were observed in the high-treatment plots at both the ZAPS areas for tardigrades and rotifers in the soil.

Hillmann (1972) studied insect populations near a 615-MW coal-burning power-generating station in Clearfield County, Pennsylvania, which emitted 172 metric tons (190 tons) of $SO_2$/day. (Atikokan emissions are projected to range from 83 to 192 metric tons (92-212 tons) of $SO_2$/day.) One site was located 1,219 m (4,000 ft) from the power plant, the other 23.5 km (14.7 miles) from the power plant. Significantly greater numbers of Aphididae and significantly lower numbers of parasitic Hymenoptera (wasps) and social Apidae (bees) were captured at the site nearest to the power plant. Since aphid numbers in the area exposed to greater amounts of $SO_2$ increased concurrently with parasitic wasp decline, Hillmann concluded that $SO_2$ may have induced host-parasite imbalance.

Freitag et al. (1973) conducted a field investigation on ground beetle populations near a Kraft paper mill in Ontario, Canada, and found that a drastic reduction in the number of carabid fauna paralleled increasing fallout of sodium sulfate ($Na_2SO_4$).

Effects of $O_3$ on insects--

The work on the effects of $O_3$ on insect systems that has been done to date has been carried out under $O_3$ levels higher than would be encountered in the BWCA-Quetico area.

Effects of $NO_x$ on insects--

As with $O_3$, very little seems to be known about the effects of oxides of nitrogen on insect systems. The work that has been done has involved higher levels than would ŀ experienced in the BWCA-Quetico area.

Effects of trace elements on insects--

Studies have shown that a large number of trace elements can move through insect systems, often accumulating in insects at the higher trophic levels. Many of these elements are toxic to insects at relatively low concentrations, and many are toxic to insects at levels lower than those that affect mammals.

The most extensive trace-element work has been carried out on substances harmful to honeybees. This work has been reviewed by Lillie (1972), Debackere (1972), Toshkov et al. (1974), and Steche (1975). Because of their extensive foraging activities, bees contact, gather, and consume these materials. Bees also are magnifiers of noxious substances in their environs. Pesticide studies indicate that pollinators smaller than honeybees may be more susceptible to toxicosis because they receive a proportionally larger dose relative to body size (Johansen 1972).

A few studies have particular relevance to problems associated with emissions from coal-fired power plants. Svoboda (1962) found that about 500 bee colonies were destroyed within a 6-km radius of a power plant that released arsenic into the air.

Hillmann (1972) found that social pollinators and parasites (which are similar in terms of trophic relations to predators) were most severely affected by power-plant emissions. He recorded a significant decrease in social insects such as bumblebees and predatory wasps near a 615-MW power plant in Pennsylvania when compared with populations at a site 23.5 km (14.7 miles) away. Hillman correlated declines in insect abundance with $SO_3^=$ levels, but did not analyze for trace elements. Many trace elements are more toxic to bees than sulfur dioxide (see review by Debackere (1972)).

Dewey (1972) found relatively high fluoride levels in the 1,005 predatory insects collected near an aluminum smelter which reportedly emitted between 1,134 and 2,837 kg/day (2,500 and 7,600 lb/day) of fluoride. Four major groups of insects were collected within a half mile of the plant: tissues of pollinators contained 5,800-58,500 pphm fluoride; predators 610-17,000 pphm; foliage feeders 2,130-25,500 pphm; cambial feeders 850-5,250 pphm. Levels in the control groups, taken at least 80 km (50 miles) away, ranged from 350 to 1,650 pphm.

Bromenshenk (1976, 1978a, b, 1979) reported that preoperational and postoperational studies of honeybees taken from commercial apiaries near two 350-MW power plants in southeastern Montana showed significant increases in the levels of fluorides in or on the tissues of adult worker honeybees. After 1 yr of operation, during which neither plant had been in continuous operation and both had operated at one-third to one-half capacity, fluorides increased by as much as twofold in bees taken from apiaries downwind and as far as 15 km away from the plants. There were no increases in fluoride levels in bee tissues upwind from the power plant.

Other elements from coal combustion also affect insect populations. Before to the development of synthetic organic insecticides, several inorganic chemicals were widely used for insect control. These included compounds of arsenic, fluoride, mercury selenium, antimony, boron, and thallium (O'Brien 1967). The first six, and possibly all seven, are released by combustion of coal in electric power generating stations. The mercury content of the coal, emission rates of Hg, deposition fluxes, and background levels in fish from lakes of the BWCA have been characterized elsewhere in this report (Table 2, Figures 7, 8, 9, 10). Based on concentrations in Saskatchewan lignite coal (Appendix C), the ratios of some other toxic elements to mercury in coal are 268-430 for fluoride, 21-34 for arsenic, 0.59-3.0 for cadmium, and 2.5-4.0 for selenium. Taking into account the concentration in precipitator fly ash, and assuming that these materials are emitted in ways similar to mercury, estimated emissions as a ratio to mercury are 233-399 for fluoride, 14-28 for arsenic, 0.42-2.4 for cadmium, and 1.3-3.2 for selenium.

Fluoride and arsenic are likely to be released in quantities much greater than mercury, and they are of particular concern with regard to long-term, low-level exposures, since many compounds of fluoride and arsenic act most effecively through slow release by weathering and rapid release in the gut (O'Brien 1967). In addition, honeybees and presumably other pollinators are magnifiers of arsenic and fluoride in their environs (Bromenshenk 1979). According to Debackere (1972) danger to bees from arsenic poisoning is greatest when: (1) the wind has blown in the same direction for extended periods, (2) precipitation has been low or infrequent, (3) in spring when blossoms are few and foraging is intense, and (4) after a heavy dew, fog, or mist. Whereas arsenic poisoning often causes sudden die-off for a few days, fluoride poisoning usually occurs as death over a long period (Lillie 1972, Debackere 1972). Both fluoride and arsenic compounds may be stored in food supplies resulting in even longer exposure periods (Bromenshenk 1978a), and severe bee kills near industrial sources of arsenic and fluoride are well documented (Lillie 1972, Debackere 1972).

In a later section on aquatic ecosystems (Section 5) concern is expressed that: (1) mercury has been found to occur in fish at levels in excess of FDA standards, (2) the sources of mercury are unknown, and (3) emissions from the Atikokan power plant may increase these levels. Whatever the source, where mercury is found, elevated levels of other injurious trace elements are also likely to be found. In view of the high toxicity of arsenic and fluoride to insects, and because large quantities of these materials (in comparison to mercury) are to be emitted by the Atikokan power plant, more information is needed about the background levels of these substances in the BWCA and in the insects, vegetation, and soil of the region. With these background data the significance for entomological systems of the worst-case concentrations and depositions could be evaluated.

Summary of effects on insects--

Although responses to threshold exposures to pollutants have not been established, a number of insect groups with strong sensory systems, particularly saphrophagous and predacious beetles, social bees (pollinators), and parasitic wasps, have been shown to be reduced in abundance at very low concentrations of air pollutants, apparently because of pollutant avoidance or disorientation, or both. Several plant-feeding insect groups increase rapidly when the activity of parasite or predator-control insects is reduced, or the vigor of host-plant species is reduced, both of which have been shown to occur from gaseous air emissions. If physiological stress is demonstrated by the host coniferous trees in the BWCA, concurrent alterations in entomological systems will occur. The available literature suggests that disturbances in the population dynamics of phytophagous forest insects may occur at levels below those manifesting visible injury to pines. Direct injury to the vegetation of the BWCA by exposures to pollutants from the Atikokan power plant, and from other regional sources if incurred, could be intensified by insect interactions.

## Amphibians

In the United States 50% of the frog and toad species breed in temporary pools formed annually by accumulated rain and melted snow. One-third of the species of salamanders in the United States that are aquatic before metamorphosing into terrestrial adults also breed in temporary ponds. Such ponds are more fragile than lakes or streams because their acidic precipitation input has little contact with soil buffer systems and is not diluted by mixing with standing water (Pough 1976).

A study of embryonic mortality of spotted salamanders (*Ambystoma maculatum*) (Pough 1976) showed less than 1% egg mortality in pools near neutrality, but more than 60% in low pH (less than 6) ponds, with an abrupt transition in mortality below pH 6. Furthermore, field results were reproducible in the laboratory, where effects of both predation and temperature were eliminated.

Other studies of anurans include one in which the breeding sites of most anurans in or near the New Jersey Pine Barrens were limited to grassy ponds and gravel pits resulting from the normally lower pH (3.6-5.2) of sphagnous pools (Gosner and Black 1957). Prestt et al. (1974) postulate that acidification of anuran breeding sites may be contributing to the recent decline in British frog populations. Pough (1976) reiterates the earlier observations of several authors that the significance of any widespread failure of salamander reproduction will have far-reaching consequences. Salamanders in temporary ponds are an important predator on dipteran larvae (flies) and an important energy source for higher trophic levels in an ecosystem (as are other anurans such as frogs). Pough also notes that these ponds are major breeding sites for many invertebrates as well. Changes in these ponds could therefore limit the breeding of numerous species, while allowing pest species to flourish.

Some changes in the acidity of standing pools in the BWCA may occur because of acidic snowmelt and acidic precipitation. If this change occurs in the spring, salamander reproduction may be affected.

## Soils

The configuration of granites, slates, and argilites and ultrabasic bedrocks in the BWCA have determined the local patterns of soils and landforms. Glacial scouring also has exposed the bedrock on many ridges and left only a shallow varying cover of till on the slopes and ravines. Although locally some soils are deep, large areas of thin rocky soils are derived from sandy glacial deposits. These soils are among the most sensitive in the Superior National Forest area (Heinselman 1977).

### Bedrock geology--

Bedrock in the Voyageur's National Park and the Boundary Waters Canoe Area shows a wide variation in rock types. All bedrock found in the two parks is part of the Precambrian (>600 m.y.) Canadian Shield and is covered by varying depths of glacial till, outwash, and lacustrine material deposited during the Wisconsin stage of glaciation. Bedrock in the VNP is part of a high grade metamorphic terrain, with schists, gneisses, migmatites, and granites as major rock types; minor feldspathic quartzite and metaconglomerate are also present. Metamorphic grade increases to the south and east. Rock types present in the VNP include 50% (of park area) metagraywacke and biotite schist, 20% schist-rich migmatite with 25-75% paleosome (a migmatite is a rock that has been raised to temperatures and pressures high enough to cause partial melting; paleosome is that portion of rock which does not melt), 12% granite, 10% granite-rich migmatite, 4% mixed metavolcanic rocks, 2% leucogranite, 1% feldspathic quartzite/metaconglomerate, 1% quartz-feldspar gneiss.

The BWCA contains rocks generally representative of a much lower metamorphic grade terrain than that seen in the VNP as well as a much wider variety of rock types. The western portion of the BWCA, that occurring west of R8W-R9W (91°25'W) boundary and north of Highway 18 (47°58'N) consists dominantly of rocks of the Vermilion Massif, a series of granitic intrusives ranging from diorite to granite. Related rocks include granite-rich migmatite, amphibolite-migmatite and biotite schists. The migmatites found in the VNP represent the northern contact zone of the Vermilion Massif with surrounding country rock (Southwick 1972). On the eastern edge of this portion are rocks of the Newton Lake Formation, a series of mafic to intermediate metavolcanic flows and tuffaceous sediments (Sims 1972), rocks of the Knife Lake Group, which include slate-graywacke, conglomerate, arkose-graywacke, agglomerate, and andesite porphyry (McLimans 1972), and rocks of the Ely Greenstone, a series of dominantly basaltic and diabasic metavolcanic flows (Sims and Viswanathan 1972).

The central portion of the BWCA, that area between R8W to R11W (91°25'W to 91°40'W) and R1W (90°31'W), below the Gunflint Trail, contains a wide variety of rock types. This area is dominated by rocks of the Duluth Gabbro Complex, a series of mafic intrusions ranging from gabbroic to troctolitic to anorthositic. Within, and surrounded by, the Duluth Complex are rocks of the North Shore volcanic group, a series of lava flows dominantly basaltic but with appreciable amounts of felsic and intermediate flows.

The remainder of the area, that north of the Duluth Gabbro Complex contact, is underlain by a variety of rock types. The majority of the Knife Lake Group occurs in the western half as do minor amounts of Ely Greenstone and rocks of the Giants Range Batholith, a series of tonalitic (quartz diorite) to granitic intrusions (Sims and Viswanathan 1972). The Saganaga Batholith, dominantly tonalitic in composition, is present east of the Knife Lake Group. Minor amounts of metabasalt, metaandesite and metadiabase (minor) are also present to the south and southwest of the Saganaga Batholith. Part of the Gunflint Iron Formation occurs along the Duluth Gabbro Complex Contact. In addition to the forementioned rock formations, small granitic to andesitic intrusives are present, and are generally associated with the Knife Lake Group.

The eastern portion of the BWCA, that between R2W (91°31'W), above the Gunflint Trail (47°54'N), and R2E (90°15'W), is dominated by the Rove Formation (graywackes and argillites) and the Logan Sills, a series of diabasic dikes and sills which intrude the Rove Formation. To the south a lesser amount of Duluth Gabbro is present. By visual estimate, the area covered by each rock type (for the entire BWCA) is:

| | |
|---|---|
| Duluth Complex | 40 |
| Vermilion Massif | 30 |
| Knife Lake Group | 8 |
| Saganaga Batholith | 5 |
| Granite-rich magmatite | 5 |
| Logan Sills | 3 |
| Rove Formation | 2 |
| North Shore Volcanic Group | 2 |
| Newton Lake Formation | 2 |
| Giants Range Batholith | 2 |
| Ely Greenstone | 1 |

Distribution of poorly buffered soils--

A number of soil surveys have been carried out on parts of the BWCA, but the survey by Prettyman (1978) of the Kawishiwi area of Minnesota covered an area central to the BWCA and included the soil-type boundaries on printed aerial photographs. Lakes and streams associated with the deeper soils in the BWCA seem less likely to show effects from acid rainfall within the immediate future.

The report by Prettyman describes 22 soil-mapping units in the Kawishiwi area. These units are grouped into roughly 12 soil types, half loosely defined (e.g., "peat and muck" and "poorly drained loamy soils"). The principal soil types covering a large acreage are the following:

| | |
|---|---|
| Barto | Gravelly coarse sandy loam |
| Conic | Gravelly sandy loam |
| Insula | Gravelly sandy loam |
| Mesaba | Gravelly sandy loam |
| Quetico Rock Complex | Loam |

Of these five types the Mesaba and Conic soils are described as usually deep soils, 51-102 cm (20-40 in.) to bedrock, whereas the Barto and Insula soils are 13-51 cm (5-20 in.) deep. The Quetico Rock Complex has soils that range from 10 to 20 cm (4 to 8 in.) deep, and although its texture is given as "loam," this texture refers to the portion of the soil that is not coarse fragments and small rocks. Thus, if the capacity of the soil to withstand additions of hydrogen ions can be measured by a combination of soil texture and total soil depth (within the specified mineralogy of the Canadian Shield bedrock types), then we can define a soil grouping within the Kawishiwi area by combining the three shallow soils, Barto, Insula, and Quetico, despite the fact that some differences in texture and geological origin can be recognized.

Chemical data on these shallow soils are quite limited. Results of a number of analyses for the Barto soils have been provided, however, by personal communication from Dr. Prettyman. These results indicate the following cation exchange capacity (CEC) and percentage base saturation:

| Soil series | Horizon | pH | CEC (meg/100g) average | Base saturation (%) |
|---|---|---|---|---|
| Barto | B 21 | 4.8 | 24.21 | 18.63 |
| | B 22 | 5.2 | 21.95 | 16.58 |
| | B 3 | 5.7 | 13.78 | 10.39 |

The data here contrast with similar analyses for Mesaba soils. The latter have 37% base saturation in the parent material horizon (compared with 10% for Barto soils). The higher base saturation in the upper horizons of Barto soils (18%) probably reflects the increased organic matter and clay content and the different type of exchange sites present there.

Effects of Acidic Precipitation on Soils --

The absence of a large soil volume for geological weathering greatly influences the potential for small watersheds to withstand changes in the rate of addition of hydrogen and sulfate ions from the atmosphere. These pollutants are likely to enter the soil environment primarily through precipitation, stem flow (precipitation draining along the trunks and stems of vegetation), and throughfall (precipitation filtering through the forest canopy). Pollutants transported long range will probably enter forest systems primarily through precipitation. Effluents from local sources may also contribute to this regional precipitation loading. In addition, quantities of local pollution will be dry deposited on vegetation. The fraction of this material which is not biologically assimilated will be subject to leaching by precipitation and will enter the soil as stem flow or throughfall. Stem flow and throughfall may be considerably enriched in pollutants compared to precipitation carrying only the regional atmospheric load (Abrahamsen et al. 1977).

The most significant soil-mediated effects may result from the fact that rainfall bearing pollutant loads initiated as $SO_2$ or $NO_x$ has depressed pH.

Effects of Acid Precipitation on Geochemical Weathering--

Since the pH of water in contact with minerals has a marked effect on weathering products that result during the breakdown of mineral, changes in the pH of precipitation also have effects on the products and rate of weathering. Through hydrolysis specific cations can be removed from the mineral, allowing a more rapid change of crystal structure. Jenny (1950) showed $H^+$ replacing $Na^+$, $K^+$, or $Ca^{2+}$ in the crystal structure or bonding with an O to form an $OH^-$ group. The $H^+$ ion is very important because its size allows easy penetration into the mineral, and its high charge-to-radius ratio has a marked disrupting influence on the crystal's charge balance (Loughnan 1969).

Birkeland (1974) determined a series of mobilities for various ions and found:

$Ca^{2+} > Na^{1+} > Mg^{2+} > K^{1+} > Si^{4+} > Fe^{3+} > Al^{3+}$.

Under the normal pH produced by background levels of carbonic acid ($H_2CO_3$), values for $Fe^{3+}$ and $Al^{3+}$ are generally so low as to be negligible. Situations do occur, however, where the pH of soil solutions is such as to allow Al to become soluble. In well-drained northern soils containing abundant organic matter a pH of < 4 is possible. The compound $Al_2O_3$ may become mobile and migrate to a less acidic area and be precipitated (Loughnan 1969).

Where precipitation exceeds evaporation and soils are very permeable, several pH dependent responses are observed:

1) Most of the $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$ is leached.

2) $Al_2O_3$ and $SiO_2$ are released.

   a. If soils are neutral to alkaline with low $Ca^{2+}$ and $Mg^{2+}$, $SiO_2$ may leave in solution as does $Na^+$ and $K^+$.

   b. If moderately acidic (4.5-6.5), $SiO_2$ and $Al_2O_3$ are immobile with the development of clay or a fine-grained mixture of gibbsite ($Al(OH)_3$) and quartz ($SiO_2$).

   c. If highly acidic and rich in humic or other organic material, $Al_2O_3$ and $Fe_2O_3$ may be removed in solution (Moore and Maynard 1929) (Figure 14).

Since background levels of $H^+$ in these major soils are traceable to the carbonic acid in water, as well as the humic reactions, additions of $H^+$ from nitric and sulfuric acid in precipitation can dominate the inorganic reactions. The separation of $Al^{3+}$ and $Fe^{3+}$ may also be seen in soils that show some evidence of podzolization, a process where Fe, Al, and organic material are leached from an eluvial (exit) horizon to an elovial (into) horizon below. Recent work suggests that Fe and Al are carried as part of a metallo-organic chelating complex, of which fulvic acids are thought to be the common chelating compounds for a number of soils. Fulvic acids are produced in the A or O horizons and chelate with $Al^{3+}$ and $Fe^{3+}$ ions or with $Al^{3+}$ and $Fe^{3+}$ hydroxy ions. Because these compounds are water soluble they can be carried downward with percolating water. At some depth in soils the complexes are destroyed and the metals deposited, but if the percolating water reaches a soil or bedrock channel, the metals can be carried with the organics to a stream or lake. Van Schuylenborgh (1965) suggested that the organic portion of the molecule may be destroyed by microbial action, with release of the cation.

Work by Schnitzer (1971) clarified the fulvic acid-metal complex transfer. Under constant pH the complexes became more insoluble as metal

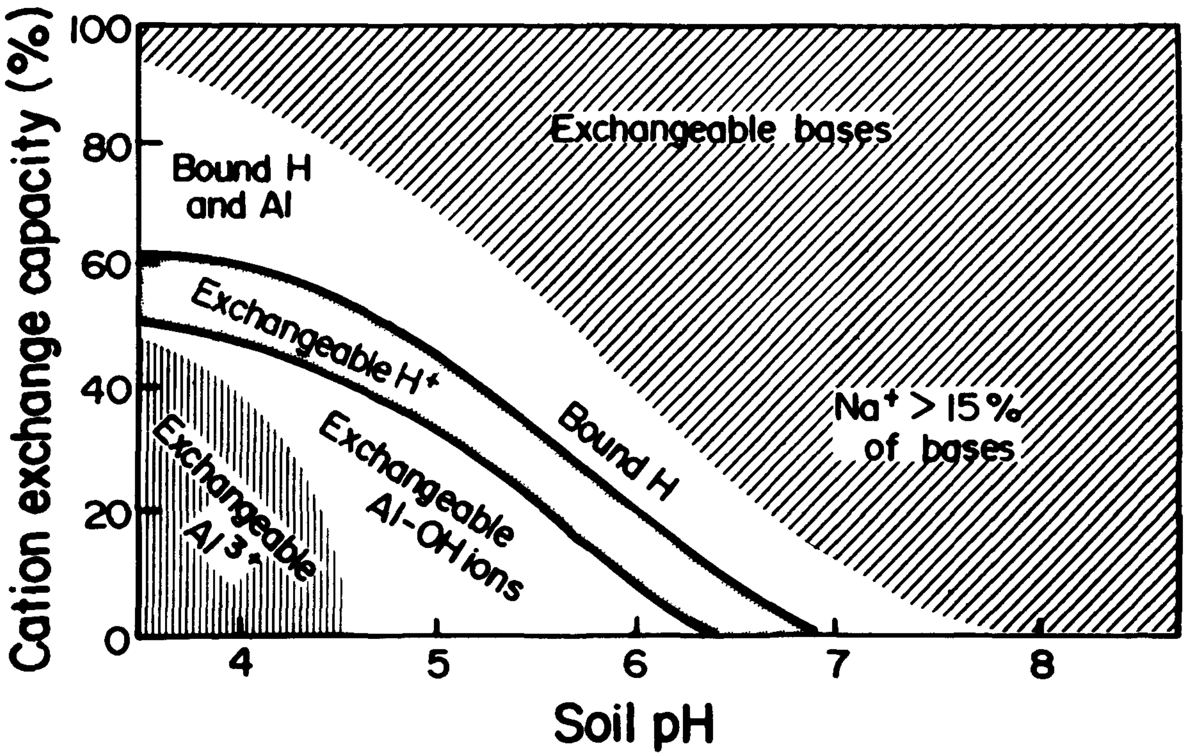



Figure 14. General exchange relationships between pH and cations. (From Buckman and Brady 1969, in Birkeland 1974).

ions were added to the fulvic acid solution; 1:1 molar $Fe^{3+}$-$Al^{3+}$-fulvic acid complexes were completely soluble while 6:1 complexes were water insoluble. Even 2:1 complexes showed decreasing solubility.

Thus transfer of $Al^{3+}$ and $Fe^{3+}$ could be envisioned as follows. Fulvic acid is formed in the A or O horizon and, being water soluble, is transported downward by percolating waters, constantly picking up $Fe^{3+}$ and $Al^{3+}$. As more metallic ions are picked up, the complex becomes insoluble and can be precipitated in the B horizon if it has not reached a bedrock surface or stream channel. Schnitzer (1971) showed that up to 56 g of iron or 27 g of aluminum can be dissolved and kept in a solution by 670 g of fulvic acid. These values are equivalent to 84 mg of iron or 40 mg of aluminum per gram of fulvic acid.

Recent experiments indicate that increased acidity of precipitation, through additions of dilute nitric and sulfuric acid, also can affect these and other reactions in the soils. Availability of nitrogen, decreased soil respiration and increased leaching of nutrient ions from the soil have been reported (Abrahamsen et al. 1977). Since acid rainfall adversely affects many other components of the soil-plant-water relationship, it has not yet been possible to demonstrate clearly the nature of causal relationships in the field. It is possible that acid damage to shallow, poorly buffered soils might initially be partly offset by the nutritional benefits gained from nitrogen compounds commonly occurring in the acid rain. Changes detected to date in soil processes are too small to affect plant growth, but the studies have been in areas of deeper soils than in the BWCA. In addition, the enhanced acidification of soils produces a continuous loss of essential cations and eventually the addition of nitrogen is of no advantage if other nutrients are not available.

The $H^+$ additions associated with the projected increase in $SO_4^=$ deposition of 0.9-1.4 kg/ha-yr over the apparent presettlement depositon of 4-5 kg/ha-yr (Section 3) appear to be an increase of consequence for element transformation and mobilization on the poorly buffered soils in this region. Elements mobilized in this fashion may be taken up by plants, may reach streams via the shallow groundwater, but most often will be carried to deep, slow-moving groundwater surfaces. Here, these elements may remain in their more toxic forms for extended periods and, in this sense an irreversible effect is produced.

## Nutrient Cycling

### Soil-mediated effects of acidity on vegetation--

Although the relationships between soil acidity and vegetation growth, metabolism, and reproduction are receiving increasing attention, many areas of uncertainty remain. The following discussion will focus on available information concerning soil-mediated effects on: (1) decomposition of organic matter; (2) effects of cation losses and mobilized toxic elements on growth of coniferous species; and (3) reproduction of coniferous species.

Any potential reduction in a soil's cation exchange capacity and essential nutrients, such as discussed in the previous section, will affect the growth of the trees it supports. In general, forest plants obtain the nutrients necessary for metabolism and growth primarily from soil. Atmospheric sources are either indirect (mediated by soil) or secondary in importance. Therefore, the potential for reduced availability of these nutrients in forest soils is of concern.

In an unmanaged forest near its climax successional state important macro- and micronutrients tend to be conserved in the soil-plant system. Most remain within the cycle of organic production, decomposition, and mineralization followed by reincorporation into living material. Leaching losses in ground water are minimal (Frink and Voigt 1977). Nutrient cycles are not closed, however. Precipitation and nitrogen fixation are important sources of nutrients to the forest (Ovington 1962), and additional supplies of nutrients are made available by weathering of soil particles. These inputs are countered by some ground-water leaching. Potential effects on plant-soil interactions may result from effects on inputs and outputs to nutrient cycles as well as soil-mediated changes in rate within the cycles.

Since $Al^{3+}$ is highly toxic to plants, the mobilization of this element by additions of $H^+$ to the soil medium can have important detrimental effects on nutrient utilization and growth. Although $Al^{3+}$ toxicity is well known for crop plants, it is only now being investigated for the common tree species (McCormick and Steiner 1978).

Sulfur and nitrogen cycles--

The capacity of a forest to utilize additional sulfur is often closely related to the nitrogen cycle. The two nutrients usually are utilized in a fixed ratio. If nitrogen is abundant, the system may be sulfur limited and have a considerable capacity to absorb anthropogenic sulfate. Such inputs of sulfates might well stimulate increased growth. In such cases $H_2SO_4$ in rainfall might not increase soil acidity or degrade the nutrient pool. However, mature timber stands are more likely to be nitrogen limited than sulfur limited. If the capacity of these systems to utilize anthropogenic sulfur inputs is exceeded, deleterious effects of $H_2SO_4$ on the ecosystem's nutrient pool are possible.

As in the sulfur cycle, overall production and consumption of $H^+$ ions in the nitrogen cycle are balanced. Loss of soil bases and acidification are still possible, however. When mineralization occurs followed by oxidation of ammonium ion to nitrate, $H^+$ ions formed will replace basic cations. These basic cations are then subject to leaching in association with nitrate ions as water passes through the soil profile if conditions allow any buildup of nitrate ion (e.g., if the system is other than nitrate limited) (Reuss 1977).

Most natural ecosystems tend to maintain low nitrate levels because nitrates formed are rapidly taken up by the vegetation. In nitrogen-limited forests anthropogenic nitrates may stimulate plant growth. This would prevent increased soil acidity due to processes within the nitrogen cycle and also accelerate sulfate uptake reducing the potential for acidification due to processes in the sulfur cycle.

Acid rain is postulated to decrease decomposition rates through adverse effects on microbial activity (Oden 1976, N. R. Glass 1978). Apparently soil pH values below 3.5 are required before effects on decomposition of pine needles can be seen (Abrahamsen et al. 1977). Negative effects of soil acidification in pine forests on microbial activity have been shown, but the effect on decomposition was unclear (Tamm et al. 1977).

The direct effects of pollutants on ground beetles cited earlier can have a marked effect on rates within the nutrient cycle. Benefits of decomposer beetles include the return of nitrogen and inorganic phosphate, the reduction of surface runoff, burial and mechanical breakdown of organic materials, decreasing wastage of organic materials, increased surface storage of nutrients, reduced loss of nutrients in runoff, and increased infiltration and storage of moisture in the soil. In addition, these arthropods serve as food for other insects and higher animals, aid in the dispersal of soil microflora and microfauna, and may compete with less desirable (from a human viewpoint) insects such as hornflies for organic material resources (Ritcher 1958, Macqueen 1975, McKinney and Morley 1975). In forest systems as much as 90% of the net primary production does not pass through herbivore food chains but is deposited on the soil as litter and is acted on by complexes of animals, fungi, and bacteria (Kurcheva 1960, Edwards and Heath 1963, Crossley 1970, Whittaker 1975, and others). Examples of resource partitioning by saprophagous arthropods are numerous, and their role in resource partitioning and their use as indicators of environmental quality has been reviewed by Cornaby (1975, 1978). He comments that they may have an exploitable role in the deactivation of noxious materials and decomposition of slowly degrading materials. Also, he points out that they may be very important as regulators of the rate of release of nutrients and as detectors of subcritical levels of pollutants in soils.

Specialists in the field of soil-litter arthropods seem to agree that these insects are susceptible to harm from pollutants and that they may affect important functional components of ecosystems. From a theoretical study Harte and Levy (1975) and Dudzek et al. (1975) concluded that damage to decomposers or nutrient pools is a potential source of instability to the entire ecosystem.

Influence of affected lichens on nitrogen inputs in forests--

The potential reduction in nitrogen-fixing lichens or in their rate of nitrogen fixation would have most effect in highly nitrogen-deficient soils, such as those in the BWCA.

Although most lichens contain only green algae, several genera contain only nitrogen-fixing blue-green algae or blue-green algae in addition to their green algae. Lobaria pulmonaria (on Thuja occidentalis and sandy rocks in northern Minnesota), many Peltigera and Nephroma species (on soils, duff, and moss), and Sterocaulon paschale (on soil) contain blue-green and green algae. Leptogium and Collema species (on soil and rock) contain only blue-green algae. The percentage of cover of these lichens and their contributions to the nitrogen regime of Minnesota forests is not presently known.

Forman and Dowden (1977) manipulated laboratory figures (Scott 1956, Millbank and Kershaw 1969, Henriksson and Simu 1971) for amounts of fixed nitrogen and determined that three Peltigera species (P. canina, P. rufescens, and P. praetextata) would fix a total of 0.05-0.6 g N $(m^2$ lichen cover$)^{-1}$ day$^{-1}$ in a spruce-fir forest in Colorado.

Denison et al. (1977) investigated the current status of $N_2$ fixation in western Washington forests and the potential effects of acid rain on this process. It is thought that even the low concentrations of $SO_2$ now found in this area have a deleterious effect on $N_2$ fixation by restricting the distribution of the ephiphytic $N_2$-fixing lichen, Lobaria pulmonaria. This species, also present in the BWCA, is found in the Pacific Northwest forests only where the mean annual $SO_2$ concentration is less than 5 $\mu g/m^3$ (0.175 pphm), a figure lower than some background levels already recorded in the BWCA (Section 3, Table 1). Lobaria pulmonaria fixes 100 times more nitrogen than does litter and 10,000 times more nitrogen than soil organisms in these acid forests. The sensitivities of Peltigera species are not known.

The rate of fixation of L. pulmonaria is about three times that of L. oregana (Denison et al. 1977), the major $N_2$ fixer of old growth and coniferous forests in the Pacific Northwest. After exposure to $H_2SO_4$ of pH 4 or less, L. oregana fixes less $N_2$.

Kallio and Varheenmaa (1974) exposed Stereocaulon paschale and Nephroma articum to the air of Turku, Finland, where maximum $SO_2$ values in 1969 were 5.36 pphm $SO_2$ (153 $\mu g$ $SO_3^=/m^3$) with $NO_3^-$ and sulfates. Nitrogen fixation decreased to 10-20% of controls. They suggest that the $SO_2$ combined with water on the lichen structures containing the blue-green algae decreases the pH of the medium sufficiently to interfere with the metabolism of the blue-green algae.

## Influence of Affected Trees on Insect Populations

Three authors have reviewed interactions among air pollutants, plants, and insects (Heagle 1973, Hay 1975, Ciesla 1975). Heagle notes "a common finding is that trees injured and weakened by pollutants are more likely to be atacked by insects that normally require weakened trees for successful reproduction." Ciesla (1975) concludes that photochemical oxidant injury to ponderosa pines in the San Bernardino Mountains predisposed the trees to bark beetle attack. The understanding of the physiological mechanisms involved needs to be determined for other combinations of pollutants, trees, and insects.

Pest insects do not always proliferate in areas subjected to air-pollution stress. In some instances declines in pest-insect populations have been observed. The difference in response appears to be a result of interactions of many variables. One variable seems to be feeding habit. Several lines of evidence indicate that stress from pollutants such as $SO_2$ and natural occurrences such as drought may reduce the tannin content of leaves (Feeny and Bostock 1968, oak leaves) and needles, which results in more free or unbound protein foliage. Thus the foliage becomes more nutritious and a "better" diet for foliage-feeding insects (G. Orians, University of Washington, personal communication, 1978).

Our understanding of the effects of air pollutants on tree-insect relations depends almost entirely on geographical historical surveys of trees severely damaged by pollutants, insects, or combinations of the two. No attempts have been made to determine dose-response thresholds. In most cases patterns of insect outbreak relative to a pollution source, deviations from normal outbreak patterns, or the appearance of insects in outbreaks that rarely reach epidemic levels have been described (Ciesla 1975). Carlson et al. (1974a) used stepwise multiple regression analyses and demonstrated that foliar fluoride content was significantly related to damage caused by complexes of foliage-feeding insects. Some of the observed insect-tree pollution interactions are summarized in Table 9.

In an attempt to identify research problems considered critical for an acceptable understanding of the interactions of air pollution and wood vegetation, Bromenshenk and Carlson (1975) concluded, "There can be no doubt that air contaminants are harmful to insect pollinators, although the exact processes are not understood. Many forest trees and shrubs would not produce seeds or reproduce themselves without insect pollinators...". Changes in the population dynamics of forest pest insects may result from a predispositon of the host to insect attack, as described earlier.

## Bioaccumulation

Many trace elements are accumulated and concentrated through food-chain processes. Organisms at higher trophic levels often have higher tissue concentrations than do their prey. Potentially toxic compounds from the Atikokan generating facility may become accessible and toxic to various organisms through this process of biological magnification. The processes by which this could occur are discussed below.

### Trace-element availability from soils and plant uptake--

Factors affecting trace-element availability include pH, organic matter content, soil drainage, soil-microorganism content, cation exchange capacity (CEC), and anion content. Plant-root components may also affect nutrient uptake by releasing organic compounds into the surrounding soil, modifying the soil environment, and thereby modifying trace-element uptake (Tiffin 1977).

TABLE 9. SUMMARY OF NATIVE INSECT RESPONSES TO $SO_2$ AND OTHER POLLUTANTS[a]

| Host | Insect | Pollutant | Source | Population response | Author |
|---|---|---|---|---|---|
| Ponderosa pine | *Dendroctonus brevicomis* (western pine bark beetle) | $SO_2$ | Smelter Kellogg, Idaho | High incidence | Evenden (1923) |
| Douglas fir | *Orgyia pseudotsugata* (Douglas fir tussock moth) | $SO_2$ | Pulp mill Missoula, Montana | Outbreaks not related to source | Carlson et al. (1974b)<br>Tunnock et al. (1974) |
| Sitka spruce (*Picea sitchensis*<br>Western hemlock (*Tsuga heterophylla*) | *Acleris gloverana* (western blackheaded budworm)<br>*Neodiprion tsugae* (hemlock sawfly)<br>*Ectropis crepuscularia* (saddle-backed looper) | $SO_2$ | Pulp mill Ketchikan, Alaska | High incidence (correlated with High foliar $SO_2$) | Laurent and Baker (1975) |
| Ponderosa pine (*Pinus ponderosa*) | *Dendroctonus brevicomis* | $SO_2$ | Smelter Trail, British Columbia | Pollutant primary agent of injury | Keen and Evenden (1929) |
| Scotch pine<br>Norway spruce | Bark beetles (several species) | $SO_2$ | Industrial | High incidence | Bosener (1969) |
| Pines | Bark beetles and other insects *Pissodes* spp. (weevil), *Ipstypographus* (engraver beetles) | $SO_2$ | Industrial (multiple source) | High incidence | Donaubauer (1968) |
| Oak | Bark beetles | $SO_2$ | Paper mill | High incidence | Kock (1935) |

(continued)

TABLE 9. (CONTINUED)

| Host | Insect | Pollutant | Source | Population response | Author |
|---|---|---|---|---|---|
| Ponderosa pine<br>Lodgepole pine | <u>Dendroctonus</u> spp.<br><u>Ips</u> spp. | $SO_2$ | Smelter<br>Trail, British Columbia | High incidence | Scheffer and Hedgcock (1955) |
| Scotch pine | <u>Tomicus piniperda</u><br><u>Melanophila cyanea</u><br>(bark beetles) | $SO_2$ | Industrial | Decreased incidence | Templin (1962) |
| Red, Scotch, Austrian pines | <u>Rhyaciona buoliana</u> | | | High incidence of <u>Rhyacionia</u>, few parasites | |
| White pine | <u>Pissodes strobi</u><br>(white pine weevil) | $SO_2$ | Smelter<br>Sudbury, Ontario | Less damage (galls) near smelter | Linzon (1958, 1966) |
| Pine and spruce | <u>Pissodes</u> spp. | $SO_2$ | Industrial | High incidence | Kudela and Novakova (1962) |
| Pines<br>Scotch | <u>Acantholyda nemoralis</u><br>(webworm) | $SO_2$ | Industrial | Decreased incidence | Sierpinski (1967) |
| Pines<br>Scotch | <u>Exotelia dodecella</u> | $SO_2$ | Industrial | Unaffected | Sierpinski (1966a, 1967) |
| Scotch pine and others | <u>Paratetranychus unungis</u><br><u>Exotelia dodecella</u><br><u>Acantholyda nemoralis</u> | $SO_2$ | Industrial | High incidence | Sierpinski (1966b, 1971) |

(continued)

TABLE 9. (CONTINUED)

| Host | Insect | Pollutant | Source | Population response | Author |
|---|---|---|---|---|---|
| Ponderosa pine | <u>Dendroctonus brevicomis</u> (western pine beetle) | $O_3$ photochemical oxidants | Urban | High incidence | Stark et al. (1968)<br>Cobb et al. (1968a,b)<br>Miller et al. (1968) |
| Oaks | <u>Biston betularia</u> (cryptic moth) | $SO_2$ | Industrial and urban | Significant positive association | Bishop et al. (1975) |
| | | smoke | | Non-significant barely positive association | |
| Spruce | <u>Adelges abietus</u> (gall louse) | smoke | Industrial | High incidence correlated with pollution damage | Ranft (1968) |
| Norway and white spruce | <u>Adelges abietus</u> | F | Industrial | High incidence correlated with pollution damage | Wentzel (1965) |
| Oaks and other deciduous trees | <u>Porthetria dispar</u> (gypsy moth) (larvae) | NaF | Laboratory oral dose, 0.05 mg | Toxic dose | Weismann and Svatarakova (1973) |
| Fir | Bark beetles and weevil | F | Industrial | Decreased incidence; F thought to be toxic | Pfeffer (1963) |

(continued)

TABLE 9. (CONTINUED)

| Host | Insect | Pollutant | Source | Population response | Author |
|---|---|---|---|---|---|
| Western hemlock Lodgepole | Ectropis crepuscularia (saddle-backed looper) Choristoneura fumiferana (spruce budworm) | F | Aluminum smelter Kitimat, British Columbia | High incidence | Silver (1961) |
| Ponderosa pine | Nuculaspis californica (black pine leaf scale) | F | Aluminum smelter The Dalles, Oregon | Infestation existed before smelter; dust and chemical sprays may have caused outbreaks | Compton et al. (1961) Edmunds (1973) |
| Lodgepole pine | Four species of insects Phenacaspis pinifoliae (pine needle scale) | F | Aluminum smelter Columbia Falls, Montana | Outbreak confined to areas where foliar fluorides were at least 30 ppm | Carlson and Dewey (1971) Carlson et al. (1974a) |
| Conifers | 33 species (4 orders, 19 families) | liquid hydrocarbon concentrate | Accidental spill Strachan, Alberta | High incidence in dead crowns | Wong and Melvin (1973) |
| Ponderosa pine | Nuculaspis californica | F dust | Smelter, roads, chicken hatchery Spokane, Washington | High incidence area of nonvisible damage; low incidence area visible $F^-$ damage | Ciesla (1975) interpretation of Johnson (1950) |

[a]In most cases, pollution doses have not been included because they were not measured. In the remaining cases levels measured were observed after damage by both pollutants and insects, and thus have little relevance to dose-response thresholds.

Soils already high in various trace elements may be more vulnerable to additional trace-element load, although in depleted or nutrient-poor soils various trace elements (e.g., Mo, B, Zn) may improve the nutrient composition. In recent studies of the environmental impact of trace elements added to soils as a result of coal combustion (Vaughan et al. 1975, Dvorak et al. 1977, Dvorak and Pentecost 1977), predictions of particulate deposition for areas proximate to the power-plant model amounted to less than 10% of the total endogenous content of trace elements. Each affected site must be examined individually, however, since these models assumed worldwide soil concentrations of trace elements and the variability factor among various soils may be as much as several hundred.

The rates and processes involving trace elements are complex, and factors controlling trace-element uptake in plants are not yet very well understood. Once absorbed into the root system, however, trace elements may be translocated to shoots which herbivorous animals may consume. Plants as well as animals vary in their sensitivity to trace-element accumulation, and different plant and animal organs respond differently with respect to trace-element uptake. Obviously, the elements that are taken up in large quantities and stored in organs preferred by certain wildlife forms constitute a hazard to each trophic level in which this occurs. Furthermore, the rate of vegetation turnover from grazing wildlife will modify the rate at which material stored in shoots is recycled to the soil.

The bioaccumulation potential in various food chains requires much more study in terrestrial animals. Food habits change seasonally, and seasonal movements may take animals out of the path of the area of particulate fallout, unless winds mix the pollutant path over a large area. This fallout may be exacerbated by secondary pollutant sources from outlying areas, such as is expected for the BWCA from the industrial north as well as areas on either side of the Mississippi River, extending down to the Gulf of Mexico.

Incremental deposition of trace elements from the Atikokan facility onto the BWCA is estimated to be comparatively small. The increase in deposition of Hg predicted in Section 3 is being further investigated.

Impact of trace elements on terrestrial vertebrates--

The penetration of trace elements into animal systems largely occurs by inhalation and ingestion (in food or water). Cutaneous absorption becomes more critical in aquatic vertebrates, especially amphibians (such as salamanders and frogs) and fish (which can absorb certain elements through their gills). Virtually no information is available on the long-term effect of low-dosage intake of various trace elements upon wildlife species, information essential to an understanding of the long-term or cumulative effects, or both, of trace-element accumulation.

Dewey's (1972) investigations show that fluorides may build up in insects of the higher trophic levels, and he expressed concern that fluoride accumulated by insects could affect insectivores up the food chain. Gordon et al. (1978) are attempting to determine that portion of the diet of deer mice which constitutes a fluoride source for mice with excessive fluoride in their femurs. Their data indicate that insects represent a considerable percentage of the diet.

Kovacevic and Danon (1952, 1959) analyzed stomachs of 136 species (34 families) of birds in Yugoslavia and found beetles representing 31 species (17 families). Numerous other studies both in Europe and the United States attest to the importance of insects as a food resource to birds. Thiele (1977) provides a review of the predators of a specific family of insects --the carabids. He lists hedgehogs, shrews, moles, bats, rodents, mice, and birds (including owls and other birds of prey).

The population of timber wolves (Canis lupus) in northern Minnesota is the largest of the continental 48 states. Because of their size wolves do not appear to be immediately vulnerable to trace-element discharge, unless it exceeds processing limits of soils and plant systems. The prey animals that are herbivores will constitute the interface between trace elements in plants and in wolves.

The eastern pine marten (Martes americana americana) is a fur-bearing carnivore of considerable economic value in past years. Since the principal regular food item for the marten is the small mammal (such as the red-backed vole Clethrionomys gapperi in the BWCA), the greatest impact of trace elements upon marten populations is likely to be exerted through small-mammal populations. Voles may be affected by selected roots with high storage levels of trace elements or through water supply (this may be obtained in food).

The bald eagle (Haliaeetus leucocephalus) and osprey (Pandion haliaetus cardinensis) rely upon fish for food items although other vertebrates appear to be eaten as well. Ospreys have been known to take several species of small mammals, other birds, reptiles, and frogs, as well as occasional crustaceans, sea snails, and beetles. The bald eagle diet in north-central Minnesota consists of 90% fish, 8% birds, and 2% mammals and invertebrates (Dunstan and Harper 1975). Obviously, trace-element effects on raptors are best considered in view of their fish diet. Scientists have determined that Hg levels in fish are already high in some lakes in northeastern Minnesota (see Sections 5 and Appendix D).

Many other changes in major or key ecosystem processes, other than those discussed, probably occur. Because of the lack of information on the effect of pollutants on insect populations, food chains, and on the composition of the ecosystems of the BWCA, it is premature to predict the potential economic or ecological damage, or both.

Too many unknown factors make reliable statements impossible concerning the effects of the Atikokan facility on trace-element fluxes through food chains. Lakes already high in Hg may experience additional loads if acid rain causes the release of existing sediment-bound Hg. Top carnivores and fish consumers, such as raptors and aquatic mammals, are likely to accumulate additional Hg, but the pace of bioaccumulation may vary considerably within The BWCA. The low rates of trace-element deposition within the BWCA from

Atikokan imply negligible short-term effects, but possible long-term consequences.

## APPLICATION OF RESEARCH FINDINGS TO THE BOUNDARY WATERS CANOE AREA

The impacts of air pollutants on terrestrial ecosystems and their components can be grouped into four major categories: 1) acute direct effects on ecosystem components; 2) acute indirect effects on components and complete ecosystems; 3) chronic direct effects on ecosystem components; and 4) chronic indirect effects on components and ecosystems. Each of these types of impacts may have significance to the continued functioning of a given ecosystem. To date the majority of data collected relate only to the acute direct effects. In some cases, however, acute indirect and chronic effects may be more important to the overall ecosystem than the acute direct effects because the former relate to factors such as forest productivity, community diversity, and ecosystem stability.

The severe limitations on data applicable to acute indirect and chronic effects indicate a limit in the "state of the art" rather than an absence of effects. These limitations have several causes: lack of long-term baseline studies; lack of instruments that can measure very low levels of air pollutants; and, perhaps most important, limitations in techniques that can first measure the subtle changes occurring in ecosystems due to low levels of pollution and then relate these changes to those levels of pollution.

Although data on direct and indirect effects from chronic low-level air pollution are limited, basic ecological principles indicate the potential for significant effects on the terrestrial ecosystems. These effects must be extrapolated from studies of short-term effects, and the limits and the sensitivity of such extrapolations must be taken into account. Through their influence on the generation of oxidants, acid particulates, and acid precipitation, the indirect effects of emissions contribute to regional loading and are likely to be the most serious effects for the Quetico-BWCA area.

In air-pollution impact studies a few characteristics remain fairly consistent regardless of the differences between two or more physical and biological areas:

1) Coniferous and lichen species within a polluted area are almost invariably the first plants to manifest symptoms of injury, usually because of toxic gases; and

2) Plant species growing along ridge tops or on any moderately elevated area will accumulate greater effects from the phytotoxic gases than the same species growing in the valleys, or riparian areas.

The following statements of projected significance of air pollutants for the terrestrial ecosystems of the BWCA are a synthesis of the research and literature previously cited and, when possible, anticipate explicit responses from applicable findings.

## Significance for Pines

The most sensitive native higher plant species for which information is available is the eastern white pine, a prominent canopy tree. This species is known to have been lost entirely from large areas subjected to frequent exposures of high $SO_2$ levels. It can persist for many years, however, with moderate levels of damage each year. In this situation growth is slowed, the trees are less resistant to insect outbreak, and longevity is reduced.

Red pine and jack pine, the other two most dominant pine species in the BWCA, may be less sensitive to $SO_2$ than eastern white pine. As such, at increased $SO_2$ levels, these species would be expected to exhibit a lesser degree of both visible and nonvisible effects than eastern white pine.

In general, most acid rain damage to plant tissues will occur over a long period of time (many growing seasons) and, therefore, will be difficult to evaluate. The earliest manifestation of acid damage in conifer needle tissues will probably be the cessation of meristem activity in the basal areas, causing the needles to be dwarfed and, in later stages, to abort and be cast prematurely from the branch (Northern Cheyenne Tribe 1976). Although slightly acidic rain in an area may not cause dwarfing during early needle development, damage of the basal tissues may occur 1-3 yr later.

If the ambient concentrations of total solid particulates, $SO_2$, $O_3$, and trace elements attributable to Atikokan are no higher than projected, it is unlikely that short-term, visible damage will occur. Several recent studies suggest, however, that growth and reproductive rates may be affected at lower ambient pollution levels than those necessary to cause visible injury, levels commensurate with $SO_2$ background levels already being recorded near Atikokan (Section 3, Table 1). The usual time for planning and developing the forest cover of a State forest, private property, or recreational area is seldom less than 50-100 yr. More often it is as much as 200 years. White pine ordinarily live 350-400 yr. Plant scientists and recreational area managers have, therefore, had to take a long-term view of their resource and look at its development over tens of decades. Over these periods, even small effects on the growth rates or lifespan of the dominant species can have major consequences for the regional vegetation.

## Significance for Lichens

Direct, visible effects on lichens are not anticipated in the BWCA within 5 yr after the projected pollution levels attributable to the Atikokan facility occur. The thresholds and time-requirement for subtle effects on species composition are not well established, but effects could be significant in a decade or two. As more pollution sources begin operation near the BWCA a complex interaction of potential lichen species substitutions, changes in nitrogen balances, and other effects may begin. Since the nitrogen-fixing species (*Lobaria pulmonaria*, many *Peltigera* spp., *Nephroma*, *Collema*, *Leptogium*, and *Stereocaulon paschale*) are present in the Minnesota coniferous forests, detrimental effects on these components of the forest ecosystem could lead to a significant loss to the nitrogen balance. Although the ultimate consequences are not expected to be great, their degree cannot be reliably predicted at this time.

Significance for Insects

The thresholds for air-pollution impacts on plant-insect relationships are unknown. Effects at the concentrations for the BWCA have not been documented. If effects occur they will probably be manifested as:

1) Injury to pollination systems dependent upon or benefited by insect pollination (primarily by native pollinators). Compiled lists of plants benefited by or dependent upon insect pollination for seed production, or utilized by insects as food resources are lengthy;

2) Changes in the pest-insect populations of conifer and hardwood forests;

3) Alteration in litter-soil subsystems resulting from harm to saprophagous and predacious insects;

4) Mobilization of zootoxins through insect food chains to small mammals and birds; and

5) Changes in key ecosystem processes or components that cannot be identified in advance because of lack of information on the functioning of insect populations in the BWCA.

Potential for the Bioaccumulation of Toxic Materials

The high density of forest vegetation in the BWCA potentially could absorb and render unavailable much of the toxic material deposited from aerial fallout. Trace elements could be expected to increase slightly in the trees themselves (needles, seeds, bark, etc.) from direct dry deposition or from secondary storage. Under the impact of acid rain the forest soils would have lower cation exchange and organic matter content. Hence, the effect of trace elements would be amplified by making the elements more available (because of low pH) and by accumulating in small herbivores and fish.

Several fish species (e.g., bullhead, suckers, pike) form much of the diet of osprey and eagle. Experimental work is needed to determine element sensitivity and rates of bioaccumulation in these top carnivores of the terrestrial system. Scientists have determined that mercury levels in fish are already high in some lakes of northeastern Minnesota. Input from the Atikokan plant itself may help shift the balance further toward harmful levels of ingestion by raptors.

The BWCA also lies within the upper Mississippi flyway for migrating birds. Incremental pollution damage to the BWCA ecosystem may harm not only indigenous biota, but also affect migrants that pass through the area to feed. Many waterfowl are sediment filter-feeders, taking both invertebrates and algae. These detrital materials may contain moderate levels of trace elements in low pH systems, injurious to various birds.

## Significance for Nutrient Cycles

Generalizations about the potential effects of acid rain on soils and soil-plant interactions must be interpreted carefully because the BWCA is a mosaic of diverse environments. Soils in the BWCA are already acid (pH 4 to pH 5.7 at various depths). In many areas there is a 5-10-cm (2-4-in.) humus layer with pH about 4, low cation exchange capacity (10-30 meq/100 g), and high buffering capacity. For even sensitive soils, however, further acidification by air pollutants whenever they are 15 cm (6 in.) or more deep will be a slow process. Probably considerable time will elapse before growth effects can be recognized. Sulfur and nitrogen entering the system in precipitation could be a small nutrient source for the system.

Effects will be first noticeable on shallow soils or bare bedrock systems. U.S. Forest Service studies have indicated that because thin, rocky soils are widespread,the BWCA lands are the least productive and most sensitive in the Superior National Forest (Heinselman 1977). Even small additions of acidity to these systems could have relatively short-term, irreversible effects.

## Lake and Watershed Chemistry in Relation to BWCA Soils

By using the over-printed, six-photo maps provided in the Kawishiwi Area Soil Report described earlier (Prettyman 1978), mapping of an area central to the BWCA was carried out on all portions in which the potentially sensitive soil types (shallow coarse soils overylying igneous bedrock) predominate. This mapping is summarized on an index sheet (Figure 15). An example of the pattern among the soils and the distribution of lakes is shown in a copy of mapsheet number 1 (Figure 16).

### Potentially sensitive headwater lakes--

Within the areas of shallow soils it is possible to recognize additional criteria to define individual lakes most likely to show changes in lake chemistry due to changes in rainfall chemistry. These criteria would include the following:

1) No stream or spring inlets (i.e., headwater lakes);
2) Hard rock basins permitting no leakage except to the lake;
3) Shallow, coarse, or negligible soils throughout the watershed;
4) The absence of any significant adjacent wetland or peat; and
5) The watershed in which the adjacent land area is of about the same or less than twice the area of the lake.

In the course of mapping Kawishiwi area soils into a "sensitive" group, 16 small lakes were identified within the mapping area, each apparently

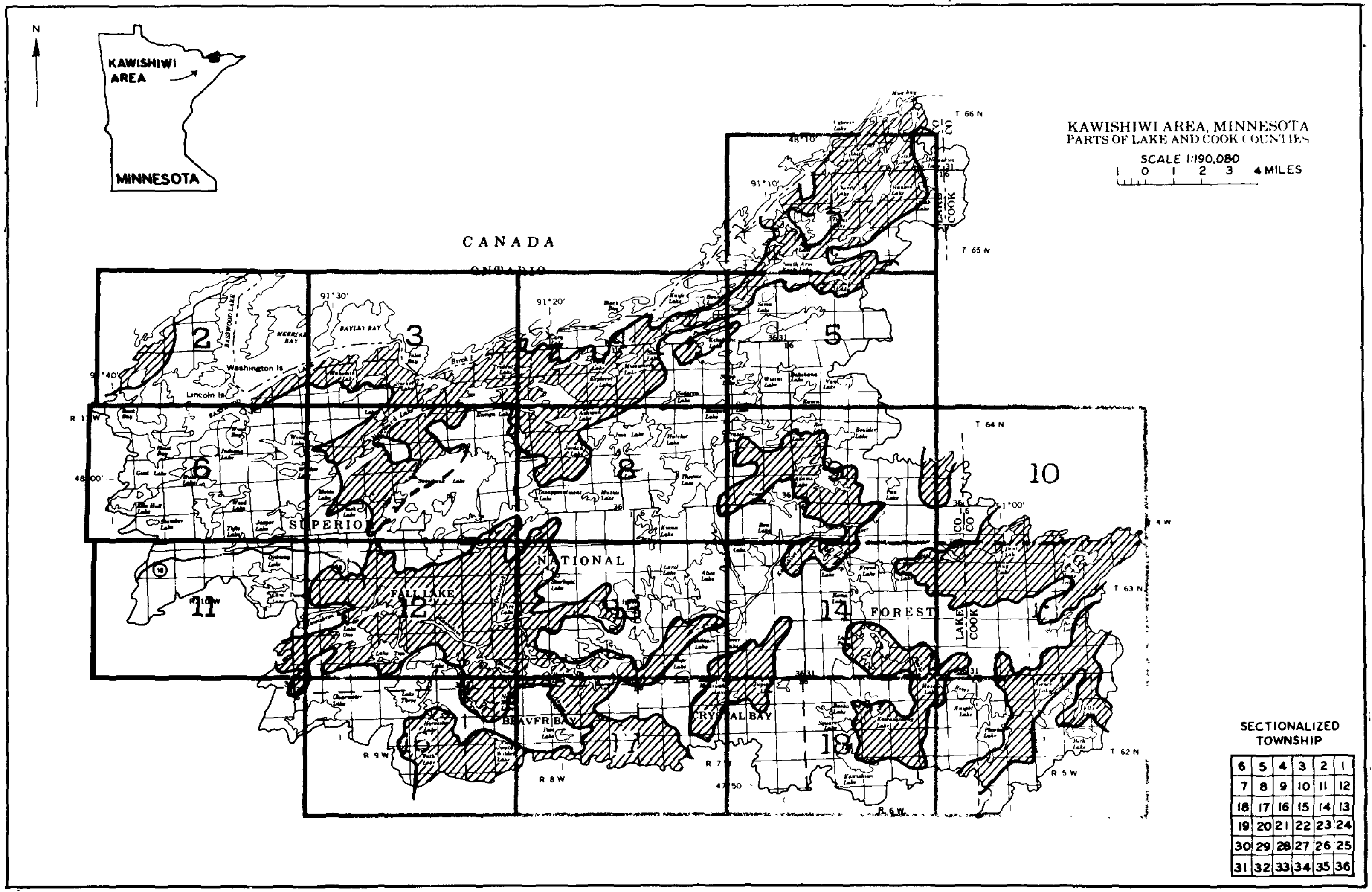



Figure 15. Outline map of the areas of sensitive soils (shaded) within the Kawishiwi Area Soils Map.

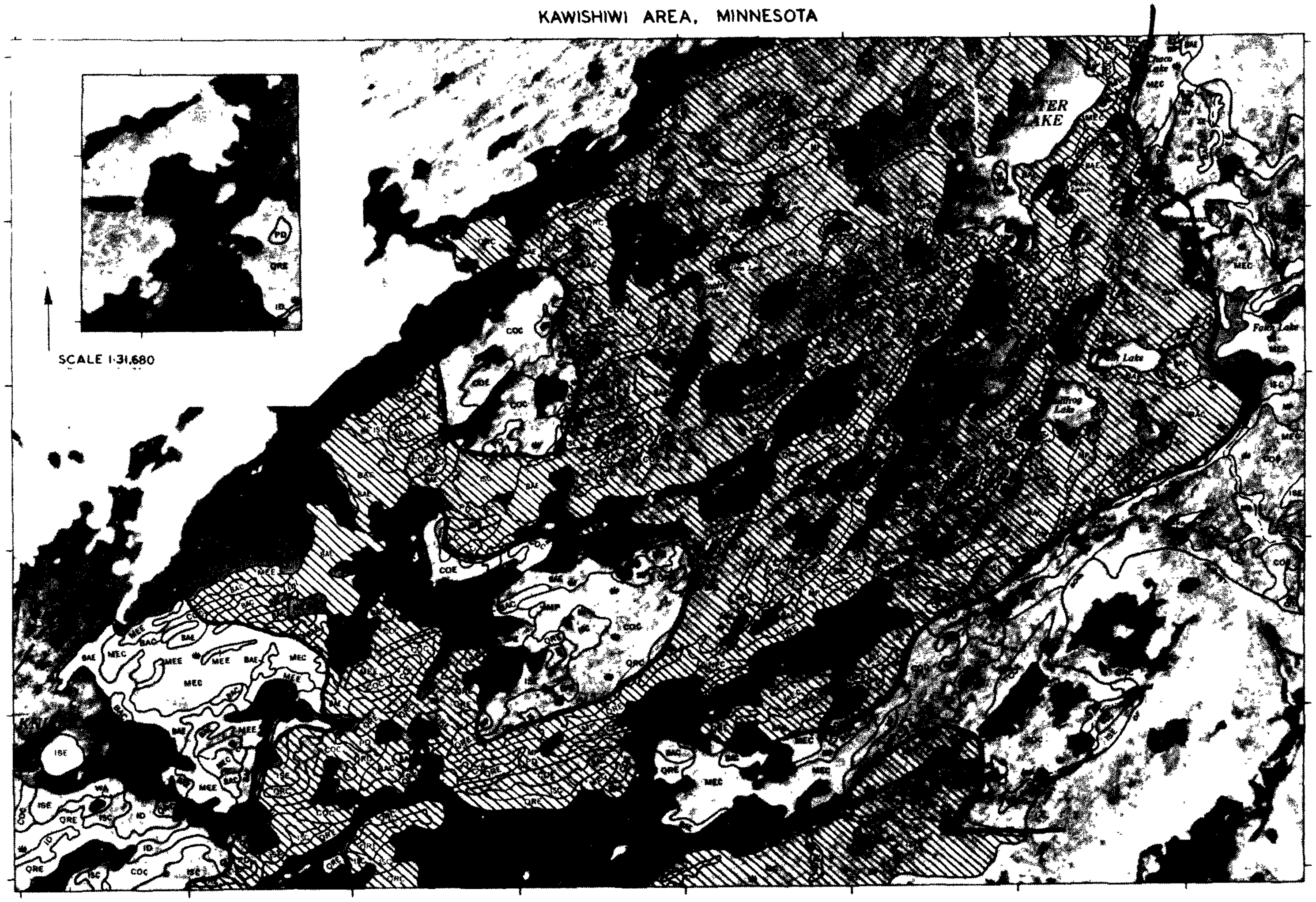



Figure 16. Sample sheet of the soil map of the Kawishiwi Area showing sensitive soil areas (shaded) and the location of six potentially sensitive lakes (arrows).

meeting most of the above criteria. This assessment has been based on the experience of the author in studies of the soils and vegetation in the Kawishiwi and BWCA areas, combined with interpretation of the soil mapping and evidence of drainage channels and wetlands from the aerial photographs. Field inspection of these and 200-300 other small lakes in this area may reveal that some of the 16 lakes identified as "susceptible" may fail to meet the above criteria fully, and that other small sensitive lakes have been missed. These 16 lakes, however, appear to be among the most likely candidates for chemical and biological change if such changes are to be found in the BWCA. It is urgent that observations of chemical characteristics be made on these lakes at the earliest possible date. The lake locations and characteristics are summarized in Table 10.

TABLE 10. POTENTIALLY SENSITIVE HEADWATER LAKES IN THE BWCA[a]

| Lake number | Sheet number[b] | Lake name | Location | Approximate lake size (acres) | Approximate watershed (acres) | Comments |
|---|---|---|---|---|---|---|
| 1 | 1 | Lake of the Clouds[c] | Center S.H.1 | 40 | 80 | studied since 1967 |
| 2 | 1 | Rivalry Lake[c] | 1 mile N. #1 | 10 | 15 | -- |
| 3 | 1 | Embla Lake | 1 mile N.E. #2 | 20 | 40 | some peat |
| 4 | 1 | Clam Lake | 2 miles S.E. #1 | 35 | 15 | -- |
| 5 | 1 | Unnamed | 2 miles N.E. #4 | 8 | 10 | -- |
| 6 | 1 | Unnamed | 1/4 mile S. Amober Lake | 15 | 15 | easterly of two lakes |
| 7 | 3 | Spigot Lake | 1/4 mile E. Sucker Lake | 25 | 40 | -- |
| 8 | 4 | Bedford Lake | 1/2 mile S. Skoda Lake | 40 | 60 | some peat |
| 9 | 5 | Unnamed | 1 mile N.W. Sema Lake | 15 | 15 | -- |
| 10 | 7 | Unnamed | 1/2 mile E. Newfound Lake | 35 | 60 | -- |
| 11 | 8 | Swing Lake | 1 mile S. Ashigan Lake | 20 | 30 | -- |
| 12 | 10 | Wisp Lake | 1 mile E. Duck Lake | 20 | 30 | long, narrow |
| 13 | 13 | Hood Lake | Center, W. side of sheet | 35 | 50 | some peat |
| 14 | 15 | Pat Lake[c] | 1/2 mile E. Bug Lake | 15 | 15 | outstanding |
| 15 | 15 | Alcove Lake | 1/2 mile W. Wine Lake | 40 | 80 | -- |
| 16 | 19 | Ella Lake | 1/2 mile E. Grace Lake | 80 | 100 | some peat |

[a] As determined by the criteria listed on page 93.

[b] In Prettyman (1978).

[c] Outstanding candidate lakes for intensive study; appear to meet all criteria.

## SECTION 5

## IMPACTS OF ACIDIFICATION ON AQUATIC ECOSYSTEMS OF THE BOUNDARY WATERS CANOE AREA (BWCA) AND VOYAGEURS NATIONAL PARK (VNP)

### INTRODUCTION

Deposition of acid from the atmosphere, with consequent severe effects upon aquatic ecosystems, is by now a well-known phenomenon (Braekke 1976, Dochinger and Seliga 1976). Both sulfuric and nitric acids are involved, and hydrochloric acid may be a much more local source (Gorham 1976). Many other toxins are deposited in addition to acids, including heavy metals, a variety of hydrocarbons, and nutrients such as nitrogen, potassium, calcium, and probably phosphorus (Gorham 1976, 1978, Lunde et al. 1976, Wright and Hendriksen 1978).

These pollutants may exert a wide range of effects upon organisms and ecosystems, particularly oligotrophic (or nutrient-poor) ecosystems. Both synergistic and antagonistic interactions are very likely. Although these have had little investigation it is known that metal toxicity may increase with increasing acidity. The acid may also have indirect effects upon the toxicity of other ecosystem components (e.g., soil-derived metals, such as aluminum and several trace metals) and upon the availability of nutrients through weathering and biological activity (e.g., N, P, K, Ca, etc.) (Glass 1977).

The impact of increased acid loading and nutrients is determined by the vulnerability of aquatic ecosystems. Geologic, physical, and chemical characteristics of the aquatic environment are important variables in determining the level of vulnerability. Biotic effects range from acute toxicity and impairment or failure of reproduction within species to lowered production and biotic diversity.

This section is a discussion of the impact of acidification on aquatic ecosystems of temperate North America and Europe and the application of these findings to the BWCA-VNP receptors. Comprehensive data on all aquatic organisms present in the BWCA-VNP are lacking, but the information discussed can be related to the BWCA-VNP by utilizing data collected in similar adjacent areas. The Minnesota Copper-Nickel Study Area (MCNSA) (a 5,515-$km^2$ area of northeastern Minnesota south of the BWCA, including Ely, Minn.) and the Experimental Lakes Area (ELA) of Ontario are located adjacent to and 150 km from, respectively, the BWCA-VNP. Because of the similar terrestrial and geological character of the areas, species present in both of these study areas can be considered to be generally representative of the species present in the BWCA-VNP. Therefore, lists of aquatic organisms found in the MCNSA are included in Appendix D (Gerhart et al. 1978, Johnson et al. 1978, Piragis et al. 1978). Specific information about the aquatic organisms in the ELA can be found in Hamilton (1971), Patalas (1971), Sakamoto (1971), Schindler and Holmgren (1971), Schindler and Noven (1971), Stockner (1971) and Stockner and Armstrong (1971). Information on the chemistry and fishes of 109 ELA lakes can be found in Armstrong and Schindler (1971), Beamish et al. (1976), Brunskill et al. (1971), Cleugh and Hauser (1971) and Schindler (1971).

## CHARACTERISTICS OF LAKES VULNERABLE TO ACIDIFICATION

Lakes in eastern Canada and the northeastern United States are generally very sensitive to acidification. Calcareous bedrock, overburden, and soil are scarce in these regions, so that surface waters are poorly buffered (Figure 17). Lakes of this type in the Adirondack Mountains of New York state and Scandinavia have been severely damaged by anthropogenic $SO_2$ sources several hundred kilometers away (Johannessen et al. 1977, Hendrey et al. 1976, Overrein 1977). Similar sources exist within a few hundred kilometers of lakes in the southern Precambrian Shield areas of North America, and it is likely that the most vulnerable waters are already affected. It therefore seems important to identify physical and chemical characteristics of these most sensitive waters so that they can be closely examined and monitored for symptoms of increasing acidity or other changes.

### Physical Factors in the Characterization of Vulnerable Lakes

For any given geological substrate, lakes with the smallest ratio of drainage area to lake volume may have the poorest buffering because of the small area of substrate available for neutralization by weathering. Lakes at higher elevations are often affected first because more precipitation usually falls in such areas, resulting in greater deposition. Such lakes also are likely to be headwaters, or at least high in the order of lakes in a chain, and likely to have less calcareous material in their drainages. Greater volume (depth) allows greater capacity for diluting acid inputs. Few exact studies of the efficiency of acidification exist because of the difficulty of quantifying acid inputs and outputs in affected areas.

The location of Atikokan is of special significance since a large portion of the area, within a 100-km radius, is in the Rainy Lake watershed (Figure 18). The rivers within the 38,100-$km^2$ watershed flow toward the U.S./Canadian border lakes. Streams and lakes east of the Laurentian Divide flow toward Lake Superior. Lakes to the west of the divide drain into the western edge of Rainy Lake where the water flows at an annual average rate of 280,000 l/s through the dam at International Falls, Minn. before it starts a northwest course through Lake of the Woods, Lake Winnipeg, and into Hudson Bay.

The entire Quetico Provincial Park and Voyageurs National Park are within the Rainy Lake basin. Most of the BWCA is included, except for the eastern section, which is part of the Lake Superior watershed (Figure 19, Figure 20). 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.

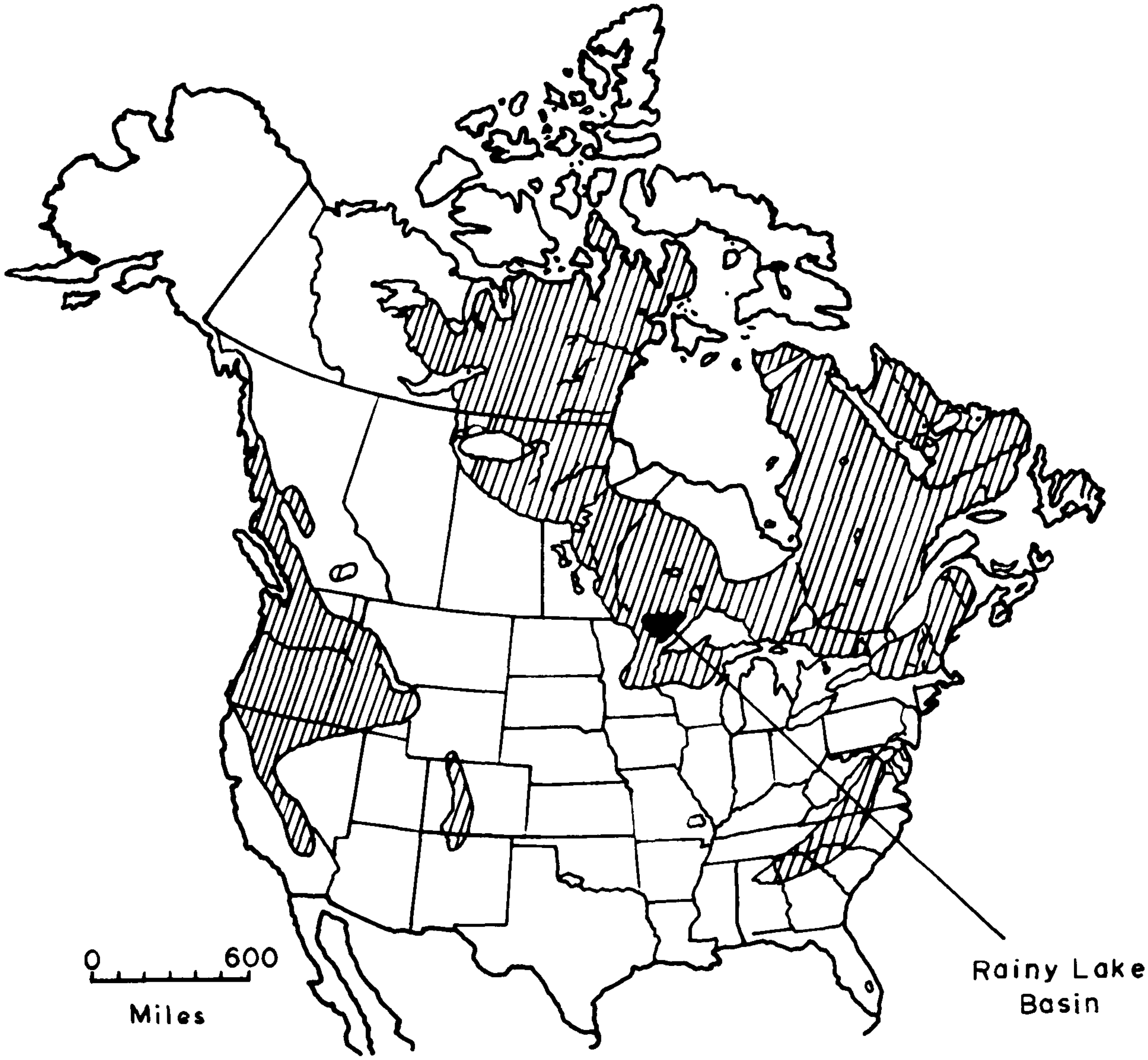



Figure 17. Regions of North America containing lakes that are sensitive to acidification by acid precipitation, based on bedrock geology. Calcareous overburden will modify this picture somewhat. (From Galloway and Cowling 1978).

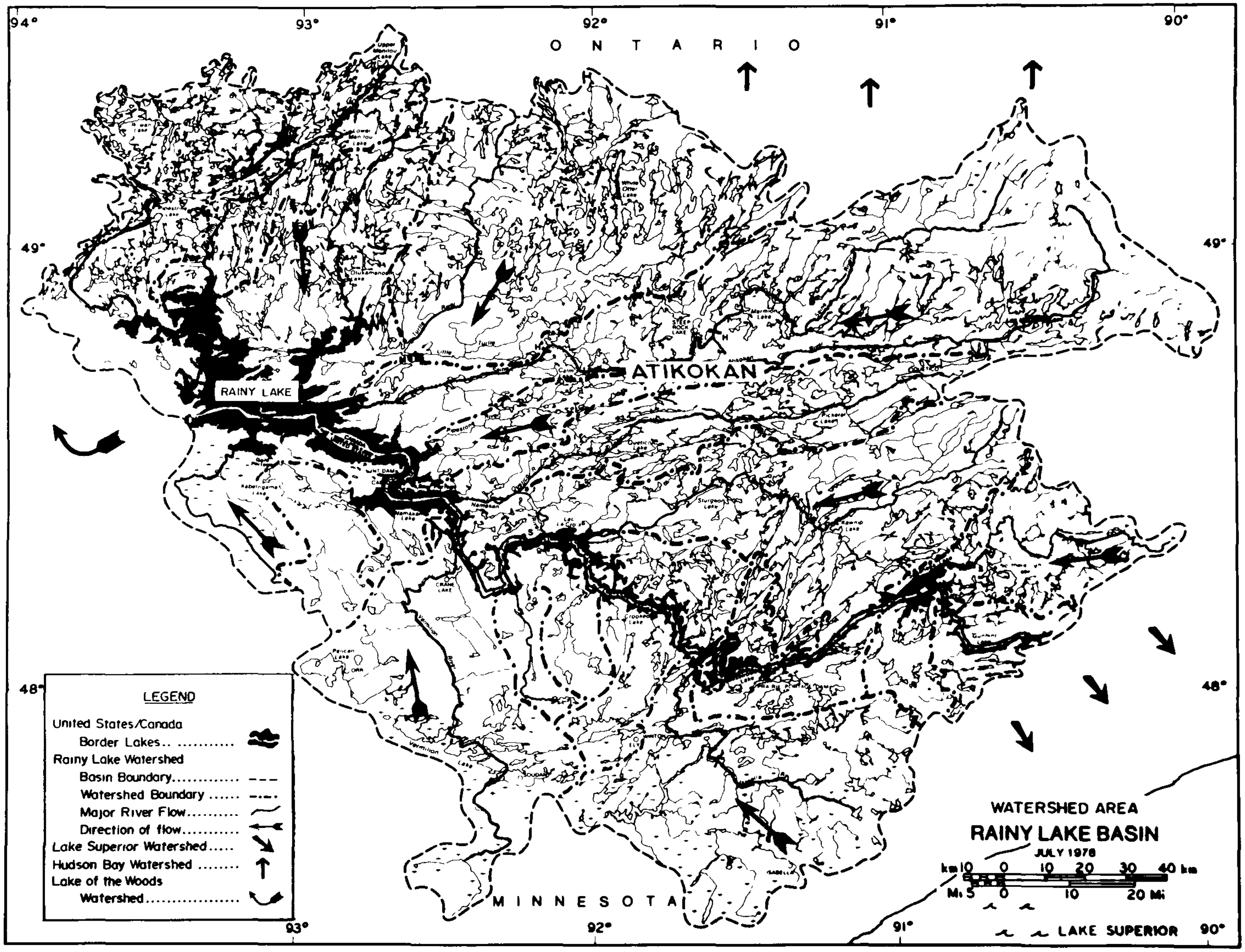



Figure 18. Rainy Lake drainage basin emphasizing major watershed areas and river-flow patterns toward U.S./Canadian border lakes. Water-flow direction of Lake Superior, Hudson Bay, and Lake of the Woods watersheds is indicated. Base map from the International Rainy Lake Board of Control 1978.

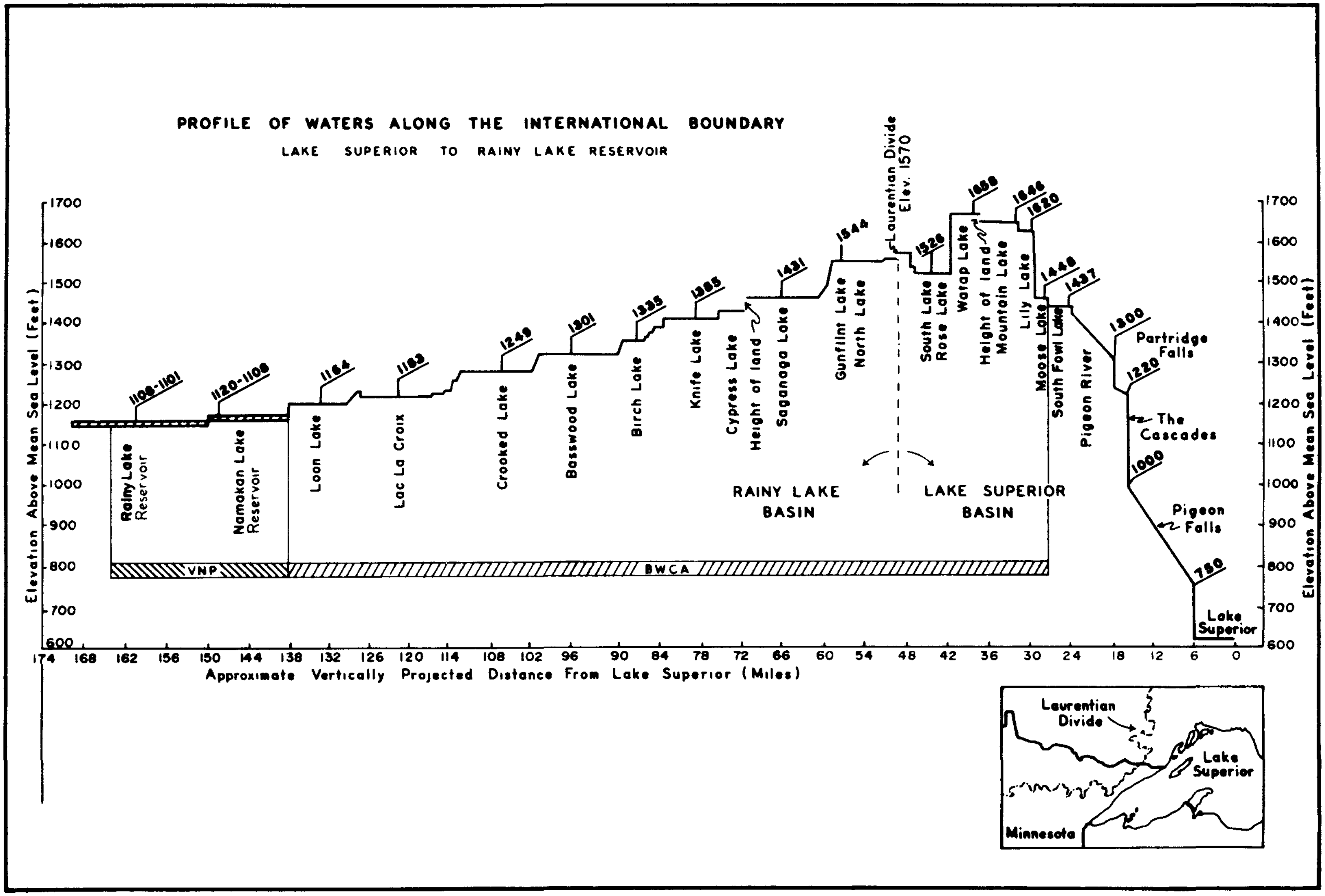



Figure 19. Profile of waters along the international boundary, Lake Superior to Rainy Lake Reservoir. (From Minnesota Pollution Control Agency 1969).

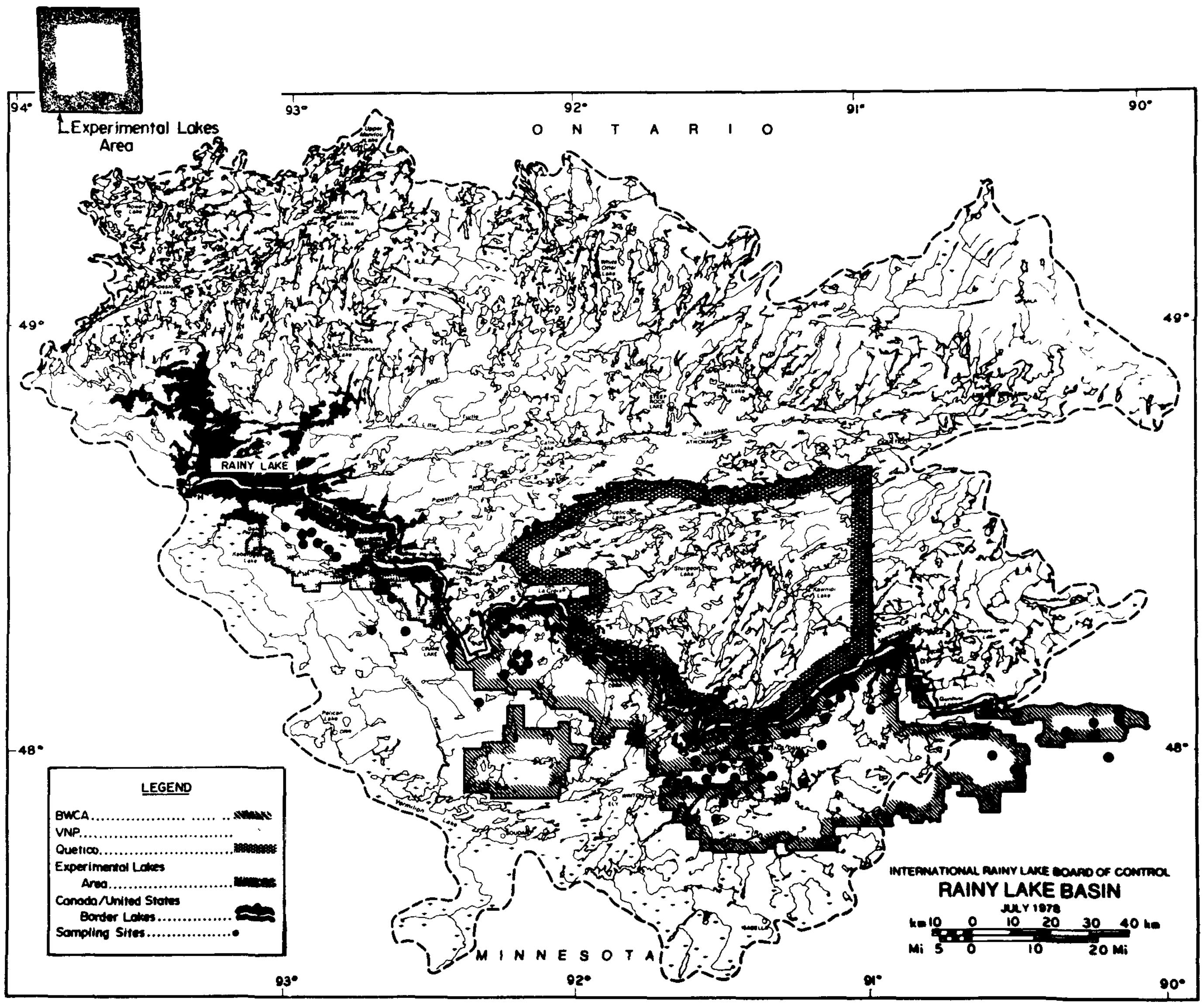



Figure 20. Park boundaries outlined on the Rainy Lake drainage basin. November 1978 EPA sampling sites. Base map from the International Rainy Lake Board of Control 1978.

Chemical Characteristics and Responses of Vulnerable Lakes

Alkalinity, or the capacity of a solution to neutralize acid, is the characteristic that reflects the sensitivity of lake water to pH change resulting from strong acid input.

Any ion that enters into chemical reaction with strong acid, significantly above the endpoint pH, can contribute to titrated alkalinity.

$$\text{Alkalinity} = [\text{Cations}] - [\text{Anions}]$$
$$\text{Alkalinity} = 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^{+}] + [K^{+}] - 2[SO_4^{2-}] - [NO_3^{-}] - [Cl^{-}]. \quad (19)$$

For the most part, alkalinity is produced by anions or molecular species of weak acids that are not fully dissociated above a pH of 4.5. In most natural water the alkalinity is practically all produced by dissolved carbonate and bicarbonate ions. A definition expressing alkalinity in terms of the "changeable" ions present is given in Eq. (20) (Deffeyes 1965):

$$\text{Alkalinity} = [HCO_3^{-}] + 2[CO_3^{2-}] + [OH^{-}] + x - [H^{+}], \quad (20)$$

with [x] giving the sum of the equivalents of noncarbonate weak acid species (e.g., organic acids, silicate, ammonia) where applicable. In humic lakes of low total alkalinity, organic acid anions (carboxylates) may make up the major fraction of the alkalinity (Beck et al. 1974). Equilibrium pH levels in these brown-water lakes will be lower than in purely bicarbonate-buffered waters because of the lower pKa values (4-5) of the carboxylic acids, compared to carbonic acid (pKa 6.3). This also means that for comparable levels of total alkalinity, a given level of strong acid input will produce a lower pH in humic water than in pure bicarbonate water. The change in hydrogen ion concentration per unit change in alkalinity ($\Delta[H^{+}]/\Delta$ Alkalinity) is thus determined by the total concentrations and species of weak acid present.

Under any system of reporting titrated alkalinity now in use the effect of all the anions that may react when a strong acid is added are lumped together and reported as an equivalent amount or a single substance or in terms of postulated ions (e.g., $CaCO_3$ mg/liter or $HCO_3^{-}$ eq/liter).

Irrespective of differences in the content of weak acids and their influence on relative pH change, the distinguishing feature of all lakes potentially sensitive to acidification is low total alkalinity. For lakes situtated in regions of hard bedrock resistant to weathering, low alkalinity is imparted by low concentrations of base-forming cations. Throughout large areas of the Precambrian Shield, carbonates are undetectably low in lake watersheds. In other areas calcareous drift deposited by receding glaciers, lacustrine clays (for example, in the Lake Agassiz basin), or marine sediments help to buffer lakes, rendering them less vulnerable to acidification. The most vulnerable lakes in granite (noncalcareous) regions have conductivities as low as 10-20 μmhos $cm^{2-}$ and alkalinities of 10-20 μeq/liter. Some BWCA-VNP lakes are as low as this in neutralizing capacity, and many approach these levels. The percentage distribution of 85 BWCA-VNP lakes based on the water alkalinity observed in November 1978 is shown in Figure 21 (Glass et al., <u>unpublished data</u>, 1979; see also Appendix D).

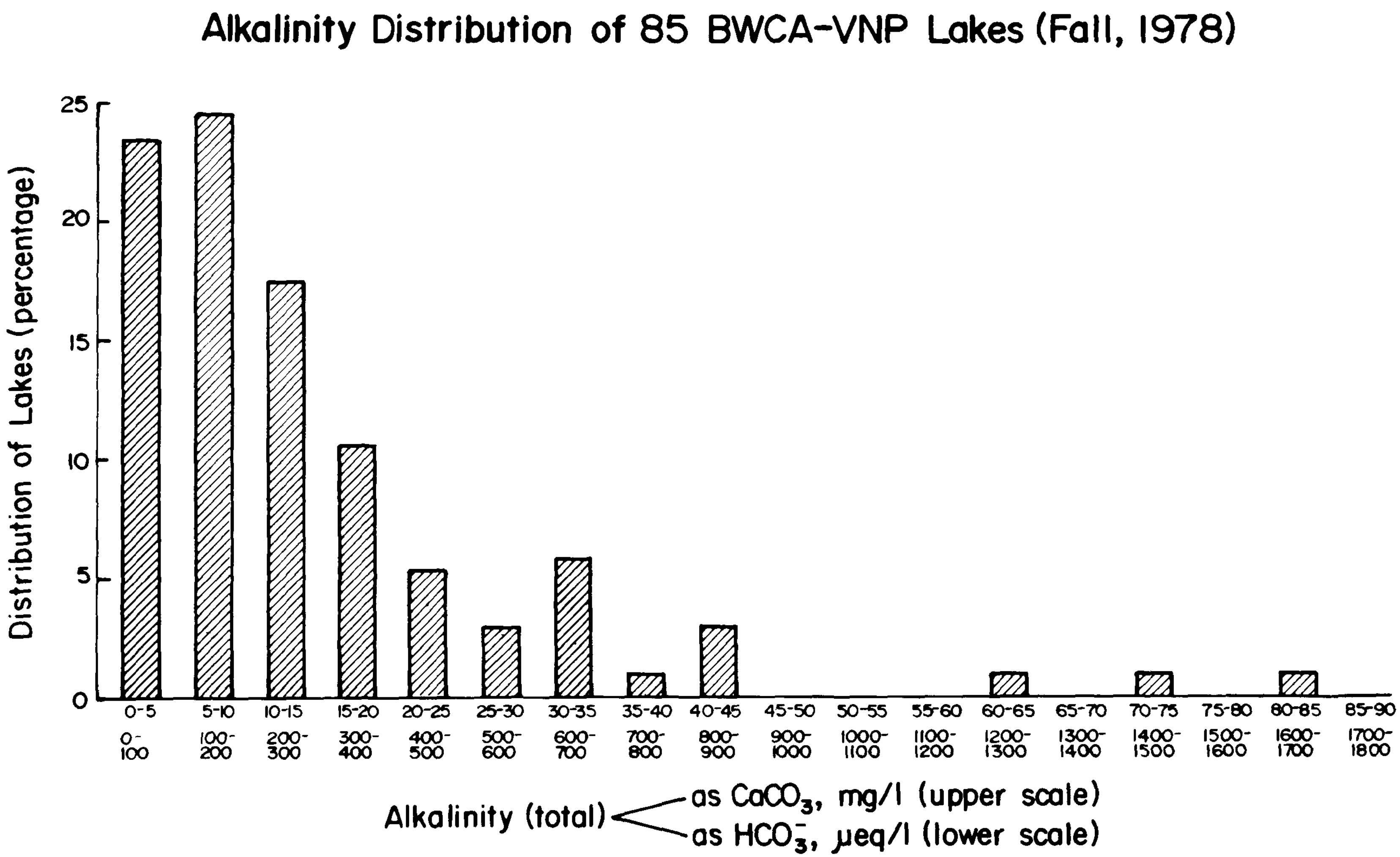



*Figure 21.* Percentage distribution of 85 BWCA-VNP lakes based on the water alkalinity observed in November 1978.

Atmospheric Acidification of BWCA-VNP Lakes

Several lines of evidence suggest that some lakes in the BWCA are at or near the threshold of serious acidification, severe enough to initiate species depletion and lowered productivity.

1) The mean annual pH of precipitation in several areas on the Laurentian Shield of eastern North America, both adjacent to and far from the BWCA, is often at or below 4.8 (Table 11). This value is the minimum mean annual pH level observed to be without major biotic consequences (so far) in southern Scandinavia (Wright and Gjessing 1976). The pH of precipitation in these Laurentian Shield areas seems likely to have declined since the mid-1950's, when it may well have been above 5.6 (cf. Likens 1976). At the present time it is frequently observed to fall (in separate precipitation events) below pH 4.5. A mean annual precipitation pH of less than 4.5 (only twice the hydrogen ion concentration at pH 4.8) is associated with severe damage to the aquatic biota in both southern Scandinavia (Wright and Gjessing 1976) and the Adirondack Mountains of New York (Schofield 1976a) and has led lake pH in many instances to fall well below 5 from initial levels well above 6.

2) Many lakes in the BWCA-VNP are somewhat acid (pH 6.1-6.3) and low in alkalinity (<100 $\mu$ equiv/liter) (Figure 22). They also exhibit calcite saturation indices (CSI) (Conroy et al. 1974, Kramer 1976) high enough to suggest great susceptibility to damage by acid loading (Table 12). Moreover, these are not the most acid lakes in the BWCA. R. F. Wright (1974) has reported one lake with a mean pH of 5.7, and it is likely that other lakes of the more than 2,000 have even lower values.

3) Sulfate loadings to northern Minnesota from historic background and distant urban-industrial sources now amount to an average of about 11 kg/ha-yr ranging from 4 to 14 kg/ha-yr (Table 1). Such loadings appear to have reached a level that is extremely critical for lake acidification. Dickson (1978) has shown that, in southern Sweden, sulfate loadings of as little as 5 kg/ha-yr appear to lower the pH of some lakes below their initial levels of about 6.5 (sensitive lakes with low neutralization capacity in their surroundings) or 7.0 (less sensitive lakes with greater neutralization capacity). In the more sensitive lakes, as sulfate loading enters the range of 10-20 kg/ha-yr, pH declines very sharply from above 6 to nearly 5 (Figure 23). Further sulfate loading produces a much slower decline in lake pH, about 60 kg/ha-yr being required to lower it to slightly above 4.

Any additional sulfate loading from the Atikokan power plant, e.g., 0.9-1.4 kg/ha-yr to some BWCA lakes and 3.4-5.1 kg/ha-yr to some Quetico lakes, is likely to tip the balance further toward the point of severe acidification effects upon aquatic ecosystems, such as have been observed in southern Scandinavia, the La Cloche Mountains of northwest Ontario, and the Adirondack Mountains of New York. In these locations, however, the most severe acidification -- to levels of pH near 4 -- has required loadings of about 60 kg/ha-yr. It may be noted that the strong acid loadings observed in southern Scandinavia, the La Cloche Mountains, and the Adirondacks have resulted in very rapid declines of lake pH. The rate of acidification has

TABLE 11. THE pH OF PRECIPITATION ON THE LAURENTIAN SHIELD OF EASTERN NORTH AMERICA

| Location | Precipitation | Period | pH | | Reference |
|---|---|---|---|---|---|
| | | | Mean | Minimum | |
| BWCA, Minn. | Rain and snow, 39 samples | 1972 | 5.6 | 5.0 | R. F. Wright (1974) |
| BWCA, Minn. | Snow, 36 sites | 1977-78 | 4.8 | 4.0 | Glass et al., unpubl. data (1979) |
| Hovland, Minn. | Rain, vol-weighted | March-Nov. 1978 | 4.8 | 4.0 | Munger and Gorham, unpubl. data (1979) |
| Ely, Minn. | Rain | 1971-75 | 5.7 | 3.7 | U.S. EPA (1975) |
| Ely, Minn. | Snow | 1971-75 | 5.2 | 4.2 | U.S. EPA (1975) |
| Rural N.E. Minn. | Snow | March 1975 | 4.9 | 4.5 | Gorham (1978) |
| Rural N.E. Minn. | Snow | Dec. 1975 | 5.2 | 4.8 | Gorham (1978) |
| ELA, W. Ont. | Rain and snow, vol-weighted | Jan.-Dec. 1975 | 5.0 | 4.3 | Schindler, unpubl. data (1978) |
| ELA, W. Ont. | Rain and snow, vol-weighted | Jan.-Dec. 1976 | 4.9 | 4.2 | Schindler, unpubl. data (1978) |
| ELA, W. Ont. | Rain and snow, vol-weighted | Jan.-Dec. 1977 | 4.7 | 3.9 | Schindler, unpubl. data (1978) |
| ELA, W. Ont. | Rain and snow, vol-weighted | Jan.-Dec. 1978 | 4.9 | 3.8 | Schindler, unpubl. data (1978) |
| LaCloche Mts., Ont. | Precipitation | Early 1970's | 4.3-4.4 | | Beamish (1976) |
| Sudbury, Ont. | Precipitation | Early 1970's | 4.5 | | Beamish (1976) |
| Nova Scotia | Rain and snow, vol-weighted | 1977-78 | 4.8 | 3.9 | Underwood, unpubl. data (1979) |

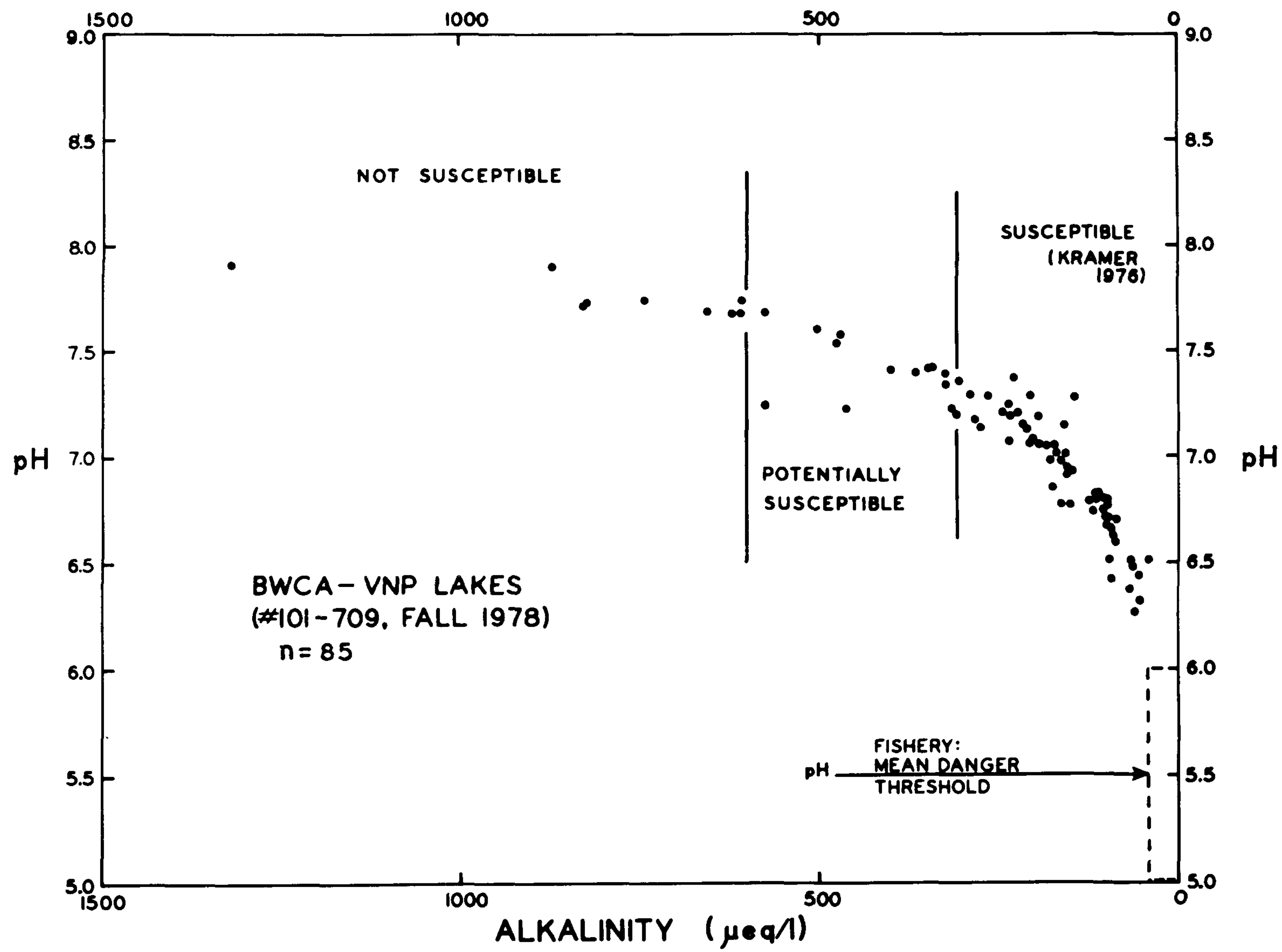



Figure 22. Relationship between pH and alkalinity in 85 BWCA-VNP lakes.

TABLE 12. CALCITE SATURATION INDICES (CSI) FOR 85 BWCA-VNP LAKES[a]

| Percentage of lakes | CSI index[b] | CSI classification |
|---|---|---|
| 10.6 | <1 | Terrain is most stable and not susceptible to change |
| 18.8 | 1-2 | Possibly susceptible to change |
| 34.1 | 2-3 | Probably susceptible to change |
| 29.4 | 3-4 | Susceptible to change |
| 7.1 | 4-5 | Highly susceptible to change |

[a]Calculated according to Conroy et al. (1974) and Kramer (1976).

[b]CSI = $p(Ca^{2+}) + p(Alk) - p(H+) + pk$, where $p(x) = -\log_{10}(x)$, pk = +2, $(Ca^{2+})$ is given as mol/liter , and (Alk) and (H+) are given as eq/liter.

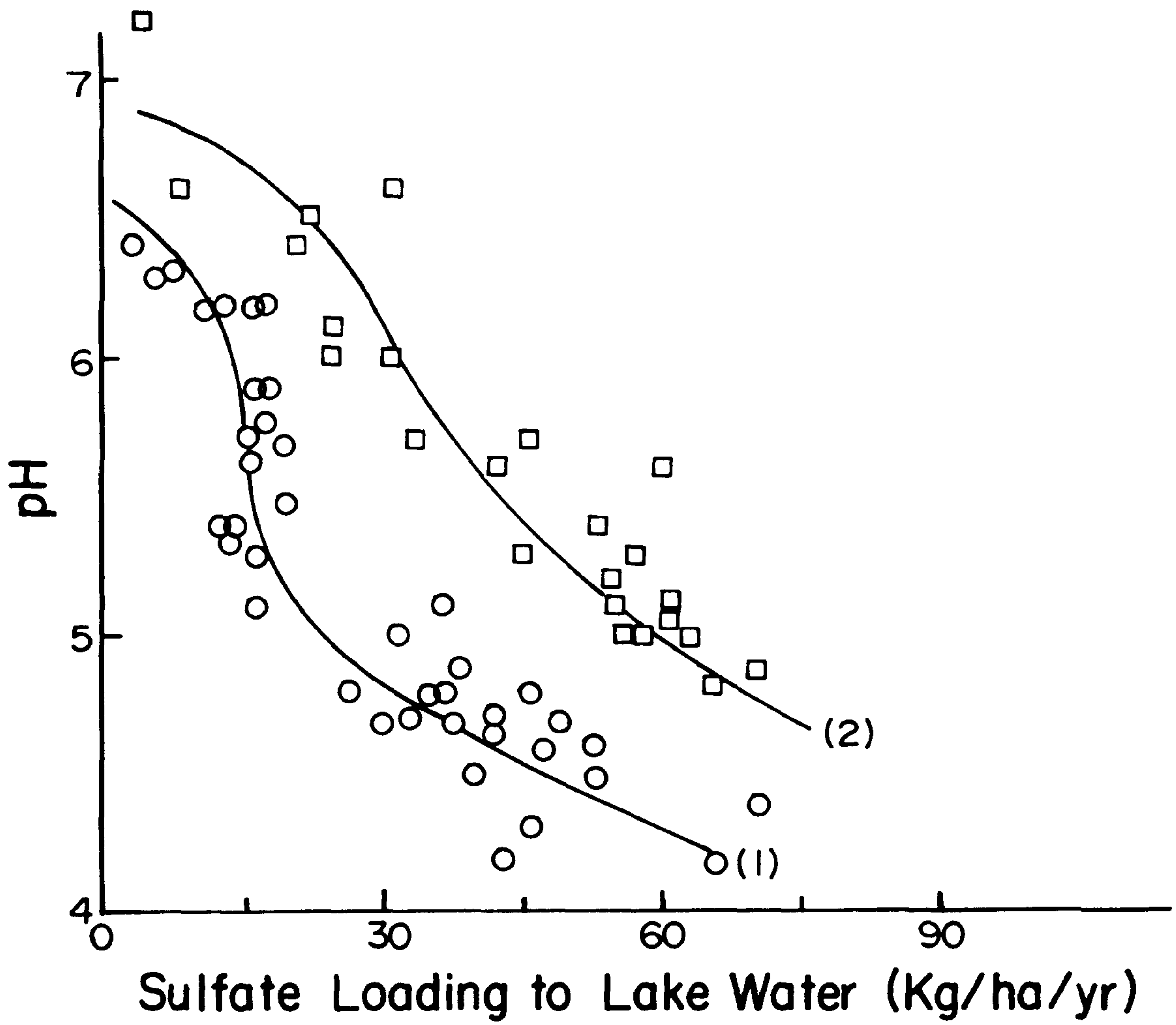



Figure 23. Relationship between acid loading and pH change for lakes in Sweden in very sensitive (1) and somewhat less sensitive (2) surroundings. (From Dickson, personal communication, 1978 and Almer, et al. 1978).

ranged between -0.02 and -0.06 pH units/yr in southern Scandinavia, where original lake pH values ranged from 6.2 to 7.3, and between -0.05 and -0.10 units/yr in eastern North America, where the original lake pH ranged from 5.0 to 6.7 (Wright and Gjessing 1976). Such rapid declines are not expected in the BWCA unless acid loadings increase considerably above present levels. Slower declines in lake pH may be occurring even with present loadings, however, and cannot be viewed with equanimity.

An experimental example illustrates the great sensitivity of lakes with low alkalinity. In 1976 and 1977 a total of 1.14 eq/liter of $H^+$ were added to the surface of an ELA lake (#223) as $H_2SO_4$ (Schindler et al. 1979). The bicarbonate content of the lake was reduced from an original value of 86 eq/liter to 10 eq/liter. Since the original pH of precipitation was 4.95, this acidification regime is equivalent to changing the pH of precipitation to 4.2 for a period of 10 years (Schindler, personal communication, 1978). Lake 223 is not one of the most vulnerable lakes in the region. Its bicarbonate value is slightly above the mean. Other lakes in the area have alkalinities as low as 8% of that of lake 223. Depending on pH levels, such lakes may be seriously affected by precipitation that has been acidified to even a few tenths of a pH unit more acid than normal. The effect of acid addition on the pH of water from selected BWCA-VNP lakes and the influence of the alkalinity and CSI of the water are shown in Figure 24. Note the large differences in acid required to reach pH 5, a value critical for most fish reproduction.

In addition to the shifts in major ion composition that constitute acidification, significant changes in certain trace metals and organic fractions of acidified lakes have been observed. Increased concentrations of aluminum, manganese, zinc, copper, and nickel have been reported in lake water from acidified regions (Dickson 1975, Schofield 1976b, Wright and Gjessing 1976, Dillon et al. 1977). These increased metal concentrations may be due in part to increased atmospheric loading (Ni, Cu) associated with specific pollutant sources, and to increased leaching from soils or lake sediment (Al, Mn, Zn). Schofield (1977) determined that 0.25-1.0 ppm aluminum leached from soil by snowmelt water at pH 4.4-5.9 was a major factor in causing severe gill damage and death among larval brook trout, a fish species found in the BWCA as well as the Adirondacks. Mobility of these metals is also enhanced at low pH levels. Increased transparency reported in some acidified lakes (Dickson 1975, Schofield 1976a) may be due to precipitation of humic and fulvic acids at low pH and high aluminum concentrations (Dickson 1977).

Marked temporal and spatial variations in strong acid and metal concentrations have been observed in lakes and streams as a result of snowmelt (Johannessen et al. 1977, Schofield 1977, Siegel 1979). During the initial phase of melting, acids stored in the snowpack are leached out by water percolating down through the snowpack. Strong acids are thus concentrated in the early fractions of meltwater leaving the snowpack. Passage of this acid meltwater through ice-covered lakes, at low levels of discharge, results in the temporary formation of a shallow (usually <1 m), but highly acid layer of surface water under the ice. This phenomenon has even been observed in moderately well-buffered lakes in the Adirondack region

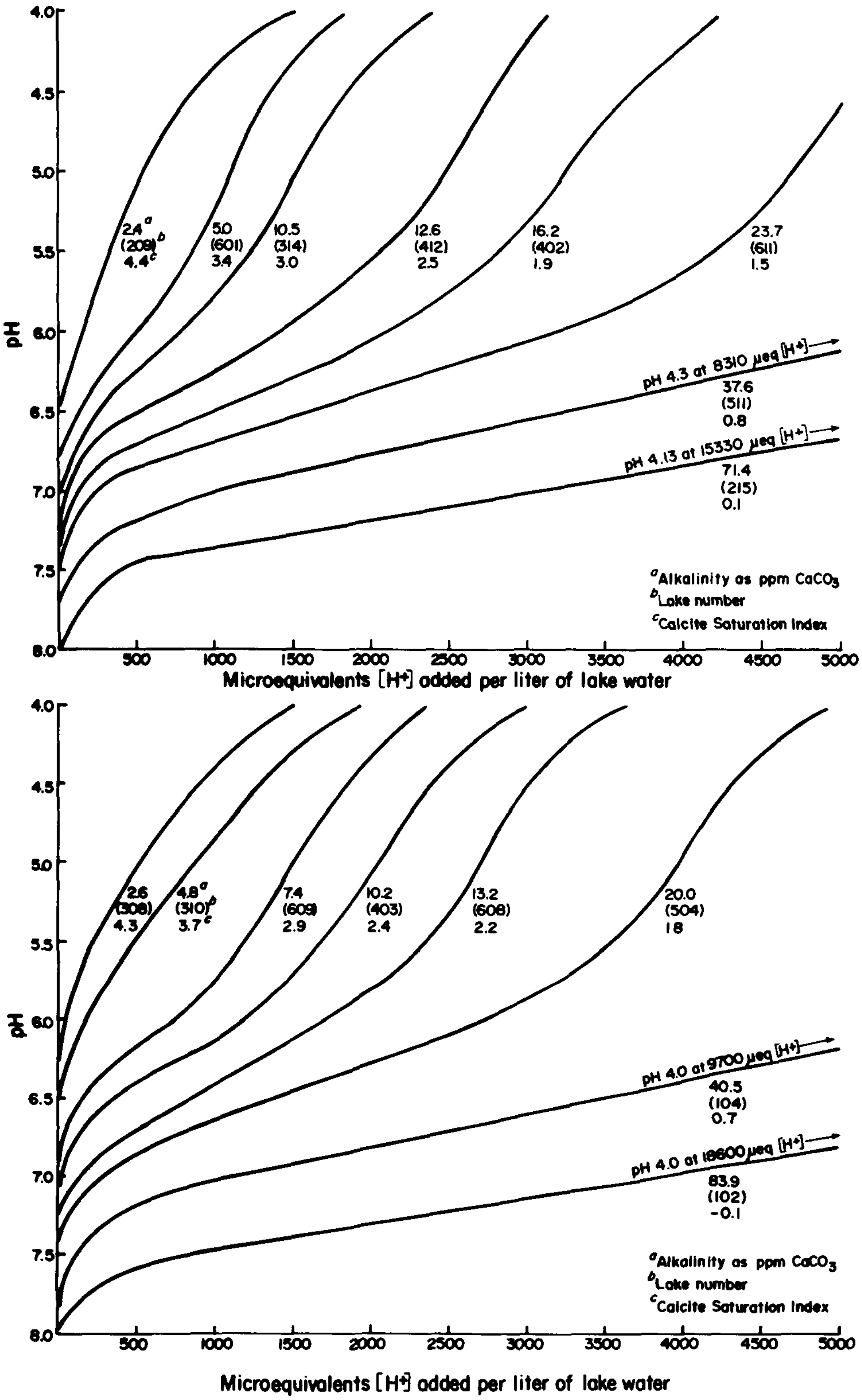



Figure 24. Effect of acid addition on the pH of water from selected BWCA-VNP lakes.

(Schofield 1976b). Sensitivity of lakes to this short-term, but intense, form of acidification is thus governed more by the physical process of acid concentration from the snowpack and transport of meltwater under ice cover than by alkalinity of the lake water alone. The degree and time of meltwater in contact with soils in the drainage system will also significantly affect acid and metal levels in the runoff. Table 13 shows snow-meltwater quality from samples collected in the BWCA-VNP in March 1978. First meltwater contains concentrations of acids two to three times the mean values for the samples. Measured snow loadings for 1977-78 are given in Appendix D.

The concentrations of most trace elements in the surface waters of the BWCA-VNP are generally low (Poldoski and Glass 1975, Glass et al., unpublished data, 1979). Because of the low concentrations of most components, increased concentrations will result in greater percentages of toxic metals present in biologically active forms (Poldoski and Glass 1975, Glass 1977).

Another concern related to acidification in northern Minnesota is the recent (1976) discovery of elevated mercury residues in fish in several BWCA lakes (Minnesota Department of Natural Resources 1978). Mean Hg levels in fish from two large lakes, Basswood and Sand Point, exceeded the 1978 FDA action level of 0.5 ppm. Figure 25 and Tables 7-9 in Appendix D provide data on the mercury levels in fish from lakes from the BWCA-VNP region. These fish are from lakes that previously would not have been considered endangered by acidification. No specific source for the mercury contamination has yet been identified. Two hypothesized sources are fallout from regional atmospheric concentrations of fossil-fuel combustion products or mobilization of mercury from bedrock geological sources, or both.

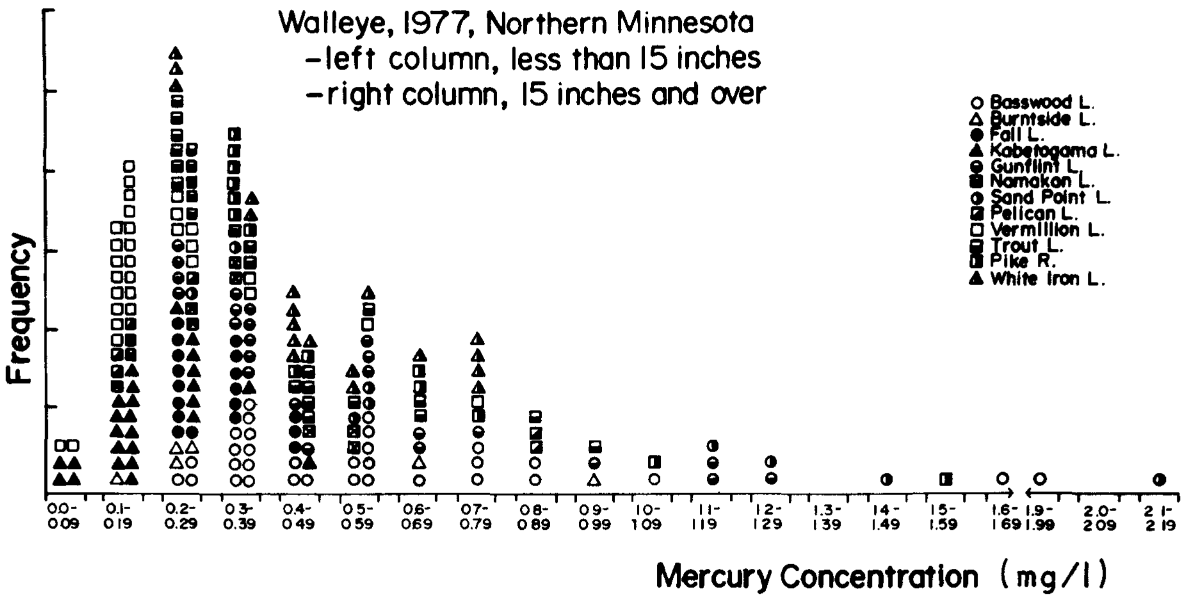
Regardless of its source, the Hg problem in the BWCA is likely to be aggravated in several ways by increased combustion-product deposition. The direct addition of more mercury is one such way (see previous discussion). Lower pH may increase the mobility of mercury from sediments and rocks. Studying the relation of acidification to mercury accumulation in fish in Sweden, Jernelov et al. (1976) and others (Brouzes et al. 1977) have found that the formation of methylmercury, the form of mercury most rapidly accumulated in tissues, is enhanced at pH levels below 6. In addition, fish are thought to take up methylmercury more rapidly at low pH. The net effect of reduced pH on accumulation is well illustrated by Figure 26 in which Hg residues in brook trout from Adirondack lakes are compared (Schofield, personal communication, 1978). Trout from acid drainage lakes had mean tissue concentrations that were three times higher than those of trout from limed, seepage, and bog lakes.

## IMPACTS UPON AQUATIC COMMUNITIES

The most obvious biological effects of acidification occur to fish populations. Less conspicuous, but no less severe damage also occurs to other organisms ranging from frogs to microbes. In fact, acidification affects organisms at all trophic levels in fresh waters. The number of species is reduced, biomass is altered, and major processes are interrupted.

TABLE 13. SNOW-MELTWATER ENRICHMENT BY DISSOLVED COMPONENTS - CONCENTRATIONS AND PERCENTAGE OF TOTAL MASS FOUND IN MELTED SNOW AS A FUNCTION OF THE PERCENTAGE MELTED (AVERAGE OF THREE SITES IN BWCA-VNP)

| Percentage snow-melt | $[H^+]$ pH % | $[NH_4^+]$ mg/l % | $[SO_4^=]$ mg/l % | $[NO_3^-]$ mg/l % | $[Cl^-]$ mg/l % | $[F^-]$ mg/l % |
|---|---|---|---|---|---|---|
| 10 | 4.26 (18) | 0.15 (14) | 1.8 (21) | 2.3 (18) | 0.15 (14) | 0.02 (14) |
| 20 | 4.25 (19) | 0.19 (18) | 1.9 (23) | 2.4 (19) | 0.16 (15) | 0.02 (14) |
| 30 | 4.30 (17) | 0.16 (15) | 1.7 (21) | 2.3 (17) | 0.15 (14) | 0.02 (14) |
| 40 | 4.46 (11) | 0.11 (11) | 1.0 (12) | 1.5 (11) | 0.11 (10) | 0.02 (14) |
| 50 | 4.63 (7) | 0.08 (8) | 0.5 (6) | 1.0 (8) | 0.11 (10) | 0.01 (7) |
| 60 | 4.71 (6) | 0.08 (8) | 0.4 (4) | 0.8 (7) | 0.08 (7) | 0.01 (7) |
| 70 | 4.76 (5) | 0.07 (7) | 0.3 (4) | 0.8 (6) | 0.09 (8) | 0.01 (7) |
| 80 | 4.80 (6) | 0.07 (7) | 0.3 (4) | 0.6 (5) | 0.08 (7) | 0.01 (7) |
| 90 | 4.82 (5) | 0.07 (7) | 0.3 (3) | 0.7 (5) | 0.09 (8) | 0.01 (7) |
| 100 | 4.86 (5) | 0.07 (7) | 0.2 (2) | 0.6 (5) | 0.07 (6) | 0.01 (7) |



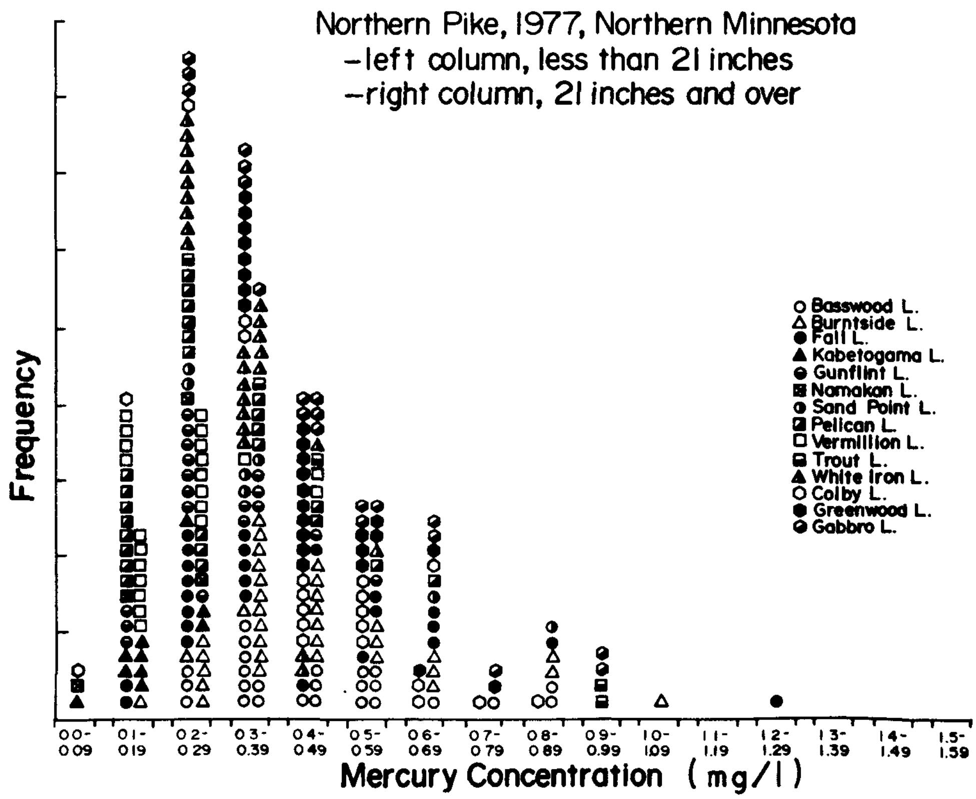




Figure 25. Relationship between frequency and mercury concentrations of walleye and northern pike taken from selected BWCA-VNP area lakes. (Data from Minnesota Department of Natural Resources 1978.)

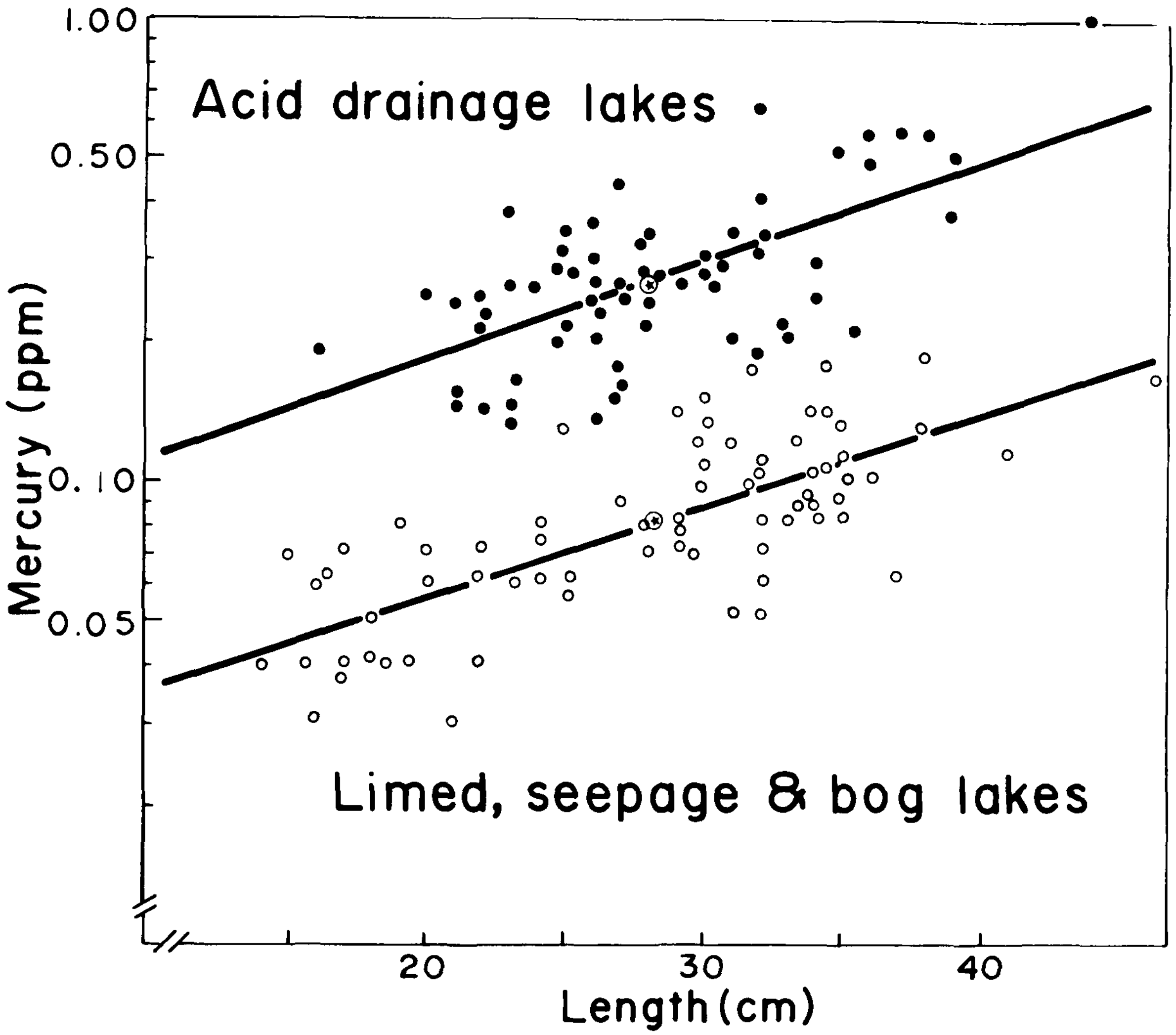



Figure 26. Regressions of log mercury concentration against total length for brook trout sampled from acid drainage lakes and limed, seepage, and bog lakes in the Adirondacks. (*, adjusted mean mercury concentrations from the two classes, for convariance analysis). (After Schofield, *personnal communication*, 1978).

Although the literature concerning effects of acid mine drainage (AMD) on freshwater ecosystems is extensive, it is not directly applicable to the acid-precipitation problem. Often the uncontaminated waters of coal mining areas have higher alkalinity and hardness than the very soft waters acidified by acid precipitation. Acid mine drainage water usually has a heavy load of iron and other heavy metals and frequently depresses the oxygen concentration of receiving waters. High turbidity and the presence of chemical floc are also common and greatly alter aquatic habitats. These factors make it very difficult to extrapolate observations from AMD situations to those in the Laurentian Shield, for example. The evidence used in this report is taken primarily from literature pertaining to acid precipitation, although some reference to AMD literature is made where relevant.

The variety of species of plants and invertebrate animals occurring in fresh waters is enormous, and the kinds of organisms present differ markedly from one locale to another even though water chemistry may be similar. It is at best difficult and probably futile to try to interpret ecosystem damage at lower trophic levels by comparing lists of species. On the other hand, changes in major processes such as primary and secondary production and decomposition can be broadly described and compared. Effects of stress on the major functional guilds may be compared from place to place. Finally, a few groups of organisms seem to be remarkably insensitive to strong mineral acidity and are common to many acid environments, whereas some other groups are clearly intolerant of pH levels below 6.0 to 5.5.

## Effects on Microbiota

The production of fish and other animal life in a lake is ultimately dependent upon the availability of organic food resources, primarily plant materials. The sources of organic materials may be divided into two major categories: autochthonous, originating by primary production in the lake, and allochthonous, transported into the lake by inflowing water, airborne litter, or dissolved in rain. The relative importance of each of these sources varies greatly from lake to lake. One principal route for both autochthonous and allochthonous organic matter into the trophic system of a lake is via the detritus (organic particulate matter).

Bacterial consumption and mineralization of organic matter, both particulate (POM) and dissolved (DOM), allows a cycling of carbon which dominates the structure and the functioning of the system and provides what Wetzel (1975) has called a fundamental stability to the system. In the deep, open water of the pelagic zone, where phytoplankton production normally provides a substantial portion of the nonrefractory organic matter, bacteria rapidly assimilate dissolved labile organic substances (DOM) derived from photosynthesis and convert them into bacterial biomass (Hellebust 1974, Fogg 1977). Only a small portion of the DOM refractory material is likely to survive longer than 24 h (Saunders and Storch 1971). The bacterial mineralization rate of POM appears to be rather slow, a few percent per day (Wiebe and Smith 1977, Cole and Likens 1979), so that this new biomass is actually available to other trophic levels. Not only do the bacteria conserve the energy stored in labile DOM, which otherwise would be lost from the system, but they also convert (at a slower rate) some of the refractory

DOM into a usable form. Fungal and bacterial communities render other POM into forms that are useful for detritivores (Boling et al. 1975). The significance of these activities to ecosystem energetics can be better appreciated when one considered that on the order of 90% of the organic carbon in the water column is DOM and that detrital POM is many times larger than the total living carbon biomass.

There are other sources of detritus in the pelagic zone. In some lakes, particularly small or shallow lakes, macrophytes and benthic algae are important sources of autochthonous organic carbon. Material from these plants may contribute significantly to detritus in the pelagic zone. In deciduous forest lakes, leaf litter falling or blown onto the surface has been found to be 200-500 g dry leaves per meter of wooded shore line (Jordan and Likens 1975, Gasith and Hasler 1976). This forest litter plus that which is added by stream inputs contributes to both DOM (after leaching) and POM.

Water-column detritus generated from all of these sources has three possible fates. It can be transformed biologically, it can sink to the sediments where it accumulates or is transformed biologically, or both, or it is lost from the system by outflow. In the first two cases, microbial activity plays a key role in removing detritus.

The inhibition of microbial decomposition can have profound effects throughout an aquatic ecosystem. Detritus removal, conservation of energy, nutrient recycling, primary production, detritivore production, and thus production at higher trophic levels can all be affected by changes in microbial activity.

Several investigations have indicated that microbial decomposition is greatly inhibited in waters affected by acid precipitation. An abnormal accumulation of coarse organic detritus has been observed on the bottoms of six Swedish lakes where the pH decreased by 1.4-1.7 units in the past three to four decades (Grahn et al. 1974). Bacterial activity apparently decreased, and in some of the lakes the sediment surfaces over large areas were made up of dense felts of fungus hyphae. In one of the lakes, Gardsjon, 85% of the bottom in the 0-2-m depth zone was covered with a thick felt of fungus. Lime treatment caused a rapid decomposition of the organic litter as well as great reductions of the fungal felt (Andersson et al. 1974), indicating that an inhibition of bacterial activities had taken place at low pH. Similar neutralizations of acidified lakes in Canada resulted in a significant increase in aerobic heterotrophic bacteria in the water column (Scheider et al. 1975). Results from field and laboratory experiments with litterbags in Norway (Hendrey et al. 1976) also indicate reduced weight loss of leaves in acidic waters. Dissolved organic carbon (DOC) in the inflowing water was found to contribute ca. 50% of allochthonous inputs and 8% of all organic carbon in Mirror Lake, while fine particulate organic carbon (FPOC) was negligible (Jordan and Likens 1975). The extent to which this DOC input is converted to bacterial biomass or otherwise enters into the energetics of a lake is not known. Observations of abnormal accumulations of organic debris have also been made in AMD waters in South Africa (Harrison 1958) and West Virginia (DeCosta, <u>personal communication</u>, 1978).

In laboratory experiments Bick and Drews (1973) found that the decomposition rate of peptone by microbiota decreased with pH and that the oxidation of ammonia ceased below pH 5. Bacterial cell counts and the species number of ciliates also decreased. Numerous other studies indicate that the microbial decomposition of organic materials is markedly reduced at pH levels commonly encountered in lakes affected by acid precipitation (Hendrey et al. 1976).

Accumulations of organic debris and extensive mats of benthic algae, as observed in the Swedish lakes (Grahn et al. 1974), both seal off the mineral sediments from interactions with the overlying water and hold organically bound nutrients that would otherwise have become available if normal decomposition had occurred. The reduction in nutrient availability can be expected to have a negative feedback effect on the organisms, further inhibiting their activities. The reduction of nutrient supplies to the water column from the sediments, because of the physical covering and from reduced mineralization of organic materials in the water itself, will lead to reduced phytoplankton productivity. These ideas have been formulated into the hypothesis of "self-accelerating oligotrophication" by Grahn et al. (1974). Qualitative observations support this hypothesis, but quantitative evaluation is lacking.

Reduction of microdecomposer activities may have a direct effect upon the invertebrates. Although certain benthic invertebrates appear to feed directly on the allochthonous detritus material, it seems that "conditioned" (colonized by microorganisms) material is preferred, and that the nutritional value of the detritus is highly increased by conditioning (Boling et al. 1975). Bacteria may also be a food source to be removed by the filtering apparatus of organisms such as the Calanoida. An inhibition of the microbiota or a reduction in microbial decomposition processes would therefore have a direct impact on the lakes' animal communities.

Because of the low temperature and lack of nutrients in the BWCA-VNP waters for in-lake energy fixation, the terrestrial production of energy in the form of plant detritus is very important for supplying energy to the food chain as well as transferring nutrients to the aquatic production system. When the decomposition and transformation of the detritus is reduced or eliminated by acidification, then less energy is available for ultimate fish production. Since the waters of the BWCA-VNP are generally infertile and support relatively low concentrations of fish, the resultant decrease in the fish crops would be expected to decrease to levels even lower than those at the present time.

## Effects on Benthic Plants

In waters affected by acid precipitation major changes occur within plant communities. Most of the available data are qualitative and descriptive although some experimentation has been done. Intact lake-sediment cores, which included the rooted macrophyte *Lobelia dortmanna*, were incubated at four pH levels (4.0, 4.5, 5.5, 6.0) at Tovdal in southern Norway. The growth and productivity of the plant ($O_2$ production) were reduced by 75% at pH 4 compared to the control (pH 4.3-5.5), and the period of flowering was delayed 10 days at the low pH (Laake 1976).

In five lakes of the Swedish west coast, a region severely affected by acid precipitation, Grahn (1977) reports that in the past three to five decades the macrophyte communities dominated by *Sphagnum* have expanded. In the sheltered and shaded locality Lake Örvattnet, in the 0-2-m depth zone, the bottom area covered by *Sphagnum* increased from 8% to 63% between 1967 and 1974. In the 4-6-m depth zone, the increase was from 4% to 30%. At the same time, pH in Örvattnet decreased 0.8 units to approximately 4.8. Similar growths of *Sphagnum* occur in other Swedish lakes, in Norwegian lakes, and in AMD water as well (Harrison 1958, Harrison and Agnew 1962, Hagström 1977). At the pH of these acid waters, essentially all of the available inorganic carbon is in the form of $CO_2$ or $H_2CO_3$. Conditions are more favorable for *Sphagnum*, an acidophile which is not able to utilize $HCO_3^-$ as do many other aquatic plants. The moss appears to simply outgrow the flowering plants under acid conditions.

In developing their hypothesis on oligotrophication, Grahn et al. (1974) have stressed two biologically important consequences of this *Sphagnum* expansion. First, *Sphagnum* has an ion-exchange capacity which results in the withdrawal of base ions such as Ca from solution, thus reducing their availability to other organisms. Secondly, dense growths of *Sphagnum* form a distinct biotype that is unsuitable for many members of the bottom fauna.

Under some acid conditions, unusual accumulations of both epiphytic and epilithic algae may occur. In the Swedish lakes Grahn et al. (1974) report that *Mougeotia* and *Batrachospermum* become important components of the benthos. In Lake Oggevatn (pH 4.6), a clear-water lake in southern Norway, not only is *Sphagnum* beginning to replace *Lobelia dortmanna* and *Isoetes lacustris*, but these macrophytes have been observed to be festooned with filamentous algae.

Heavy growths of filamentous algae and mosses occur not only in acidified lakes, but have also been reported in streams in Norway affected by acidification. In experiments in artificial stream channels using water and the naturally seeded algae from an acidified brook (pH 4.3-5.5), increasing the acidity to pH 4 by addition of sulfuric acid led to an increased accumulation of algae compared to an unmodified control (Hendrey 1976). The flora was dominated by *Binuclearia tatrana*, *Mougeotia* sp., *Eunotia lunaris*, *Tabellaria flocculosa*, and *Dinobryon* sp., each accounting for at least 20% of the flora at one time or another. The rate of radioactive carbon uptake per unit of chlorophyll in the channels, measured on two occasions, was lower in the acid channel by approximately 30%, suggesting greater algal biomass accumulation at low pH despite lower productivity.

Several factors may contribute to these unusual accumulations of certain algae. The intolerance of various species to low pH or consequent chemical changes (Moss 1973) will allow just a few algal species to utilize the nutrients available in these predominantly oligotrophic waters. Many species of invertebrates are absent at low pH, and removal of algae by grazing is probably diminished. Microbial decomposition is inhibited, as was previously noted, which also reduces the removal of algal mass.

In the BWCA-VNP, reduction in growth and production of benthic plants will probably not be important since the lakes most likely to be acidified are the same lakes that have few, if any, aquatic plants. If indeed the two were to co-exist, then decreases in benthic plants could reduce juvenile fish recruitment for those species which utilize macrophyte beds for nursery areas. The biomass of benthic plants usually enters the detrital food chain and reductions in this energy source could reduce fish standing crops. If filamentous algae were to be established during acidification, the visual aesthetics of pristine lake shorelines could be reduced.

## Effects on Phytoplankton

There is no consistency among various investigations as to which phytoplankton taxa are likely to be dominant under conditions of acidification. The Pyrrophyta may be more common (e.g., species of Peridinium and Gymnodinium) than others in lakes near pH 4.0. With decreasing pH in the range 6.0-4.0, many species of the Chlorophyta are eliminated, although a few tolerant forms are found in the acid range. In their survey of 155 Swedish west coast lakes, Almer et al. (1974) found that blue-green algae became less important with decreasing pH, but Kwiatkowski and Roff (1976) found the opposite to be true in lakes of the Sudbury, Ontario, region.

Conspicuous decreases occur, however, in phytoplankton species number, species diversity, biomass, and production per unit volume ($mg/m^3$) with decreasing pH. Lake clarity and the compensation depth increase with lake acidification, so that primary production ($mg/m^2$), although lower in acid than non-acid lakes, is not as severely depressed as is production per unit volume (Johnson et al. 1970, Almer et al. 1974, Hendrey and Wright 1976, Kwiatkowski and Roff 1976). The low phytoplankton biomass (<1 mg/liter has been correlated with the concentration of available phosphorus, which generally decreases with lower lake pH (Almer et al. 1974). Low availability of inorganic carbon has also been suggested as a factor limiting primary production in acidic lakes (King 1970, Johnson et al. 1970).

In the BWCA-VNP, if production is decreased, the energy available for food-chain transfer is reduced, and an effect on total fish production would be expected. If the grazing zooplankton are reduced before the phytoplankton are affected, the fish population will respond to the zooplankton while the algal populations will not be utilized, possibly removing nutrients from the production system without being recycled.

## Effects on Invertebrates

Zooplankton analyzed from net samples collected from 84 lakes in Sweden showed that acidification caused the elimination of many species and led to simplification of zooplankton communities (Almer et al. 1974). Crustacean zooplankton were sampled in 57 lakes during a Norwegian lake survey in 1974 (Hendrey and Wright 1976), and the number of species decreased with pH. The distributions and associations of crustacean zooplankton in 47 lakes of a region of Ontario affected by acid precipitation were strongly related to pH and to the number of fish species present in the lakes. However, fish and zooplankton were each correlated with the same limnological variables, especially pH (Sprules 1975a, 1975b). Zooplankton communities become less complex with fewer species present as acidity increases. Food supply, feeding habits, and grazing of zooplankton will probably be altered following acidification, as a consequence of decreased biomass and species composition of planktonic algae and bacteria. Parsons (1968) reported that in streams continuously polluted by AMD the number of zooplankton species was small compared to the numbers of individuals; greater numbers were found in less polluted conditions downstream.

Surveys at many sites receiving acid precipitation in Norway, Sweden, and North America (Andersson et al. 1974, Conroy et al. 1975, Hendrey and Wright 1976, Borgstrøm et al. 1976) have shown that waters affected by acid precipitation have fewer species of benthic invertebrates than localities that are less acid. In 832 lakes J. Ökland (1969) found no snails at pH values below 5.2; snails were rare in the pH range 5.2-5.8 and occurred less frequently in the pH range 5.8-6.6 than in more neutral or alkaline waters. The amphipod Gammarus lacustris, an important element in the diet of trout in Norwegian lakes where it occurs, is not found in lakes with pH less than 6.0 (K. A. Ökland 1969). Experimental investigations have shown that the adults of this species cannot tolerate 24-48 h of exposure to pH 5.0 (Borgstrøm and Hendrey 1976).

In the River Duddon in England, pH is the overriding factor that prevents permanent colonization by a number of species of benthic invertebrates, primarily herbivores, of the upper acidified reaches of the river (Sutcliffe and Carrick 1973). In the more acid tributaries (pH <5.7) the fauna consisted of an impoverished plecopteran community. Ephemeroptera, Trichoptera, Ancylus (Gastropoda), and Gammarus (Amphipoda) were absent. The epiphytic algal flora was reduced (in contrast to increases noted in Norway), and litter decomposition was retarded. The food supply of the herbivores was apparently decreased, and this may have played a role in the simplification of the benthic fauna. Quantitative data concerning the effects of low pH on the benthic fauna are also available for some acid Norwegian lakes (Hendrey et al. 1976), where notably low standing crops have been observed.

Many studies of invertebrate communities in streams receiving AMD have been conducted. Comparisons are usually made between affected and unaffected zones or tributaries, and experimental acidification has been performed (Herricks and Cairns 1974). The numbers of species, species diversity, and biomass are usually greatly reduced. Generally, in AMD waters Chironomidae (midges) and Sialis (alderfly) are the most tolerant macroinvertebrates. The order Trichoptera has more tolerant species than does Ephemeroptera (mayflies) (Harrison 1958, Harrison and Agnew 1962, Dinsmore 1968, Parsons 1968, 1977, Dills and Rogers 1974, Wojcik and Butler 1977).

This order of tolerance is essentially the same as that in waters acidified by acid precipitation. However, the Hemiptera, Notonectidae (backswimmer), Corixidae (waterboatman), and Gerridae (water strider) are often abundant in acidified soft waters at pH as low as 4.0. This pattern of distribution may, in part, be due to lack of fish predation, as well as the partial adaptation of these invertebrates to terrestrial living.

Benthic plant communities in lakes may be greatly altered as a consequence of lake or stream acidification (as discussed above). Under these conditions, benthic invertebrate populations may be affected by starvation, evacuation, or extinction due to the loss of preferred habitat. Chironomids (Oliver 1971) and other benthic invertebrates (Cummins 1973) present in many of the poorly buffered northeastern lakes have diverse feeding habits and habitats. These invertebrates, in many situations, will be affected by altered decomposition cycles and variations in available foods caused by increased acidification.

The tolerance of aquatic invertebrates to low pH varies over their life cycles, and the emergence of adult insects seems to be a period particularly sensitive to lower pH levels. Bell (1971) and Moss (1973), in similar studies with Trichoptera and Ephemeroptera, found emergence patterns to be affected at pH levels that were higher than the 30-day survival limits. Many species of aquatic insects emerge early in the spring, even through cracks in the ice and snow cover. Because of the contamination of spring meltwaters by atmospheric pollutants, including heavy metals (Hagen and Langeland 1973, Hultberg 1977, Johannessen et al. 1977, Henriksen and Wright 1976), the early emergers must, in many cases, be exposed to the least desirable water conditions.

Changes in invertebrate communities will influence other components of the food chains. Benthic invertebrates assist with the essential function of removing dead organic material. In litterbag experiments the effects of invertebrates on leaf decomposition were much more evident at higher pH than at low pH (Hendry et al. 1976). A reduction of grazing by benthic invertebrates may also contribute to the accumulation of attached algae in acidified lakes and streams.

A short reach of Norris Brook, a tributary to Hubbard Brook in New Hampshire, was acidified to pH 4 in the spring and summer of 1977 to evaluate the effects of acidification on a stream ecosystem. Excessive accumulations of algae occurred, bacterial biomass and heterotrophic activity per unit of organic matter were reduced, and both invertebrate diversity and biomass decreased (Hall and Likens, unpublished data, 1979).

In unstressed lake ecosystems a continuous emergence of different insect species tends to be available to predators from spring to autumn. In acid-stressed ecosystems the variety of prey is reduced, and periods may be expected to occur in which the amount of prey available to fish, waterfowl, songbirds, and other predators is diminished.

In the BWCA-VNP the zooplankton and benthos are the algal grazers and detritivores that transfer energy from vegetable to animal biomass. Factors adversely affecting these organisms will adversely affect the transfer of energy through the food chains and ultimately affect the fish product.

## Effect on Vertebrates-Fish

The loss of fish species with increasing acidity has been well documented in Scandinavia and in North America. In Sweden, Hultberg and Stenson (1970) collected all of the fish in two lakes acidified by acid precipitation. At a pH of 4.8 one lake contained a single yellow perch and seven eels; the other lake at pH 4.6 contained 26 northern pike and 19 eels and had lost its former perch population. Jensen and Snekvik (1972) recorded the elimination of salmon and trout populations from many rivers and lakes in southern Norway. In Canada Beamish and Harvey (1972) described the loss of eight species of fish from a lake as the pH fell from 6.8 to 4.4. Beamish et al. (1975) recorded the loss of fish from another lake undergoing acidification, and Harvey (1975) reviewed the effects of acidification on the fish populations in a group of 68 lakes.

The tolerance of fishes to low pH has been studied under laboratory conditions for half a century. This effort has been directed at recording the death of fishes in relation to hydrogen ion concentration and duration of exposure (Douderoff and Katz 1950, Lloyd and Jordan 1964, European Inland Fisheries Advisory Commission 1969, Rooney 1973). The results of these works are statements of criteria or pH tolerance of various fish species.

In the natural environment fishes may be exposed to adverse levels of acidity throughout their life. Thus pH will act to control their survival or well-being at the most critical stage or time in their life history. Accumulation of acidic snow gives rise to spring runoff of acid water which coincides with the time of spawning of many fish species. Headwater lakes undergo more rapid acidification than those lower in the watershed, as a function of flushing rate and buffering capacity of the drainage basin. Thus, fish tend to be lost first from headwater lakes.

One of the effects commonly observed in populations of acid-stressed fishes is a failure to reproduce successfully, often manifest by an absence of young fish (Hultberg and Stenson 1970, Beamish and Harvey 1972, Ryan and Harvey 1977). The cause of this reproductive failure varies from species to species. In one population of white suckers, females failed to reach spawning condition (Beamish and Harvey 1972); physiologically these fish did not show the normal pattern in protein-bound serum calcium (Beamish et al. 1975). Lockhart and Lutz (1977) have also proposed disruption of Ca metabolism as an explanation for losses of fish from acid lakes. Another mechanism of action is the disruption of spawning behavior (Conroy et al. 1974).

In some species spawning is successful, but recruitment into year class 0 is lacking, indicating lesser tolerance of eggs and larvae (Milbrink and Johansson 1975) or greater susceptibility of young or small fish such as Robinson et al. (1976) found for brook trout. Two recent laboratory chronic exposures (Menendez 1976, Smith 1977) have demonstrated a reduction in the hatchability of brook trout embryos at pH 6.0 and lower. Both investigators commented that continual exposure to pH values below 6.5 would be highly detrimental. Trojnar (1977a) observed reduced hatchability of brook trout embryos at pH 5.6. In a study of lake trout in the acidified lake number 223 of the ELA, L. Kennedy (personal communication, 1978) found that egg weights were lower and survival was drastically reduced at a pH of 5.75. The absence of a previous year class indicated that similar effects might have occurred when the pH was 6.0. These data indicate that the lake trout, one of the most sought after and valuable fish species in the BWCA-VNP, is highly vulnerable to the effects of acidification.

Other species found in the BWCA area are also very sensitive to low pH. Mount (1973) observed a reduction in embryo production and hatchability at pH 5.9 in fathead minnows. A pH of 5.6 was marginal for vital life functions. A reduction in the development of white suckers to the swim-up (early larval) stage occurred at pH 5.3 and lower (Trojnar 1977b). Embryo production, embryo fertility, and fry growth were impaired at pH 6.0 and lower among flagfish (Jordanella floridae), a species not found in the BWCA (Craig and Baski 1977). Generally speaking, several fish species have been found to be sensitive to pH levels around 6.0 or a little above.

Laboratory-determined effects appear to agree closely with field observations made in the LaCloche Mountain lakes area near Sudbury, Ontario. The pH values at which various species disappeared from lakes are shown in Table 14 (Beamish 1976).

Acute physiological effects of acid have also been investigated. It is known that brook trout suffer malfunction of sodium regulation and lose excessive amounts of this ion to the water (Packer and Dunson 1970). These authors suggest (1972) that anoxia may be the primary cause of death in fishes exposed to very low pH. Leivestad and Muniz (1976) also observed an inability of acid-stressed fish to regulate plasma sodium and chloride levels. Mudge et al. (1977) found evidence of an inhibition of RNA synthesis and presumably of steroidogenesis in interrenal tissue.

Whatever the mechanism of action of the acid stress, serious changes in the population structure can result. Beamish and Harvey (1972) noted the complete absence of one age class (5-year-old fish) in a population of white suckers, probably resulting from an acid pulse 5 yr earlier. In another population of white suckers, older animals were lost in response to gradual acidification, and maximum age declined from 16 yr to 7 yr (Beamish et al. 1975). Spinal deformity resulting from disintegration of several vertebrae in adult fish was also observed.

The more common effect of acidification is to reduce the population to a small number of older individuals. This change has been observed in Scandinavia (Hultberg and Stenson 1970) and in a group of acid-stressed lakes in Canada (Ryan and Harvey 1977). In some species the growth rate of survivors increased, presumably in response to reduced competition for food.

These changes in the form of populations precedes their extinction. There is a long and increasing list of water bodies from which some or all fish populations have been lost because of low pH. Major rivers in southern Norway have reduced populations of trout and salmon, and large kills have been recorded in association with acid precipitation (Jensen and Snekvik 1972). Schofield (1975, 1976a) described the acidification and loss of fishes from a large group of lakes in the Adirondack Mountains. Lakes at pH 4.5-5 yielded no fish in response to survey netting. In the LaCloche Mountains of Ontario a study of 67 lakes yielded 28 that had lost the majority of their fish; many of these lakes had supported good sport fisheries until relatively recently (Beamish 1976). Many of the remaining lakes showed reduced numbers of fishes, perhaps influenced by changes in other populations of organisms (see section on effects on invertebrates).

TABLE 14. APPROXIMATE pH AT WHICH FISH IN THE LACLOCHE MOUNTAIN LAKES, ONTARIO, STOPPED REPRODUCTION[a]

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

[a]After Beamish (1976).

Most likely the early effects of acidification of BWCA-VNP lakes will be a decrease in fish production, and very quickly direct effects on the fish community will be apparent. Loss of production followed by loss of desirable species and complete elimination of fish would be expected in the sensitive lakes in the BWCA-VNP. Little or no effect is expected for nonsensitive lakes and watersheds.

## Effects on Other Vertebrates

Vertebrate animals other than fishes have received scant attention. Birds and mammals that feed on fish are faced with a reduction or loss of food supply. In the LaCloche Mountain lakes, for example, loons continued to nest on and attempted to fish in lakes that had lost much or all of their fish life.

Amphibians are especially prone to acidification of shallow surface waters. Pough (1976) has described effects of acid precipitation on spotted salamanders (Ambystoma jeffersonianum and A. maculatum), which breed in temporary rain pools. Below pH 5 and 7, respectively, these species suffered high mortality during hatching in laboratory tests. This mortality was associated with distinctive embryonic malformations. The development of salamander eggs in five ponds near Ithaca, New York, ranging from pH 4.5 to 7.0 was observed. An abrupt transition from low to high mortality occurred below pH 6. Although a synergistic effect of several stresses may have been possible, the studies suggested that pH was the critical variable. Pough (1976) cites studies which indicate a decline in British frog populations.

Hagström (1977) has investigated frog populations in Tranevatten, a lake acidified by acid precipitation, near Gothenburg, Sweden. The lake pH has declined to 4.0-4.5, and all fish have been eliminated. The frog species Rana temporaria is being eliminated as well. Currently, only adults 8-10 years old are found. Many eggs were observed in 1974, but few were found in 1977. The few larva observed in 1977 subsequently died. A toad species, Bufo bufo, is also being eliminated from this lake.

Frogs and salamanders are important predators on invertebrates in lakes and puddles or pools, including mosquitoes and other pests. In turn, they are themselves important prey for higher trophic levels in an ecosystem (Pough 1976).

## SUMMARY

Acid precipitation, by causing increased acidity in lakes, streams, pools, and puddles, can cause slight to severe alteration in communities of aquatic organisms. The effects are similar to those observed in waters receiving acid mine drainage, but the toxicology and chemistry are not as greatly complicated by the presence of high concentrations of heavy metals, chemical flocs, turbidity, etc. Bacterial decomposition is reduced, and fungi dominate saprotrophic communities. Organic debris accumulates and nutrient salts are taken up by plants tolerant of low pH (mosses, filamentous algae) and by fungi. Thick mats of these organisms and organic debris may develop which inhibit sediment-to-water nutrient exchange. Phytoplankton species diversity and production are reduced, although biomass accumulations may be high due to reduced grazing. Zooplankton and benthic invertebrate species diversity and biomass are reduced. Ultimately the remaining benthic fauna consists of tubificids and Chironomus (midge) larvae in the sediments. Some tolerant species of stoneflies and mayflies persist, as does the alderfly. Air-breathing insects (water boatman, backswimmer, water strider) may become abundant. Fish populations are reduced or eliminated; some of the most sought-after species (brook trout, walleye, smallmouth bass) are the most sensitive and therefore are among the first to be affected. Toxicity or elevated tissue concentrations of metals may result either from direct deposition or increased mobilization, or both. Amphibian species may be eliminated. Finally, either the populations or the activities of terrestrial vertebrates utilizing aquatic organisms for food (or recreation) are likely to be altered.

Acidification of the BWCA-VNP will affect the fish communities in some of the lakes, either by reducing populations, changing species composition, or directly eliminating fish from the lakes. As the acid load increases or continues, more lakes will fall in the affected category. Although the small headwater lakes in poorly buffered watersheds are the most likely candidates for impact, the importance of these lakes in the total recreational picture is unknown. However, as more lakes are eventually affected, the general objectives of wilderness management for the BWCA-VNP will be violated. Operation of the Atikokan generating facility will add about 10% to the total sulfate deposition on the area and increase the acid content by 25 to 30%. These quantities should be judged in relation to the shortening of the time period within the above effects are expected to be observed.

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## APPENDIX A

## WET REMOVAL RATES FOR $SO_2$ GAS AND $SO_4^=$ AEROSOL

In most models describing pollutant transport, transformation, and removal one typically finds an equation of the form

$$\frac{dn}{dt} = -\lambda n + S, \tag{A-1}$$

where n represents the mass concentration of pollutant and $\lambda$ represents a rainout or washout coefficient. The symbol S denotes all other pollutant sources and sinks such as photochemical production, chemical conversions, and dry deposition. If we neglect these additional source-sink terms and consider only the wet removal processes, the solution to (A-1) becomes

$$n = n_o \exp(-\lambda t), \tag{A-2}$$

where $n_o$ represents the initial concentration of pollutant. When used as a description for wet removal of pollutants, Eq. (A-2) is generally applied over some vertical depth of the atmosphere such as the mixing layer, the cloud layer, or the troposphere.

Although wet removal is generally considered to be described by first-order expressions such as Eq. (A-1), it is not intuitively obvious that it should be, or can be, described in such a manner. Indeed, we will show that the first-order assumption is not strictly correct. However, a first-order expression can be approximated after considering basic principles. The following derivation will clearly illustrate the conditions under which the application of Eq. (A-1) is appropriate and will determine the form of $\lambda$ for the wet removal of $SO_2$ gas and $SO_4^=$ aerosol.

### WET REMOVAL OF POLLUTANTS

An exact description of the local time variation of pollutant concentration results from applying the basic continuity equation; i.e.,

$$\frac{\partial n}{\partial t} = -\nabla \cdot n\bar{v} + \frac{\partial n_p v_f}{\partial z}, \tag{A-3}$$

where $n_p$ is the concentration of pollutant associated with falling precipitation particles. Here $\bar{v}$ represents the three-dimensional wind vector with the vertical component described by

$$v_3 = w - v_f, \tag{A-4}$$

where w is the vertical wind speed and $v_f$ (positive) is the fall speed of precipitation particles. Application of Eq. (A-3) for the description of wet removal implies that pollutant is carried to and from the volume of interest only by the wind and falling precipitation. Assuming that boundary-layer flow in the atmosphere is nondivergent and rearranging Eq. (A-3) in terms of a substantial derivative results in a form analogous to Eq. (A-1),

$$\frac{dn}{dt} = \frac{\partial n_p v_f}{\partial z} . \tag{A-5}$$

Integration over height, z, provides the desired expression for describing the wet removal of pollutants from the atmosphere;

$$\frac{d\bar{n}}{dt} = \frac{(n_p v_f)_z - (n_p v_f)_{z_o}}{z - z_o} , \tag{A-6}$$

where $\bar{n}$ represents the vertical average over a column extending from $z_o$ to z. Therefore instead of finding that pollutant removal is directly proportional to the pollutant concentration as in Eq. (A-1), we find that removal is actually determined by the vertical flux divergence of pollutant in the column under consideration. The rate of mass (concentration) removal is a consequence of the mass flux of pollutant into the top of a volume minus the mass flux of pollutant out the bottom.

For wet removal the mass flux of pollutant past a particular level can be represented by the precipitation rate, j, multiplied by the pollutant concentration of the precipitation water, C, where j has the units of a water flux and C has units of mass of pollutant per mass of water. Thus, the flux divergence can be represented by

$$\frac{d\bar{n}}{dt} = \frac{(jC)_z - (jC)_{z_o}}{z - z_o} . \tag{A-7}$$

A major difficulty in describing the wet removal of pollutants is determination of the vertical extent of the region being scavenged. Modelers often wish to determine pollutant removal for a layer of fixed thickness and generally apply Eq. (A-1) to a surface layer of air. However, unless the surface layer encompasses the entire vertical extent of the region being cleansed by precipitation, such an approach will produce only a crude approximation to the true removal. As Eq. (A-7) illustrates, both the flux into and out of the surface layer must be considered. Without the assistance of detailed vertical profiles of precipitation rates and pollutant concentration, the flux into the top of a surface layer will be indeterminate. Currently detailed vertical profiles of precipitation and pollutant concentration are unavailable. Thus we find our first restriction to apply Eq. (A-7) or Eq. (A-1); *the layer under consideration must extend to heights where the wet, downward flux of pollutant is near zero.*

WET REMOVAL OF SULFATE AEROSOL

Figure A-1 represents the simplest case for wet removal. Sulfate aerosol removal is considered, and the removal model described by Scott (1978) is employed. Briefly, the model assumes that in the portion of the figure above cloud base, cloud droplets are nucleated on sulfate condensation nuclei. Large collector particles (snowflakes) then enter the box from above and, as they descend, grow to larger sizes primarily by accretion of the cloud droplets. The process envisioned here is one of precipitation development in a cold cloud by the Bergeron process. The sweeping out of a dirty layer of cloud water above the cloud base by relatively pure collector particles is the major removal mechanism. The region of the cloud where precipitation growth is primarily by accretion of cloud droplets is designated as the riming zone. Since the snowflakes are assumed to be relatively sulfate free when they enter the riming zone, the wet, downward pollutant flux at the top of riming zone is zero.

The thickness of the riming zone can be estimated from the fall speed of a typical collector particle and from the time required for the particles to grow to raindrop sizes. By utilizing the work of Kessler (1969), the fall speed of the median volume drop can be expressed in terms of the precipitation rate as

$$v_f = 3.89\ J^{0.105}\ (\mathrm{m/s}), \qquad \text{(A-8)}$$

where here, J represents the precipitation rate in mm $h^{-1}$. In continuous rainfalls, precipitation rates generally average between 0.5 and 1.0 mm $h^{-1}$. For such rainfall rates the median volume drop diameter is roughly between 0.7 and 1.0 mm. Millimeter-sized ice particles can be produced by riming in 5-13 min in mixed phase clouds with water concentrations near 1 g $m^{-3}$ (Hindman and Johnson 1972, Scott 1976). Therefore, a time of 9 min is felt to be an appropriate estimate for the time collector particles remain in the riming zone while growing to precipitation sizes.

Taking the height of the riming zone to be defined by collector particle velocity [Eq. (A-8)], and multiplying by the time of collector-particle growth in the riming zone gives the riming zone thickness, $\Delta z$, as

$$\Delta z = 2100\ J^{0.105}\ (\mathrm{m}). \qquad \text{(A-9)}$$

Thus, the thickness of the riming zone is generally near 2,000 m and weakly depends upon precipitation rate.

The distance from the ground to cloud base in a precipitating cloud is typically small compared to 2,000 m. Therefore, $\Delta z$ can be considered to represent the distance from the ground to the top of the riming zone. Since $z-z_0 \approx \Delta z$, the flux divergence over the entire column extending from the ground to the top of the riming zone can then be evaluated by computing only the pollutant flux at the surface.

The concentration of sulfate in the precipitation water reaching the surface can be described in terms of the sulfate concentration of the air being drawn into the cloud base. Fitting curve 3 of Figure 2 in Scott (1978) with a least square curve for $0.13<J<2.5$ gives the surface-water concentration

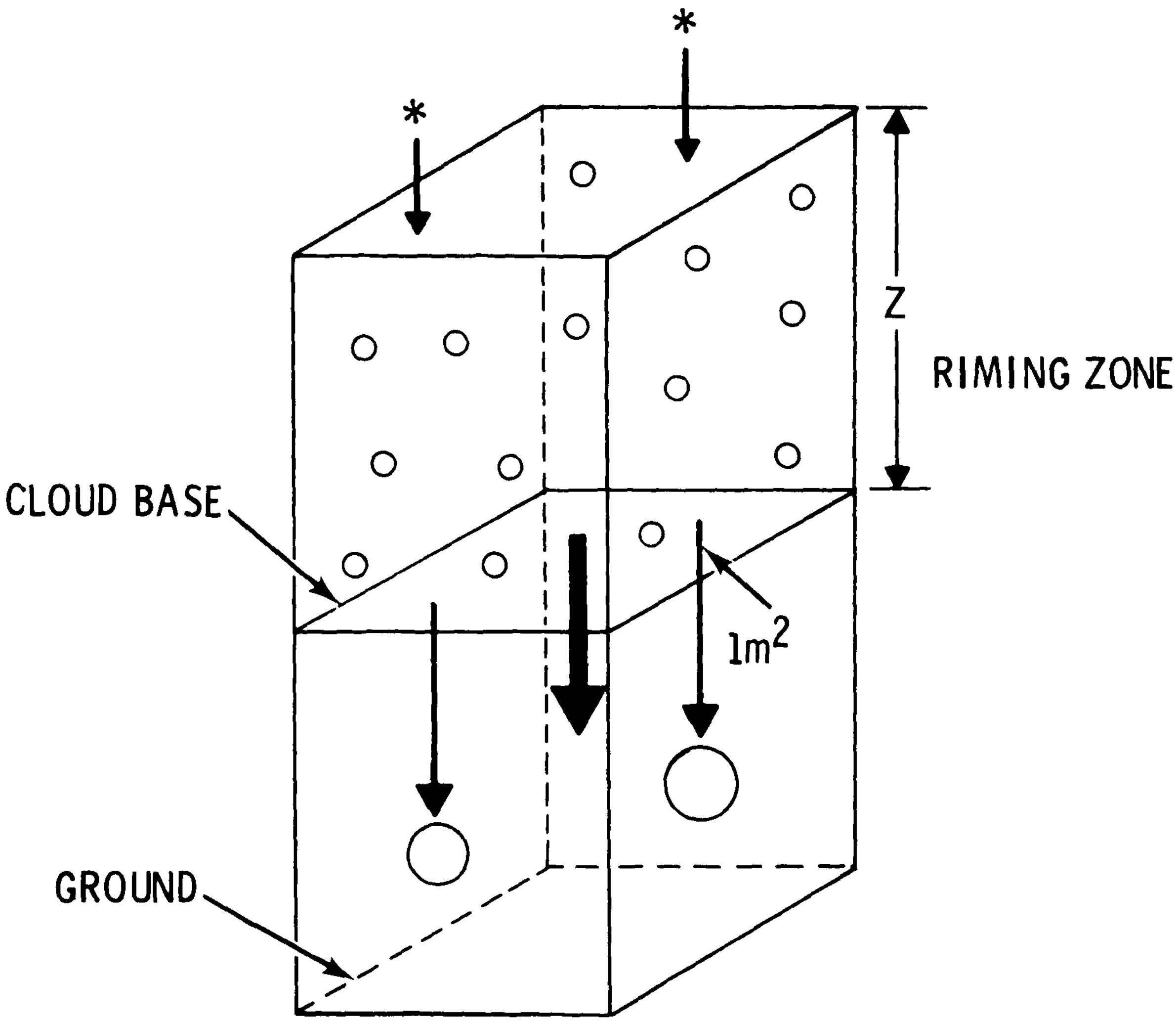


Figure A-1. The volume considered for sulfate removal. The symbols represent: *, ice particles; 0, liquid drops; o, cloud droplets; →, the direction of the sulfate flux at the upper and lower boundaries of the volume.

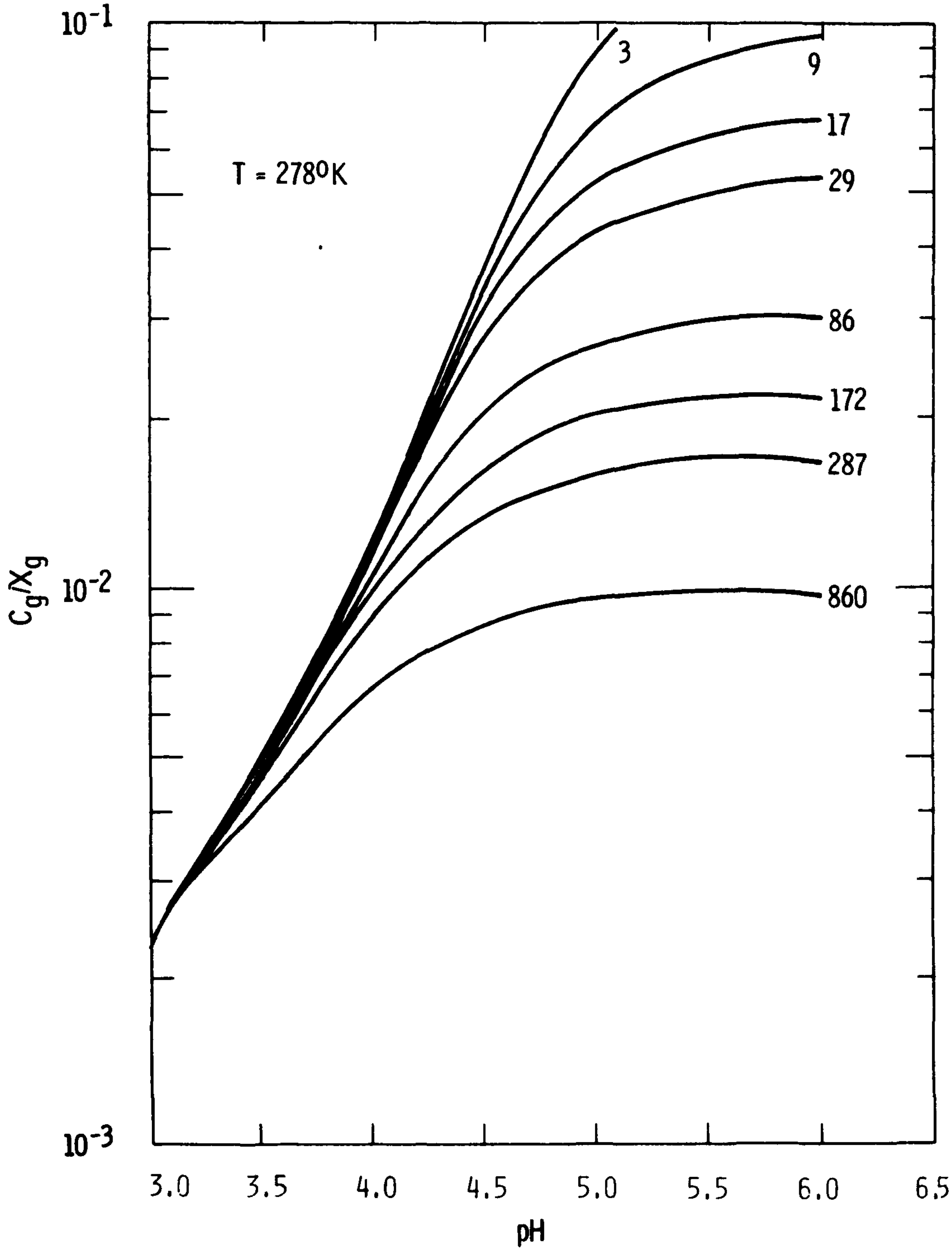


Figure A-2. Curves of $C_g/x_g$ as a function of pH. The labels for the curves represent $SO_2$ air concentrations ($\mu g/m^3$). The units of $C_g$ and $x_g$ are grams of dissolved $SO_2$ per gram of water and grams of air-borne $SO_2$ per cubic meter of air, respectively.

of sulfate (grams of sulfate per gram of water) as

$$C = 0.46\ x_g(SO_4^=)J^{-0.27}, \qquad \text{(A-10)}$$

where $x_g(SO_4^=)$ is the clear air concentration of sulfate (grams of sulfate per $m^3$ of air) being drawn into the cloud at cloud base. Generally, the subcloud air is well mixed, and the sulfate concentration should be fairly uniform between the ground and cloud base. Therefore we approximate $x_g$ with the surface-air concentration of sulfate.

If we combine Eq. (A-7), (A-9), and (A-10), the wet removal rate for sulfate can be expressed as

$$\frac{d\bar{x}(SO_4^=)}{dt} = -\ 0.22\ x_g(SO_4^=)J^{0.625}, \qquad \text{(A-11)}$$

where $\bar{X}(SO_4^=)$ represents the average $SO_4^=$ aerosol concentration (grams of sulfate per $m^3$ of air) in the layer extending from the ground to the top of the riming zone.

REMOVAL OF $SO_2$ BY SNOW

Much of the preceding material can be used to describe the wet removal of $SO_2$. For the simplest case, that of $SO_2$ scavenging by snow, a direct analogy follows. Here we assume that the bulk of $SO_2$ picked up by frozen collector particles occurs as these particles capture cloud droplets in the riming zone. The dissolved $SO_2$ in these cloud droplets is assumed to be in equilibrium with the environment, which, if the $SO_2$ air concentration decreases monotonically with height, implies that the droplets at the upper portions of the riming zone will contain less $SO_2$ than those droplets near cloud base. As the snowflakes collect cloud droplets, the droplets will freeze rapidly and will have no opportunity to adjust to new equilibrium values as they are carried to lower levels in the cloud.

Since the wet, downward flux of $SO_2$ through the upper boundary of the riming zone is negligible, the $SO_2$ removal rate by snow is determined by evaluating the pollutant flux at the ground. Written in terms of flux divergence over the riming zone, the wet $SO_2$ removal rate is given by

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{snow} = -\ \frac{JC}{\Delta z}$$

$$= 0.48\ J^{0.9}C, \qquad \text{(A-12)}$$

where C represents the dissolved $SO_2$ concentration in the snowflakes arriving at the ground.

From Scott (1978) the final concentration of pollutant in a collector particle passing through the riming zone is given by

$$C = \bar{C}[1 - \exp(-2\bar{m})], \qquad \text{(A-13)}$$

where $\bar{C}$ is the vertical average of the $SO_2$ water concentration in the riming zone and $\bar{m}$ is the vertical average of the cloud water concentration. Then, taking $\bar{C}$ to equal the arithmetic average of the equilibrium concentration at the ground, $C_g$, and at the top of the riming zone, and setting the upper level concentration equal to zero results in

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{snow} = - 0.24\ C_g J^{0.9}(1-\exp(-2\bar{m})). \qquad \text{(A-14)}$$

Furthermore, Scott (1978) has presented an expression relating precipitation rate to cloud water concentration:

$$\bar{m} = 1.56 + 0.44 \ln J. \qquad \text{(A-15)}$$

Equation (A-15) was intended to generalize all precipitation events. However, no liquid water needs to be present in snow clouds. Caution should be exercised when applying it to snowfalls, particularly when precipitation rates are very light.

Values of $C_g$ can be obtained from Figure A-2 which presents equlibrium concentrations of $SO_2$ as a function of pH and $SO_2$ air concentration. The curves of Figure A-2 result from the simultaneous solution of three equilibrium equations describing the dissociation of $SO_2$ in water (e.g., see Appendix A, Easter and Hobbs 1974).

REMOVAL OF $SO_2$ BY RAIN

To extend these concepts to $SO_2$ removal by rain scavenging, consider the features illustrated in Figure A-3. Again the riming zone is represented by the distance $(z-z_o)$, and the freezing level height is designated by $(z_f-z_o)$. For this model, snowflakes, as before, are assumed to accrete cloud droplets containing dissolved $SO_2$ and then to melt to raindrops after falling through the freezing level. In applying the flux divergence concept, the vertical fluxes in and out of each of the two boxes in Figure A-3 must be considered. In the upper box the only change in $SO_2$ concentration results from a downward flux through the freezing level. As in the purely snow case, the amount removed is

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{ice} = \frac{-j(z_f)\ C(z_f)}{(z-z_f)}, \qquad \text{(A-16)}$$

where both the precipitation rate and the $SO_2$ concentration in the snow are evaluated at the freezing level. Below the freezing level the removal due to rain is

$$\left.\frac{dX(SO_2)}{dt}\right|_{liquid} = \frac{j(z_f)\ C(z_f) - j(z_o)\ C(z_o)}{(z_f-z_o)}, \qquad \text{(A-17)}$$

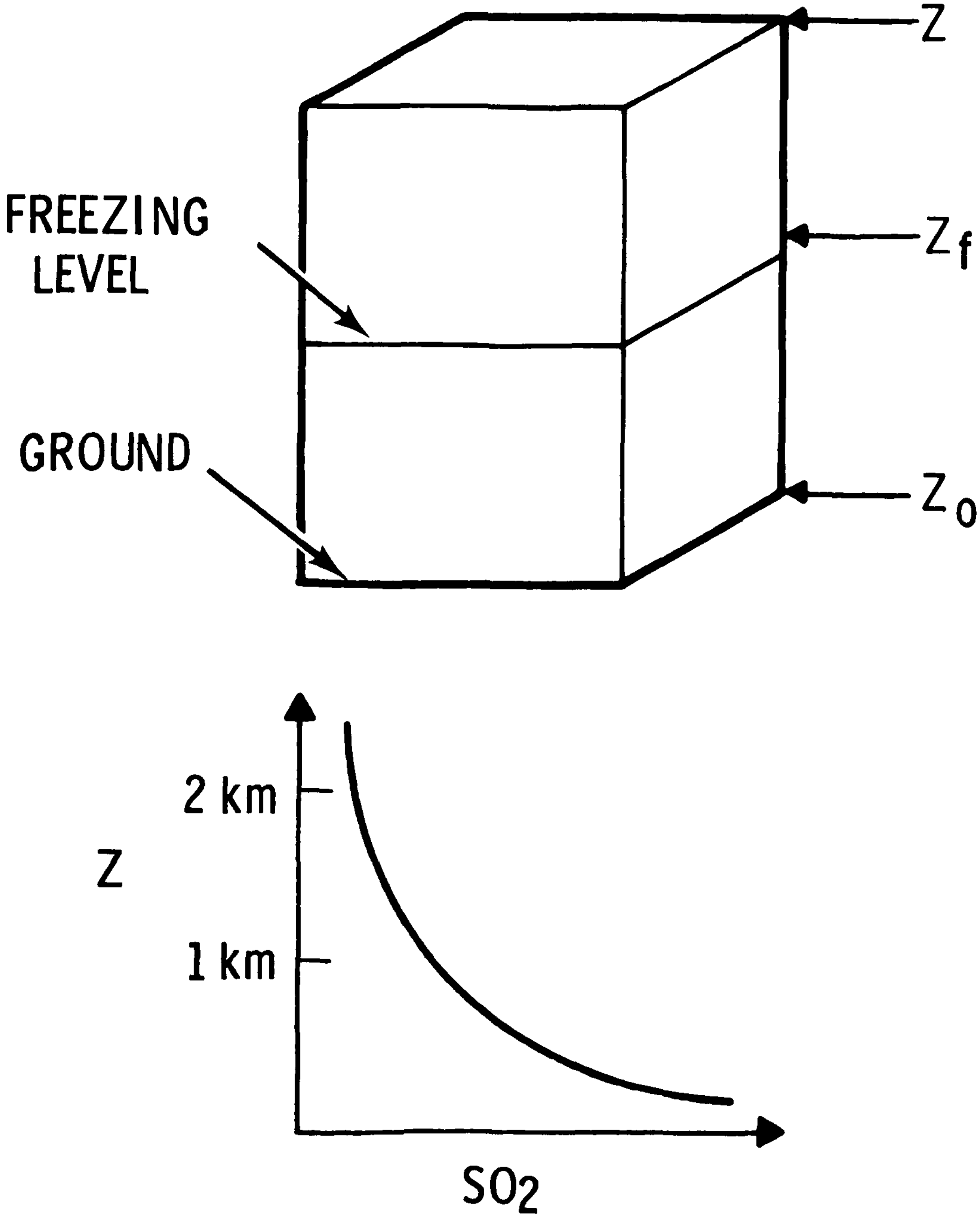


Figure A-3. The volume considered for wet $SO_2$ removal by snow and rain. The ground is at $z_o$ and the top of the riming zone is at z. The freezing level is at $z_f$. The air concentration of $SO_2$ is assumed to decrease with height.

where $j(z_o)$ and $C(z_o)$ are ground values. Below the freezing level the $SO_2$ concentration in the drops is assumed to be determined solely by establishing an equilibrium concentration between the dissolved and airborne $SO_2$.

To derive a removal rate that is analogous to the previous removal rates and applied over the entire region being scavenged (the top of the riming zone to the ground) a weighted average over both boxes is performed:

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{rain} = \frac{(z-z_f)\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{ice} + (z_f-z_o)\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{liquid}}{(z-z_o)} . \qquad (18)$$

Substituting Eq. (A-16) and (A-17) into Eq. (A-18) results in the desired expression for $SO_2$ removal by rain:

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{rain} = -\ 0.48\ J^{0.9} C_g . \qquad (A\text{-}19)$$

Comparison between Eq. (A-14) and Eq. (A-19) illustrates that the rain removal rate of $SO_2$ can exceed the snow removal rate by a factor of two or more at equivalent precipitation rates. In particular, as the cloud water concentration goes to zero, the wet removal of $SO_2$ by the snow riming mechanism postulated above becomes negligible.

For both Eq. (A-14) and (A-19) the ground-level concentration of dissolved $SO_2$ is related through the curves of Figure A-2 to the ground level $SO_2$ air concentration, $X(SO_2)$. That is,

$$C_g = \beta\ X(SO_2). \qquad (A\text{-}20)$$

Thus, the expressions describing wet removal of $SO_2$ and $SO_4^=$ [Eq. (A-11), (A-14), and (A-19)] can be generalized to

$$\frac{d\bar{X}}{dt} = -\ K\ X_g J^a . \qquad (A\text{-}21)$$

Notice that Eq. (A-21) is not an exact first-order expression, as was assumed a priori in Eq. (A-1). The average wet removal of $SO_2$ and $SO_4^=$ for a layer depends not on the average pollutant concentration in the layer, but upon the surface-level concentration in the layer. If the surface-level concentration, $X_g$, can be expressed in terms of a layer average, then the first-order relationship of Eq. (A-1) will result. For example, suppose the surface-level concentrations of $SO_2$ and $SO_4^=$ decrease linearly to zero at the top of the riming zone. Then $X_g = 2\bar{X}$ and

$$\frac{d\bar{X}(SO_4^=)}{dt} = -\ 0.44\ \bar{X}(SO_4)J^{0.625}$$

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{snow} = -0.48\ \beta\ \bar{X}(SO_4)J^{0.9}\ (1-\exp(-2\bar{m})) \qquad \text{(A-22)}$$

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{rain} = -0.96\ \beta\ \bar{X}(SO_2)J^{0.9}.$$

Another common situation is to assume a Gaussain profile for a plume. Then

$$X_g = \bar{X}\ \ \Delta z/\ [1.25\,\sigma_z\ \mathrm{erf}(\Delta z/(1.41\sigma_z))], \qquad \text{(A-23)}$$

$$= \gamma\bar{X}\ .$$

Substitution of Eq. (A-23) into Eq. (A-11), and (A-19) gives

$$\frac{d\bar{X}(SO_4^=)}{dt}\ \ \beta\gamma = -\ 0.22\ \gamma\ \bar{X}(SO_4^=)J^{\ 0.625},$$

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{snow} = -\ 0.24\ \ \beta\gamma\ \bar{X}(SO_2)\ J^{0.9}\ (1-\exp(2\bar{m})), \qquad \text{(A-24)}$$

$$\left.\frac{d\bar{X}(SO_2)}{dt}\right|_{rain} = -\ 0.48\ \beta\gamma\ \bar{X}(SO_2)\ J^{0.9}.$$

WET FLUX OF SULFUR AND PRECIPITATION pH

After procedures for computing removal rates of $SO_2$ and $SO_4^=$ by precipitation have been developed, calculations to determine sulfur depostion and rainwater acidity follow directly. In fact, the flux of $SO_2$ or $SO_4^=$ is obtained by multiplying Eq. (A-21) by the region being scavenged, $\Delta z$, which is defined by Eq. (A-9). As for pH, the major portion of acidity found in rainwater can be attributed to the incorporation of sulfate (Granat 1977). Indeed, as Figure A-4 illustrates, a good approximation to rainwater pH results from assuming two hydrogen ions for every sulfate ion (Dana 1978). The figure presents precipitation chemistry data collected from the MAP3S precipitation chemistry network and suggests that during the summer months when nitrate concentrations in precipitation water are the lowest, the two hydrogen to one sulfate ion is regularly observed. During the winter months when nitrates play a greater role in determining rainfall acidity, there is an excess of hydrogen ions; the molar ratio of hydrogen to sulfate is then greater than 2. Still, at pH values less than 4.3, the assumption of $[H]/[SO_4^=] = 2$ is quite good. Thus, determination of the sulfate concentration in precipitation water should provide accurate estimates of rainfall pH.

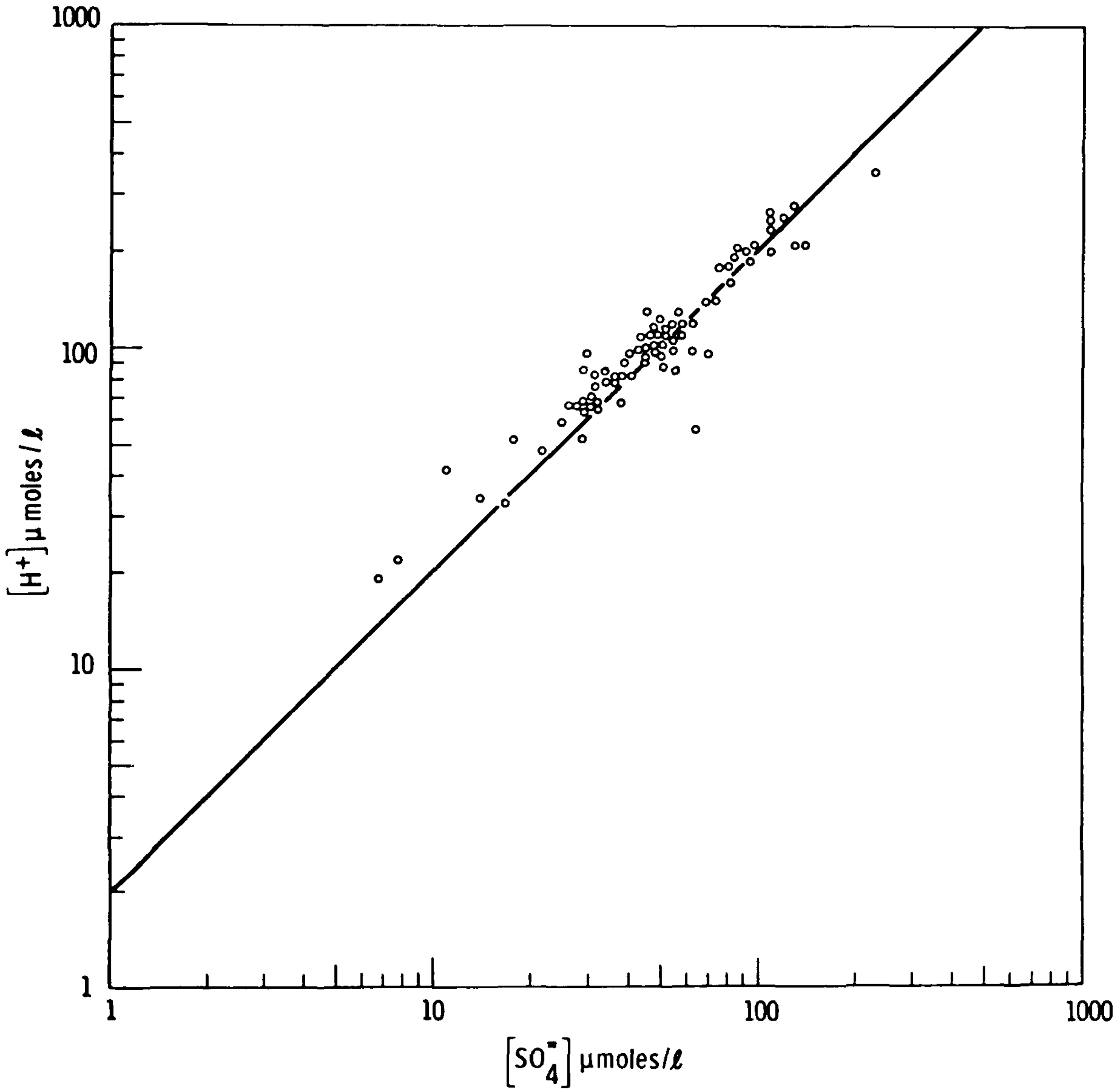


Figure A-4(a). Observed relationships between the ion concentrations of H and $SO_4^=$ for summer 1977. The solid line represents two hydrogen moles for every sulfate mole; the circles represent data points.

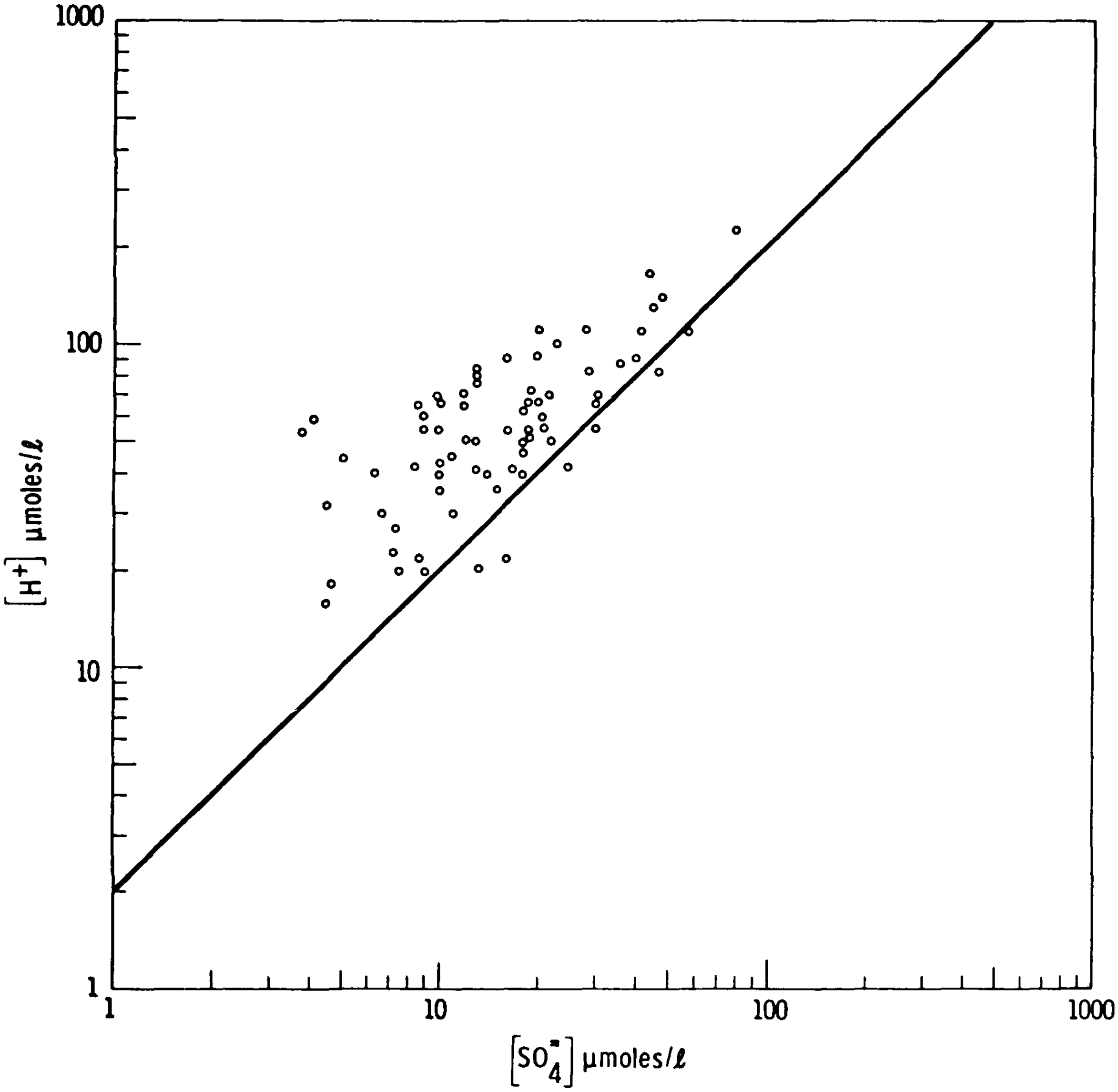


Figure A-4(b). Observed relationships between the ion concentrations of H and $SO_4^=$ for winter 1977-78. The solid line represents two hydrogen moles for every sulfate mole; the circles represent data points.

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APPENDIX B

SIMPLE MODEL CALCULATIONS OF EMISSIONS APPLIED TO ATIKOKAN

Annual averages, 3-h, and 24-h worst-case concentrations and deposition fluxes may be estimated by using simplified models. These calculations provide a comparison with the more complicated grid model.

## ANNUAL AVERAGE CONCENTRATIONS

The single box model approach is used. Since all possible meteorological conditions occur in a year we may consider that the plume is uniformly mixed in a cylindrical box. Assume that the wind blows with equal frequency in all directions. From conservation of mass,

$$Q = 2\pi \ x \ L \ U \ C.$$

or

$$C = \frac{Q}{2\pi \ x \ LU} .$$

Let C be the annual ambient air concentration ($\mu g/m^3$) at distance x (m) from the source Q (g/s). Let U be the average annual wind speed (m/s) through the average mixed layer of height L(m). Let us now divide this result by 2 to account for the time when the plume is in stable air and hence not dispersing to the ground. The equation to be evaluated is then

$$C = \frac{4}{4\pi \ x \ LU} .$$

Holtzworth (1972) gives the mean annual day time value of L at International Falls as 1,300 m and the mean annual wind U as 7.2 m/s. We choose x = 80 km as the distance from Atikokan to the center of the BWCA. For the indicated emission rates, Q, the annual average concentrations, C, are as follows:

| Species | $Q(\frac{g}{s})$ | $C(\frac{\mu g}{m^3})$ | C(ppb) |
|---|---|---|---|
| $SO_2$ | 2,230 | 0.24 | 0.09 |
| $SO_4^=$ | 335[a] | 0.04 | 0.01 |
| PM | 328 | 0.04 | --- |
| Hg | 0.0290 | $3 \times 10^{-6}$ | 0.001 |
| NOX as $NO_2$ | 1,320 | 0.14 | 0.005 |

[a] Assumed 2%/h conversion of $SO_2$ to $SO_4^=$ plus 2% conversion in the stack.

The EPA CRSTER model, which runs a Gaussian plume calculation for every hour of the year, gave an annual average $SO_2$ concentration at 80 km due south of 0.25 $\mu g/m^3$ (Goklany, personal communication, 1978).

THREE-HOUR WORST-CASE CONCENTRATIONS

Assume that the plume is fully trapped and calculate the plume centerline concentration for neutral stability at 80 km downwind. The Gaussian plume result is

$$C = \frac{Q}{\sqrt{2\pi\sigma_y}\ LU} .$$

Because of plume meandering an average concentration across the plume is more appropriate than the centerline value. The width of the plume is taken as 4.3 $\sigma_y$ and the result is

$$\bar{C} = \frac{0.4\ Q}{\sqrt{2\pi\sigma}\ _y\ LU} .$$

For neutral stability $\sigma_y$ = 0.13 x 0.903, and assuming x = 80 km, u = 5 m/s, and L = 500 m, we have

$$\bar{C} = \frac{Q(g/s)}{106.5} .$$

In order for this to represent a 3-h average concentration the wind would have to blow steadily in one direction for 7 h since the travel to the receptor is about 4 h. Hence, this is an upper limit to the real situation. The results of this 3-h calculation are as follows:

| Species | $Q(\frac{g}{s})$ | $C(\frac{\mu g}{m^3})$ | $C(ppb)$ |
|---|---|---|---|
| $SO_2$ | 2,230 | 21 | 8 |
| $SO_4^=$ | 335 | 3 | 1 |
| PM | 328 | 3 | --- |
| Hg | 0.0290 | 0.0003 | $4 \times 10^{-5}$ |
| NOX as $NO_2$ | 1,320 | 12 | 6 |

The EPA CRSTER model calculated the highest 3-h concentration of $SO_2$ at 80 km south-southeast as 20 $\mu g/m^3$.

TWENTY-FOUR-HOUR WORST-CASE CONCENTRATIONS

The 24-h case cannot be calculated without having actual meteorological data because conditions do not persist in the atmosphere for 24 h. The EPA CRSTER model calculated the highest 24-h $SO_2$ concentration 80 km south of Atikokan as 5 $\mu g/m^3$. Taking this in relation to the emissions we have the following 24-h worst-case concentrations:

| Species | $Q(\frac{g}{s})$ | $C(\frac{\mu g}{m^3})$ | C(ppb) |
|---|---|---|---|
| $SO_2$ | 2,230 | 5 | 2 |
| $SO_4^=$ | 335 | 1 | 0.2 |
| PM | 328 | 1 | --- |
| Hg | 0.0290 | 0.00006 | $7 \times 10^{-6}$ |
| NOX as $NO_2$ | 1,320 | 3 | 1.6 |

ANNUAL AVERAGE DRY DEPOSITION

The annual average dry deposition flux may be estimated by multiplying an effective depositive velocity, $V_D$, by the annual average concentration:

$$F_{DRY} = C\ V_D\ (\mu g/m^2 \text{ per second}),$$

or

$$F_{DRY} = 315\ C\ V_D\ (\text{kg/ha-yr}).$$

This assumes that the ambient air concentration is not significantly decreased because of dry deposition upwind of the receptor point in question. Hence the calculation is an upper limit. The annual average dry deposition fluxes are as follows:

| Species | $V_D$(cm/s) | $F_{DRY}$(kg/ha-yr) |
|---|---|---|
| $SO_2$ | 1 | 0.75 |
| $SO_4^=$ | 0.1 | 0.014 |
| PM | 0.1 | 0.014 |
| Hg | 0.1 | $1 \times 10^{-6}$ |
| NOX as $NO_2$ | 0.5 | 0.22 |

WET DEPOSITION FLUXES

For typical rainfall rates of 1 mm/h continuous rainfalls, the procedure outlined in Appendix A yields a concentration of 1.8 mg/liter for the sulfate in precipitation if we assume an average sulfate concentration of 3 $\mu g/m^3$ in the air. By assuming two hydrogen moles for every sulfate mole, the sulfate concentration converts to a rainfall pH of 4.4, and $\beta = 0.0237$. The removal rate for 21 $\mu g/m^3$ of $SO_2$ is

$$W_{SO_2} = 0.24\ (\mu g/m^3 \text{ per hour}),$$

and for 3 $\mu g/m^3$ of $SO_4^=$ is

$$W_{SO_4^=} = 1.0\ (\mu g/m^3 \text{ per hour}).$$

If we use a height of 1,300 m for the mixed layer, the deposition rate due to rain is

$$F_{WET}(SO_2) = 3 \text{ (g/ha-h)},$$

$$F_{WET}(SO_4^{=}) = 13 \text{ (g/ha-h)}.$$

For snow let us assume a typical precipitation rate of 0.5 mm/h. Then $\bar{m} = 1.25$ and

$$W_{SO_2} = 0.23 \text{ (}\mu g/m^3 \text{ per hour)},$$

$$W_{SO_4^{=}} = 0.63 \text{ (}\mu g/m^3 \text{ per hour)}.$$

If we use 1,300 m for the mixed layer, the deposition rate due to snow is

$$F_{WET}(SO_2) = 3 \text{ (g/ha-h)},$$

$$F_{WET}(SO_4^{=}) = 8 \text{ (g/ha-h)}.$$

Wet deposition of particulate matter may be estimated by using an appropriate wash-out coefficient, $\lambda$. The wash-out coefficient is a function of particle size and the droplet size. The fly-ash particles that escape the electrostatic precipitation will be predominantly in the 0.1-1-m range, and we have selected a wash-out coefficient of 0.036 per hour. For mercury we assume a wash-out coefficient of 0.005 per hour. The scavenging mechanism for NOX is not known. The equation to be used is

$$F_{WET} = \lambda C Z_m \text{ (}\mu g/m^2 \text{ per hour)}.$$

If we use a height of 1,300 m for the mixed layer, the deposition rate in the plume due to rain is

$$F_{WET}(PM) = 1.4 \text{ (g/ha-h)},$$

$$F_{WET}(Hg) = 4 \times 10^{-6} \text{ (g/ha-h)}.$$

ANNUAL AVERAGE DEPOSITION

During the model year of 1964 there were 43 h of rain and 46 h of snow when the winds were from the northeast to northwest. This information may be used to calculate an annual average wet deposition flux. Since the plume would cover roughly a 15° sector at any given time, however, we should use only one-sixth of this time. The estimated annual average deposition fluxes due to Atikokan are summarized below:

| Deposition (kg/ha-yr) | $SO_2$ | $SO_4^{=}$ | PM | Hg |
|---|---|---|---|---|
| Rain | 0.02 | 0.10 | 0.01 | $3 \times 10^{-8}$ |
| Snow | 0.02 | 0.06 | 0.01 | $3 \times 10^{-8}$ |
| Dry | 0.75 | 0.01 | 0.01 | $1 \times 10^{-6}$ |
| Total | 0.79 | 0.17 | 0.03 | $1 \times 10^{-6}$ |

The deposition rates for $SO_4^{=}$ are probably an upper limit because up-wind removal between Atikokan and the BWCA due to wet and dry deposition would decrease the concentrations used in the calculation. The wet deposition of $SO_2$ might be increased since the pH of the rain would be less and therefore the scavenging coefficient would be greater.

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APPENDIX C

REPRESENTATIVE ANALYSIS OF COAL AND FLY ASH FOR MAJOR AND TRACE COMPONENTS: SOUTHERN SASKATCHEWAN LIGNITE[a]

| Component | Coal | Ash | Component | Coal | Ash |
|---|---|---|---|---|---|
| Aluminum (%) | 1.7 | 9.4 | Lithium (ppm) | 9 | - |
| Antimony (ppm) | 1.1 | 2.1 | Magnesium (%) | 0.45 | 2.5 |
| Arsenic (ppm) | 6.8 | 19 | Manganese (ppm) | 180 | 400 |
| Ash (%) | 22 | - | Mercury (ppm) | 0.3 | - |
| Barium (%) | 0.05 | 0.50 | Molybdenum (ppm) | 9 | 20 |
| Beryllium (ppm) | <0.14 | 3 | Nickel (ppm) | 37 | 39 |
| Bismuth (ppm) | 9 | - | Phosphorus (%) | 0.15 | - |
| Boron (ppm) | 37 | 400 | Potassium (%) | 0.4 | - |
| Bromine (ppm) | 2.7 | 2.0 | Rubidium (ppm) | - | 40 |
| Cadmium (ppm) | <0.6 | 1.8 | Silicon (%) | 4 | - |
| Calcium (%) | 1.8 | 8.1 | Selenium (ppm) | 0.8 | <3 |
| Cerium (ppm) | - | 112 | Silver (ppm) | - | 0.4 |
| Cesium (ppm) | - | 3 | Sodium (%) | 0.2 | 2 |
| Chlorine (ppm) | - | 460 | Strontium (%) | 0.02 | 0.2 |
| Chromium (ppm) | 25 | 60 | Sulfur (%) | 0.8 | 0.48 |
| Cobalt (ppm) | 9 | 9 | Tantalum (ppm) | - | 1.7 |
| Copper (ppm) | 46 | 43 | Tellurium (ppm) | - | 90 |
| Fluorine (ppm) | 86 | 94 | Thallium (ppm) | <0.5 | - |
| Gallium (ppm) | - | 1,090 | Thorium (ppm) | - | 14 |
| Gold (ppm) | - | 0.005 | Titanium (%) | 0.05 | - |
| Hafnium (ppm) | - | 12 | Tungsten (ppm) | - | 2.5 |
| Heat content (BTU) | 8,600 | - | Uranium (ppm) | 8 | 11 |
| Holmium (ppm) | - | 6 | Vanadium (ppm) | 20 | 70 |
| Iron (%) | 0.6 | 2.2 | Zinc (ppm) | 40 | 20 |
| Lead (ppm) | <29 | 30 | Zirconium (ppm) | 80 | 240 |

[a]G. E. Glass, unpublished data, 1979.

APPENDIX D

DATA PERTINENT TO THE AQUATIC ECOSYSTEMS OF THE BOUNDARY WATERS CANOE AREA

TABLE D-1. FISHES KNOWN TO BE PRESENT IN THE BWCA AND BORDER LAKES OF MINNESOTA[a]

| | |
|---|---|
| Silver lamprey, Ichthyomyzon unicuspis | Northern redhorse, Moxostoma macrolepidotum |
| Lake sturgeon, Acipenser fulvescens | White sucker, Catostomus commersoni |
| Goldeye, Hiodon alosoides | Longnose sucker, Catostomus catostomus |
| Mooneye, Hiodon tergisus | Brown bullhead, Ictalurus nebulosus |
| Brook trout, Salvelinus fontinalis | Black bullhead, Ictalurus melas |
| Lake trout, Salvelinus namaycush | Tadpole madtom, Noturus gyrinus |
| Rainbow trout, Salmo gairdneri | Trout-perch, Percopsis omiscomaycus |
| Lake whitefish, Coregonus clupeaformis | Burbot, Lota lota |
| Cisco, Coregonus artedi | Brook stickleback, Culaea inconstans |
| Central mudminnow, Umbra limi | Largemouth bass, Micropterus salmoides |
| Northern pike, Esox lucius | Smallmouth bass, Micropterus dolomieui |
| Muskellunge, Esox masquinongy | Rock bass, Ambloplites rupestris |
| Longnose dace, Rhinichthys cataractae | Green sunfish, Lepomis cyanellus |
| Lake chub, Couesius plumbeus | Bluegill, Lepomis macrochirus |
| Creek chub, Semotilus atromaculatus | Pumpkinseed, Lepomis gibbosus |
| Pearl dace, Semotilus margarita | Black crappie, Pomoxis nigromaculatus |
| Northern redbelly dace, Chrosomus eos | Yellow perch, Perca flavescens |
| Finescale dace, Chrosomus neogaeus | Sauger, Stizostedion canadense |
| Golden shiner, Notemigonus crysoleucas | Walleye, Stizostedion vitreum vitreum |
| Bluntnose minnow, Pimephales notatus | Log perch, Percina caprodes |
| Fathead minnow, Pimephales promelas | River darter, Percina shumardi |
| Mimic shiner, Notropis volucellus | Johnny darter, Etheostoma nigrum |
| Common shiner, Notropis cornutus | Iowa darter, Etheostoma exile |
| Spottail shiner, Notropis hudsonius | Mottled sculpin, Cottus bairdi |
| Blacknose shiner, Notropis heterolepis | Slimy sculpin, Cottus cognatus |
| Brassy minnow, Hybognathus hankinsoni | |

[a]Data from:
Eddy S., and J. Underhill. 1974. Northern Fishes. Univ. Minnesota Press, Minneapolis, Minn. 414 p. Records of Minnesota Department of Natural Resources Area Fisheries Headquarters in Ely, Finland, and Grand Marais, Minn., personal communication.

TABLE D-2. LAKE BENTHIC INVERTEBRATES COLLECTED FROM FIVE LARGE LAKES[a] IN SUPERIOR NATIONAL FOREST IN 1976[b]

PLECOPTERA
- Capniidae
- *Acroneuria lycorias*
- *Perlinella drymo*

EPHEMEROPTERA
- *Isonychia* sp.
- Siphlonuridae
- *Siphlonurus* sp.
- *Siphlonurus marshalli*
- Heptageniidae
- *Arthroplea bipunctata*
- *Stenacron* sp.
- *Stenacron candidum*
- *Stenacron interpunctatum*
- *Stenacron minnetonka*
- *Stenonema* sp.
- *Stenonemn tripunctatum*
- *Siphloplecton interlineatum*
- Bactidae
- *Callibactis* sp.
- *Clocon* sp.
- Leptophlebiidae
- *Leptophlebia* sp.
- *Ephemerella* sp.
- *Ephemerella versimilis*
- *Ephemerella temporalis*
- *Caenis* sp.
- *Ephemera simulans*
- *Hexagenia* sp.
- *Hexagenia limbata*

ODONATA
- Coenagrionidae
- *Enallagma* sp.
- Comphidae
- *Dromogomphus spinosus*
- *Hagenius brevistylus*
- *Acshnidae*
- *Acshna* sp.
- *Basiaeschna janata*
- *Boycria* sp.
- *Boycria vinosa*
- *Didymops transversa*
- *Macromia* sp.

ODONTA (continued)
- *Macromia illinoiensis*
- *Somatochlora williamsoni*
- *Notonecta* sp.
- *Ranatra* sp.
- *Belostroma* sp.
- *Lethocerus* sp.
- Corixidae

TRICHOPTERA
- *Nyctiophylax moestus*
- *Polycentropus cinereus*
- *Polycentropus interrupta*
- Hydroptillidae
- *Agraylea* sp.
- *Hydroptila* sp.
- *Ochrotrichia* sp.
- *Agrypnia improba*
- *Banksiola crotchi*
- *Phrygabea cinerea*
- *Ptilostomis* sp.
- Limnephilidae
- *Gramotaulis* sp.
- *Nemotaulius hostilis*
- *Pycnopsyche guttifer*
- *Agarodes distinctum*
- *Molanna* sp.
- *Molanna blenda*
- *Molanne tryphena*
- *Helicopysche borealis*
- *Ceraclea* sp.
- *Ceraclea neffi*
- *Ceraclea resurgens*
- *Triaenodes injusta*
- *Triaenodes tarda*

MEGALOPTERA
- *Chauloideg rastricornis*
- *Sialis* sp.

COLEOPTERA
- *Haliplus* sp.
- Dytiscidae
- Cyrinidae
- *Dineutus* sp.

(continued)

Table D-2. (continued)

COLEOPTERA (continued)
- *Cyrinus* sp.
- Hydrophilidae
- *Ectopria nervosa*
- *Dubiraphia* sp.
- *Macronychus glabratus*
- *Donacia* sp.

DIPTERA
- Tabenidae
- *Aedes* sp.
- Chironomidae
- *Clinotanypus* sp.
- *Conchapelopia* sp.
- *Dicrotendipes* sp.
- *Endochironomus* sp.
- *Eukiefferriella* sp.
- *Glyptotendipes* sp.
- *Larsia* sp.
- *Palpomyia* group
- *Polypedilum* sp.
- *Procladius* sp.
- *Stenochironomus* sp.
- *Xenochironomus* sp.
- *Chironomidae pupae*

DECAPODA

CRUSTACEA
- *Crangonyx* sp.
- *Hyalella azteca*

NEMATODA

TURBELLARIA

HIRUDINEA

OLIGOCHAETA

GASTROPODA
- *of. Amnicola limosa*
- *Carpeloma decisum*
- *Perrissia* sp.
- *Cyraulus* sp.
- *Hellsoma anceps*
- *H. carpanulata*
- *H. corpulentum*
- *H. trivolvis*
- *Helisomi* sp.
- *Physa gvrina*
- *Sphaerium strintinum*
- *Stagnicola* sp.

PELECYPODS
- Sphaeriidae

OTHER
- Lepidoptera

[a]Birch, Colby, Gabbro, Seven Beaver, and White Iron Lakes.

[b]Collections made by the Minnesota Copper-Nickel Study Group (MCNSG) (Johnson et al. 1978).

TABLE D-3. ZOOPLANKTON COLLECTED FROM FIVE LARGE LAKES[a] IN SUPERIOR NATIONAL FOREST IN 1976 AND 1977[b]

| | |
|---|---|
| ROTIFERA | CLADOCERA |
| Keratella cochlearis | Bosimina longirostris |
| Polyarthra vulgaris | Daphnia galeata mendotae |
| Synchaeta sp. | Holopedium gibberum |
| Conchilus sp. | Daphnia retrocurva |
| Kellicottia congispina | Diaphanosoma sp. |
| Trichocera cylindrica | Chydorus sphaericus |
| Kellicottia bostoniensis | Ceriodaphnia lacustris |
| Collotheca sp. | Daphnia pulex |
| Trichocera similis | Leptodora kindtii |
| Filinia longiseta | Daphnia shodleri |
| Keratella quadrata | Alona circumfimbriata |
| Ploesoma truncatum | Ceriodaphnia quadrangula |
| Pompholyx sulcata | Alona guttata |
| Trichocera porcellus | Ceriodaphnia sp. |
| Hexathra sp. | Chydorus bicornutus |
| Ploesoma lenticulare | Daphnia catawba |
| Lecane sp. | Daphnia longiremis |
| Trichocera multicrinis | D. parvula |
| Asplanchna sp. | D. sp. |
| Lophochavis salpine | |
| Trichocera weberi | COPEPODA |
| Brachionus sp. | Tropocyclops prasinus (Cyclopoida) |
| Lophocharis sp. | |
| Trichocera clongata | Cyclops bicuspidatus thomasi (Cyclopoida) |
| Trichocera longiseta | |
| Ascomorpha sp. | Diaptomus oregonensis (Calanoida) |
| Enthlanis dilatata | |
| Hexarthra mira | Epischura lacustris (Calanoida) |
| Ploesoma hudsoni | |
| Testudinella patina | Cyclops vernalis (Cyclopoida) |
| Trichocera sp. | |
| Trichotria tetractis | Mesocyclops edax (Cyclopoida) |
| Ascomorpha ovalis | |
| A. saltans | Diaptomus minutus (Calanoida) |
| Bdelloid sp. | |
| Brachionus quadridentatus | Ergasilis chautaquaensis (Cyclopoida) |
| Cephalodella intuda | |
| Euchlanis sp. | Macrocyclops albidus (Cyclopoida) |
| Keritella hiemalis | |
| K. paludosa | Eucyclops agilis (Cyclopoida) |
| K. serrulata | |
| K. taurocephala | Orthocyclops modestus (Cyclopoida) |
| Notholca acuminata | |
| Notholca sp. | Diaptomus sicilis (Calanoida) |
| Rotaria peturia | |
| Synchaeta stylata | |

[a]Birch, Colby, Gabbro, Seven Beaver, and White Iron Lakes.

[b]Collections made by the Minnesota Copper-Nickel Study Group (MCNSG) (Piragis et al. 1978).

TABLE D-4. PHYTOPLANKTON COLLECTED FROM FIVE LARGE LAKES[a] IN SUPERIOR NATIONAL FOREST DURING THE FALL AND SUMMER OF 1976 AND 1977[b]

BACILLARIOPHYTA
- Asterionella formosa
- Cyclotella bodanica
- Fragilaria crotonensis
- Melosira ambigua
- Melosira distans
- Nitzschia sp.
- Tabellaria fenestrata

CHLOROPHYTA
- Ankistrodesmus falcatus including varieties aricularis & mirabilis
- Botryococcus Braunii
- Oocystis sp.

CYANOPHYTA
- Agmenellum quadruplicatum (Merismopedia glauca)
- Aphanocapsa delicatissima
- Coelosphaerium Kuetzingianum

CHRYSOPHYTA
- Dinobryon bavaricum
- Dinobryon divergens
- Dinobryon sertularia var. protuberans

CRYPTOPHYTA
- Cryptononas erosa

PYRRHOPHYTA
- Ceratim hirundinella

[a]Birch, Colby, Gabbro, Seven Beaver, and White Iron Lakes.

[b]Collections made by the Minnesota Copper-Nickel Study Group (MCNSG) (Gerhart et al. 1978).

TABLE D-5. BWCA-VNP WATER QUALITY NOVEMBER 1978. FIELD + DESCRIPTION DATA USEPA -- BY G. E. GLASS, ET AL., ERL-D USEPA (LAKES WITHIN AND NEAR THE BWCA AND VNP SAMPLED 11-6,7,8,9-78 and 11-15,16,17-78)

| Number | Lake name | Location: TN, R section | Location: BWCA[a] | Location: VNP[a] | Elevation (ft) | Depth of probe measurement (m) | Probe temp. (°C) | Probe Conductivity (μmho/cm²) | Probe % transmittance | Conductivity @ 25° (μmho/cm²) | pH @ 6°C ERL-D | Alkalinity[b] total as $CaCO_3$ (mg/l) ERL-D | CSI[c] | Lake Characteristics: Surface area hectare | Lake Characteristics: Watershed area hectare |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 101 | No name | 63,11W,24 | - | - | 1430 | 0.43 | 4.26 | 45.9 | 70.2 | 67 | 7.23 | 23.6a | 1.67 | 3 | 58 |
| 102 | Pea Soup | 63,10W,18 | - | - | 1450 | 0.48 | 3.82 | 109.5 | 86.3 | 186 | 7.99 | 85.6a | -0.14 | 4 | 89 |
| 103 | Dan L. | 63,10W,17 | - | - | 1495 | 0.83 | 5.61 | 94.1 | 75.6 | 144 | 7.92 | 66.2a | 0.12 | 3 | 17 |
| 104 | Kaminela | 63,10W,14 | - | - | 1515 | 0.70 | 4.93 | 60.4 | 65.6 | 90 | 7.72 | 41.1a | 0.74 | 8 | 47 |
| 105 | No name | 63,9W,10 | - | - | 1450 | 1.16 | 4.95 | 23.7 | 58.8 | 29 | 6.43 | 4.7a | 3.73 | 5 | 98 |
| 201 | Charm | 67,14W,16 | x | - | 1246 | 0.92 | 4.52 | 17.8 | 70.9 | 21 | 6.37 | 3.1a | 4.21 | 14 | 179 |
| 202 | Thumb | 67,14W,18 | x | - | 1227 | 0.91 | 5.62 | 19.1 | 83.5 | 22 | 6.52 | 3.3a | 4.03 | 28 | 692 |
| 203 | Fat | 67,15W,14 | x | - | 1305 | 1.09 | 6.79 | 18.4 | 87.6 | 20 | 6.70 | 4.4a | 3.68 | 43 | 251 |
| 204 | Norway | 67,15W,4 | x | - | 1235 | 0.96 | 5.76 | 22.3 | 82.5 | 27 | 6.72 | 5.0a | 2.53 | 23 | 199 |
| 205 | North | 67,15W,3 | x | - | 1184 | 0.72 | 3.06 | 21.1 | 74.5 | 27 | 6.79 | 6.1a | 3.41 | 32 | 1812 |
| 206 | Dovre | 67,16W,20 | x | - | 1172 | 1.16 | 4.52 | 19.6 | 69.2 | 25 | 6.80 | 5.0a | 3.47 | 47 | 1472 |
| 207 | No name | 67,16W,29 | x | - | 1280 | 1.00 | 4.42 | 16.5 | 78.0 | 18 | 6.49 | 3.1a | 4.17 | 9 | 69 |
| 208 | Ruby* | 66,14W,6 | x | - | 1320 | 1.08 | 3.97 | 22.4 | 86.2 | 26 | 6.74 | 5.9a | 3.49 | 27 | 186 |
| 209 | Warpaint* | 66,14W,7 | x | - | 1330 | 1.20 | 3.25 | 16.7 | 84.5 | 19 | 6.32 | 2.7a | 4.43 | 18 | 71 |
| 210 | Aquwata* | 66,14W,8 | x | - | 1277 | 1.24 | 3.53 | 18.2 | 80.7 | 20 | 6.44 | 2.7a | 4.28 | 16 | 126 |
| 211 | Emerald* | 66,14W,8 | x | - | 1319 | 1.35 | 3.74 | 18.9 | 84.6 | 22 | 6.83 | 5.4a | 3.31 | 42 | 374 |
| 212 | Griddle | 64,9W,2F | x | - | 1455 | 0.70 | 3.80 | 31.2 | 67.7 | 48 | 7.22 | 15.7a | 2.20 | 10 | 104 |
| 213 | Flash | 64,9W,28 | - | - | 1455 | 0.89 | 4.94 | 45.8 | 87.0 | 68 | 7.60 | 27.2a | 1.20 | 32 | 120 |
| 214 | Ennis | 63,9W,33 | - | - | 1450 | | Water sample only | | | 89 | - | 36.0a | 1.07 | 8 | 37 |
| 215 | No name | 64,10W,36 | - | - | 1410 | | Water sample only | | | 154 | - | 73.2a | 0.10 | 3 | 21 |
| 301 | No name | 69,17W,32 | - | x | 1130 | 1.07 | 3.52 | 32.5 | 76.1 | 50 | 7.41 | 18.7 | 1.88 | 7 | 38 |
| 302 | Tooth | 68,18W,3 | - | x | 1183 | 0.96 | 5.58 | 26.1 | 81.4 | 35 | 7.05 | 9.1 | 2.79 | 23 | 192 |
| 303 | Spring | 68,18W,15 | - | - | 1162 | 1.07 | 6.87 | 29.2 | 86.2 | 38 | 7.21 | 11.2 | 2.52 | 89 | 406 |
| 304 | Wiyapka | 68,18W,17 | - | x | 1185 | 1.15 | 4.38 | 25.8 | 65.9 | 34 | 6.77 | 8.1 | 3.02 | 21 | 372 |
| 305 | Weir | 70,19W,34 | - | x | 1159 | 1.51 | 4.27 | 18.4 | 68.4 | 21 | 6.63 | 4.5 | 3.70 | 26 | 1499 |
| 306 | No name | 70,20W,30 | - | x | 1275 | 1.02 | 4.78 | 21.2 | 77.1 | 25 | 6.60 | 4.4 | 3.70 | 7 | 83 |
| 307 | No name | 70,20W,30 | - | x | 1185 | 1.04 | 4.59 | 19.7 | 71.1 | 25 | 6.65 | 4.6 | 3.57 | 3 | 123 |
| 308 | Shoepack | 70,20W,34 | - | x | 1195 | 1.02 | 4.71 | 19.6 | 74.6 | 25 | 6.26 | 3.0a | 4.27 | 128 | 1126 |
| 309 | Little Shoepack | 69,20W,3 | - | x | 1215 | 1.09 | 4.13 | 19.9 | 79.0 | 25 | 6.71 | 4.9 | 3.36 | 69 | 146 |
| 310 | Quarterline | 69,20W,12 | - | x | 1175 | 1.13 | 4.61 | 20.4 | 71.7 | 26 | 6.51 | 4.8 | 3.71 | 7 | 66 |
| 311 | Fishmouth | 70,19W,21 | - | x | 1157 | 1.13 | 4.97 | 22.7 | 82.6 | 28 | 7.02 | 7.8 | 3.01 | 12 | 56 |
| 312 | Loiten | 70,20W,19 | - | x | 1188 | 1.12 | 6.07 | 25.5 | 84.5 | 33 | 6.80 | 5.6 | 3.31 | 39 | 294 |
| 313 | Locator | 70,21W,22 | - | x | 1143 | 1.37 | 6.14 | 24.5 | 81.8 | 30 | 6.75 | 5.2 | 3.39 | 53 | 1386 |
| 314 | Tin Can Mike | 64,11W,5 | x | - | 1305 | 0.90 | 5.50 | 22.0 | 83.0 | 30 | 6.92 | 7.5 | 3.04 | 56 | 311 |
| 315 | Sandpit | 64,11W,7 | - | - | 1307 | 1.06 | 6.11 | 23.7 | 83.0 | 30 | 7.05 | 8.7 | 2.85 | 23 | 161 |
| 316 | Louis | 64,12W,12 | - | - | 1435 | 1.27 | 5.66 | 19.4 | 87.4 | 23 | 6.83 | 5.5 | 3.40 | 8 | 34 |
| 401 | Totem | 66,6W,35 | x | - | 1455 | 1.07 | 4.50 | 53.0 | 76.7 | 82 | 7.68 | 34.2 | 0.99 | 6 | 26 |
| 402 | Embla | 66,6W,33 | x | - | 1490 | 1.15 | 4.00 | 35.2 | 83.5 | 51 | 7.34 | 16.2 | 1.87 | 4 | 20 |
| 403 | L. of the Clouds | 65,6W,4 | x | - | 1515 | 1.14 | 5.40 | 31.1 | 89.3 | 41 | 7.15 | 10.7a | 2.39 | 11 | 87 |
| 404 | Clam | 65,6W,10 | x | - | 1475 | 1.01 | 3.73 | 47.1 | 90.0 | 71 | 7.68 | 28.8 | 1.07 | 8 | 22 |

(continued)

TABLE D-5. (continued)

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 405 | No name | 65,6W,18 | x | - | 1462 | 1.31 | 5.99 | 41.5 | 88.9 | 58 | 7.57 | 23.7 | 1.42 | 5 | 11 |
| 406 | Rog | 65,5W,16 | x | - | 1495 | 1.58 | 6.52 | 66.7 | 85.4 | 99 | 7.90 | 43.6 | 0.95 | 22 | 62 |
| 407 | Cup | 65,6W,11 | x | - | 1510 | 1.00 | 4.81 | 29.5 | 78.5 | 41 | 7.07 | 10.2 | 2.45 | 7 | 51 |
| 408 | Dutton | 65,6W,6 | x | - | 1510 | 1.19 | 5.48 | 33.7 | 86.9 | 46 | 7.28 | 16.2 | 1.94 | 12 | 52 |
| 409 | Sema | 65,7W,25 | x | - | 1424 | 1.20 | 6.08 | 54.5 | 84.2 | 77 | 7.74 | 30.4 | 0.98 | 29 | 154 |
| 410 | Museum | 63,8W,15 | x | - | 1570 | 1.04 | 4.50 | 23.2 | 79.3 | 31 | 6.98 | 8.0 | 3.07 | 23 | 121 |
| 411 | Hood | 63,8W,17 | x | - | 1590 | 1.18 | 3.93 | 25.3 | 83.2 | 35 | 7.06 | 9.6 | 2.83 | 10 | 79 |
| 412 | Harmony | 64,7W,28 | x | - | 1530 | 1.07 | 5.62 | 31.3 | 84.7 | 41 | 7.21 | 12.6 | 2.47 | 10 | 45 |
| 413 | Balmy | 64,7W,13 | x | - | 1610 | 1.03 | 4.65 | 42.7 | 84.3 | 61 | 7.14 | 13.9 | 2.21 | 4 | 38 |
| 414 | Redface | 64,7W,4 | x | - | 1515 | 1.00 | 4.28 | 35.8 | 6.7 | 50 | 7.20 | 15.4 | 2.01 | 4 | 16 |
| 415 | Beford | 64,7W,5 | x | - | 1490 | -- | -- | 46.0 | -- | 81 | 7.67 | 30.4 | 1.06 | 11 | 66 |
| 501 | Hustler | 66,14W,4 | x | - | 1245 | 1.30 | 4.20 | 18.8 | 83.7 | 33 | 6.52 | 3.6 | 3.95 | 125 | 1057 |
| 502 | Herriman | 66,16W,5 | x | - | 1270 | 1.54 | 2.71 | 20.6 | 78.4 | 25 | 6.80 | 5.7 | 3.35 | 18 | 139 |
| 503 | Lower Pawness | 66,15W,15 | x | - | 1235 | 1.02 | 3.01 | 18.6 | 63.5 | 24 | 6.68 | 4.9 | 3.52 | 67 | 21191 |
| 504 | Franklin | 67,18W,11 | - | - | 1200 | 1.12 | 2.98 | 35.2 | 80.4 | 50 | 7.42 | 20.0 | 1.83 | 60 | 196 |
| 505 | Long | 67,18W,7 | - | - | 1221 | 1.12 | 1.85 | 58.5 | 76.6 | 94 | 7.71 | 41.4 | 0.88 | 188 | 4198 |
| 506 | King William Narrows | 67,17W,1 | - | x | 1119 | 1.11 | 3.91 | 41.6 | 77.0 | 59 | 7.42 | 17.6 | 1.78 | 56 | 277250 |
| 507 | Pauline | 65,16W,12 | - | - | 1330 | 1.05 | 2.12 | 19.8 | 70.2 | 24 | 6.78 | 4.9 | 3.42 | 23 | 97 |
| 508 | Rock Island | 63,9W,33 | x | - | 1490 | 0.95 | 1.85 | 25.2 | 65.5 | 36 | 6.77 | 7.5 | 3.14 | 23 | 291 |
| 509 | Jordan | 64,8W,23 | x | - | 1490 | 1.34 | 3.79 | 28.4 | 80.4 | 38 | 7.13 | 10.5 | 2.56 | 62 | 3706 |
| 510 | Ashigan | 64,8W,15 | x | - | 1401 | 1.14 | 4.18 | 49.8 | 81.7 | 72 | 7.67 | 31.0 | 1.07 | 62 | 201 |
| 511 | Frog | 64,8W,4 | x | - | 1395 | 1.24 | 2.64 | 57.7 | 82.3 | 75 | 7.74 | 37.2a | 0.78 | 19 | 54 |
| 512 | Splash | 64,8W,7 | x | - | 1350 | 1.24 | 2.07 | 34.4 | 84.4 | 49 | 7.39 | 16.1 | 1.90 | 38 | 20760 |
| 513 | Indiana | 64,10W,15 | x | - | 1310 | 1.28 | 3.88 | 31.0 | 82.6 | 41 | 7.17 | 14.2 | 2.30 | 56 | 140 |
| 601 | Greenwood | 64,2E,21 | - | - | 1869 | 1.01 | 3.25 | 19.4 | 84.9 | 26 | 6.80 | 5.0 | 3.39 | 825 | 2634 |
| 602 | Crystal | 64,2E,5 | x | - | 1689 | 1.09 | 4.55 | 26.5 | 88.8 | 35 | 7.18 | 9.8 | 2.65 | 84 | 286 |
| 603 | West Pike | 65,2E,27 | x | - | 1556 | 1.05 | 5.21 | 33.4 | 88.9 | 44 | 7.19 | 11.7 | 2.42 | 303 | 3546 |
| 604 | Pemmican | 65,2E,22 | x | - | 1775 | 1.05 | 3.04 | 32.6 | 83.9 | 45 | 7.25 | 11.9 | 2.32 | 10 | 54 |
| 605 | Gogebic | 65,2E,30 | x | - | 1672 | 1.09 | 3.18 | 37.2 | 84.9 | 53 | 7.35 | 15.3 | 2.07 | 25 | 126 |
| 606 | Rocky | 64,1E,2 | x | - | 1618 | 0.97 | 2.79 | 37.6 | 83.5 | 53 | 7.24 | 13.3 | 2.22 | 31 | 309 |
| 607 | Ram | 63,1W,9 | x | - | 1900 | 0.92 | 2.64 | 27.1 | 80.8 | 38 | 7.29 | 14.5 | 2.27 | 27 | 68 |
| 608 | Little Trout | 63,1W,5 | x | - | 1810 | 0.98 | 2.71 | 30.8 | 87.2 | 43 | 7.28 | 13.2 | 2.24 | 52 | 196 |
| 609 | Gaskin | 64,2W,22 | x | - | 1869 | 1.12 | 3.03 | 25.5 | 86.4 | 33 | 6.93 | 7.4 | 2.94 | 166 | 3331 |
| 610 | Partridge | 65,1W,30 | x | - | 1770 | 1.31 | 3.94 | 40.5 | 83.8 | 58 | 7.39 | 18.3 | 1.82 | 47 | 286 |
| 611 | Topper | 65,2W,27 | - | - | 1820 | 0.95 | 2.99 | 44.1 | 87.5 | 65 | 7.54 | 23.7 | 1.51 | 19 | 87 |
| 612 | Tepee | 66,4W,34 | - | - | 1490 | 1.06 | 3.19 | 25.9 | 73.5 | 34 | 7.08 | 10.1 | 2.59 | 36 | 149 |
| 701 | Sawbill | 62,4W,7 | x | - | 1787 | 1.02 | 2.14 | 23.7 | 80.5 | 32 | 6.98 | 8.9 | 2.93 | 354 | 5714 |
| 702 | Alton | 62,5W,1 | x | - | 1802 | 1.09 | 2.90 | 24.2 | 83.5 | 32 | 6.85 | 8.7 | 3.02 | 397 | 1142 |
| 703 | Alice | 63,7W,9 | x | - | 1514 | 1.12 | 3.49 | 22.4 | 80.7 | 28 | 6.95 | 7.6 | 2.99 | 613 | 37637 |
| 704 | Insula | 63,8W,13 | x | - | 1512 | 1.26 | 2.61 | 23.0 | 83.2 | 29 | 7.15 | 7.9 | 2.78 | 1271 | 47579 |
| 705 | Snowbank | 64,8W,19 | x | - | 1425 | 1.03 | 5.08 | 29.9 | 83.6 | 40 | 7.07 | 11.8 | 2.45 | 1886 | 6950 |
| 706 | Lake Two | 63,9W,27 | x | - | 1485 | 1.01 | 2.48 | 22.8 | 80.2 | 31 | 7.02 | 8.3 | 2.87 | 214 | 61845 |

(continued)

TABLE D-5. (continued)

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 707 | Clearwater | 62,9,5 | x | - | 1510 | 1.08 | 2.62 | 26.3 | 84.9 | 35 | 7.37 | 11.3 | 2.65 | 253 | 1792 |
| 708 | Peltro | 62,9,8 | x | - | 1510 | 1.09 | 2.89 | 25.0 | 86.4 | 32 | 7.29 | 10.4 | 2.52 | 134 | 330 |
| 709 | Gabbro | 62,10,14 | x | - | 1453 | 0.75 | 1.55 | 37.5 | 70.5 | 58 | 7.64 | 22.1 | 1.49 | 552 | 103070 |

[a] x = within, - = not within

[b] Potentiometric titration of low alkalinity ($\leq$ 20 mg/l $CaCO_3$) Standard Methods, 14th ed., Section 403.4d employing a radiometer DTS-600 series digital titration system.

[c] Calcite saturation Indices (CSI) calculated to Conroy, Jeffries and Kramer (1974), and Kramer (1974)

* Initial sampling 11-7-78 (water sample); second sampling 11-15-78 (probe data collected)

TABLE D-6 SUMMARY OF SNOW DATA FROM THE BWCA-VNP, MARCH 1978. (COMPONENT CONCENTRATIONS IN MELTED SNOW AND CALCULATED LOADINGS)

| Components: | $H^+$ as H | $NH_4^+$ as N | $SO_4^{-2}$ as $SO_4$ | $NO_3^-$ as $NO_3$ | $Cl^-$ as Cl | $F^-$ as F | B as B | Cr as Cr | Mn as Mn | Hg as Hg |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | dissolved / acid exchangeable | dissolved / acid exchangeable | dissolved / acid exchangeable | total |
| Canopy Type: | | | | | | | | | | |
| Coniferous (19 sites, mean moisture content of snow 9 cm) | | | | | | | | | | |
| Mean concentration (mg/l) | 0.0139 (pH 4.85) | 0.089 | 1.80 | 1.33 | 0.27 | 0.025 | <0.005 / 0.0021<* | <0.005 / 0.0014<* | 0.012<* / 0.0052 | 0.000 014<* |
| Mean loading kg/ha | 0.0121 | 0.075 | 1.62 | 1.15 | 0.24 | 0.020 | <0.005 / 0.0016<* | <0.005 / 0.0013<* | 0.011<* / 0.0046 | 0.000 013<* |
| Deciduous (17 sites, mean moisture content of snow 13 cm) | | | | | | | | | | |
| Mean contentration (mg/l) | 0.0170 (pH 4.77) | 0.11 | 1.08 | 1.20 | 0.15 | 0.020 | <0.005 / 0.0018<* | <0.005 / 0.0014<* | 0.008<* / 0.004<* | 0.000 011<* |
| Mean loading kg/ha | 0.0225 | 0.10 | 1.41 | 1.46 | 0.27 | 0.019 | <0.005 / 0.0017<* | <0.005 / 0.0018<* | 0.009<* / 0.004<* | 0.000 015<* |
| Mean Watershed Values (assuming coniferous 60%, deciduous 40%) | | | | | | | | | | |
| Mean concentration (mg/l) | 0.0151 (pH 4.82) | 0.099 | 1.53 | 1.29 | 0.22 | 0.023 | <0.005 / 0.0020<* | <0.005 / 0.0014<* | 0.011<* / 0.005 | 0.000 013<* |
| Mean loading kg/ha | 0.0163 | 0.086 | 1.53 | 1.29 | 0.22 | 0.020 | <0.005 / 0.0010<* | <0.005 / 0.0015<* | 0.010<* / 0.005 | 0.000 013<* |

*< Computed values of the mean over-estimate of the acutal value because the non-measureable values were entered as the numerical less-than value, rather than zero.

TABLE D-7. MERCURY CONCENTRATIONS IN FISH FROM SELECTED NORTHERN MINNESOTA LAKES[a]

| Lake | Species | Number of fish | Range, length (inches) | Range, ppm Hg | Expected size (inches) at the 0.5 ppm threshold |
|---|---|---|---|---|---|
| Vermilion | Walleye | 30 | 12.4 - 23.0 | 0.09 - 0.73 | 25 |
| | Northern pike | 22 | 17.6 - 33.0 | 0.10 - 0.47 | N/A[b] |
| Trout | Walleye | 25 | 14.0 - 21.4 | 0.20 - 0.95 | 18 |
| | Northern pike | 5 | 20.0 - 30.0 | 0.25 - 0.98 | 24 |
| | Lake trout | 15 | 15.0 - 24.8 | 0.11 - 0.50 | |
| | Smallmouth bass | 5 | 11.3 - 14.8 | 0.28 - 0.42 | |
| Pelican | Walleye | 6 | 9.5 - 25.9 | 0.10 - 0.87 | 20 |
| | Northern pike | 25 | 10.8 - 28.2 | 0.13 - 0.69 | 30 |
| | Smallmouth bass | 5 | 13.1 - 15.4 | 0.13 - 0.36 | |
| Basswood | Walleye | 28 | 12.5 - 29.0 | 0.24 - 1.95 | 15 |
| | Northern pike | 25 | 15.5 - 25.5 | 0.23 - 0.86 | 21 |
| Sand Point | Walleye | 8 | 11.8 - 21.0 | 0.25 - 2.67 | 13 |
| | Northern pike | 7 | 19.2 - 24.5 | 0.21 - 0.83 | 22 |
| Namakan | Walleye | 10 | 11.5 - 17.5 | 0.13 - 0.58 | >30 |
| | Northern pike | 4 | 15.5 - 23.3 | 0.09 - 0.28 | N/A |
| Kabetogama | Walleye | 26 | 9.4 - 21.3 | 0.03 - 0.40 | >30 |
| | Northern pike | 10 | 15.8 - 30.5 | 0.09 - 0.24 | |
| Burntside | Walleye | 6 | 11.2 - 24.0 | 0.18 - 0.95 | 17 |
| | Northern pike | 34 | 19.5 - 32.0 | 0.19 - 1.01 | 28 |
| | Lake trout | 4 | 21.0 - 28.0 | 0.37 - 0.76 | |
| | Smallmouth bass | 9 | 9.0 - 18.0 | 0.27 - 0.65 | |
| White Iron | Walleye | 26 | 11.0 - 21.5 | 0.26 - 0.78 | 15 |
| | Northern pike | 25 | 15.2 - 23.7 | 0.21 - 0.58 | 24 |
| | White suckers | 20 | 12.8 - 20.0 | 0.03 - 0.27 | |
| | Yellow perch | 25 | 5.2 - 10.6 | 0.10 - 0.68 | |
| Fall | Walleye | 24 | 9.3 - 18.8 | 0.21 - 0.53 | 25 |
| | Northern pike | 25 | 14.0 - 40.7 | 0.15 - 1.29 | 23 |
| | White suckers | 24 | 8.8 - 22.1 | 0.04 - 0.35 | |
| | Yellow perch | 24 | 5.2 - 11.3 | 0.09 - 0.50 | |
| Gunflint | Walleye | 24 | 10.0 - 26.0 | 0.21 - 1.23 | 16 |
| | Northern pike | 18 | 14.0 - 28.0 | 0.12 - 0.56 | 29 |
| Colby | Northern pike | 20 | 6.7 - 21.0 | 0.09 - 0.80 | 18 (est.) |
| | White suckers | 21 | 13.1 - 19.6 | 0.09 - 0.62 | |
| | Yellow perch | 25 | 5.3 - 8.6 | 0.15 - 0.53 | |
| Greenwood | Northern pike | 25 | 14.9 - 27.7 | 0.31 - 0.75 | 19 (est.) |
| | White suckers | 25 | 8.5 - 18.8 | 0.07 - 0.56 | |
| | Yellow perch | 25 | 5.4 - 10.9 | 0.08 - 0.68 | |
| Gabbro | Northern pike | 21 | 17.6 - 34.5 | 0.22 - 0.95 | 22 (est.) |
| | White suckers | 25 | 8.8 - 22.0 | 0.03 - 0.20 | |
| | Yellow perch | 25 | 5.7 - 9.6 | 0.08 - 0.88 | |
| Pike River | Walleye | 8 | 14.2 - 29.0 | 0.46 - 1.50 | |

[a] Data from: Minnesota Department of Natural Resources. 1978. Mercury levels in eleven northeastern lakes, 1977. Spec. Publ., Ecol. Serv. Sect. (mimeo). 34 p.

[b] N/A = not applicable.

TABLE D-8. RELATIVE SIZES (INCHES) AND MERCURY CONTENT (PPM) OF WALLEYE FROM 12 NORTHERN MINNESOTA WATERS, 1977[a]

| Water | Total number of fish | 0.5 ppm Hg and over | Under 0.5 ppm Hg | Under 15 in. | 15 in. and over | Under 15 in., under 0.5 ppm | Under 15 in., 0.5 ppm and over Hg | 15 in. and over, under 0.5 ppm | 15 in. and over, 0.5 ppm and over |
|---|---|---|---|---|---|---|---|---|---|
| Basswood L. | 28 | 16 | 12 | 9 | 19 | 7 | 2 | 5 | 14 |
| Burntside L. | 6 | 2 | 4 | 3 | 3 | 3 | 0 | 1 | 2 |
| Fall L. | 24 | 2 | 22 | 17 | 7 | 17 | 0 | 5 | 2 |
| Kabetogama L. | 26 | 0 | 26 | 8 | 18 | 8 | 0 | 18 | 0 |
| Gunflint L. | 24 | 10 | 14 | 8 | 16 | 8 | 0 | 6 | 10 |
| Namakan L. | 10 | 2 | 8 | 5 | 5 | 3 | 2 | 5 | 0 |
| Sand Point L. | 8 | 6 | 2 | 2 | 6 | 1 | 1 | 1 | 5 |
| Pelican L. | 6 | 2 | 4 | 2 | 4 | 2 | 0 | 2 | 2 |
| Vermilion L. | 30 | 2 | 28 | 12 | 18 | 12 | 0 | 16 | 2 |
| Trout L. | 25 | 6 | 19 | 9 | 16 | 8 | 1 | 11 | 5 |
| Pike River | 8 | 5 | 3 | 1 | 7 | 1 | 0 | 2 | 5 |
| White Iron L. | 26 | 9 | 17 | 17 | 9 | 14 | 3 | 3 | 6 |
| Total | 221 | 62 | 159 | 93 | 128 | 84 | 9 | 75 | 53 |
| Percentage (based on 211 fish)[b] | 100 | 28 | 72 | 42 | 58 | 38 | 4 | 34 | 24 |

[a] Data from Minnesota Department of Natural Resources (1978). Mercury levels in eleven northeastern lakes, 1977. Spec. Publ., Ecol. Serv. Sect. (mimeo). 34 p.

[b] Of 128 fish 15 in. and over, 59% contained under 0.5 ppm Hg and 41% contained 0.5 ppm Hg and over. Of 93 fish under 15 in., 90% contained under 0.5 ppm Hg and 10% contained 0.5 ppm and over.

TABLE D-9. RELATIVE SIZES (INCHES) AND MERCURY CONTENT (PPM) OF NORTHERN PIKE FROM 14 NORTHERN MINNESOTA LAKES, 1977[a]

| Water | Total number of fish | 0.5 ppm and over | Under 0.5 ppm | Under 21 in. | 21 in. and over | Under 21 in., under 0.5 ppm | Under 21 in., 0.5 ppm and over | 21 in. and over, under 0.5 ppm | 21 in. and over, 0.5 ppm and over |
|---|---|---|---|---|---|---|---|---|---|
| Basswood L. | 25 | 10 | 15 | 13 | 12 | 10 | 3 | 5 | 7 |
| Burntside L. | 34 | 8 | 26 | 2 | 32 | 2 | 0 | 24 | 8 |
| Fall L. | 25 | 8 | 17 | 17 | 8 | 16 | 1 | 1 | 7 |
| Kabetogama L. | 10 | 0 | 10 | 4 | 6 | 4 | 0 | 6 | 0 |
| Gunflint L. | 18 | 1 | 17 | 12 | 6 | 12 | 0 | 5 | 1 |
| Namakan L. | 4 | 0 | 4 | 3 | 1 | 3 | 0 | 1 | 0 |
| Sand Point L. | 7 | 5 | 2 | 4 | 3 | 4 | 0 | 1 | 2 |
| Pelican L. | 25 | 2 | 23 | 14 | 11 | 14 | 0 | 9 | 2 |
| Vermilion L. | 22 | 0 | 22 | 5 | 17 | 5 | 0 | 17 | 0 |
| Trout L. | 5 | 2 | 3 | 1 | 4 | 1 | 0 | 2 | 2 |
| White Iron L. | 25 | 1 | 24 | 18 | 7 | 18 | 0 | 6 | 1 |
| Colby L. | 20 | 9 | 11 | 19 | 1 | 11 | 8 | 0 | 1 |
| Greenwood L. | 25 | 7 | 18 | 22 | 3 | 18 | 4 | 0 | 3 |
| Gabbro L. | 21 | 12 | 9 | 10 | 11 | 8 | 2 | 4 | 7 |
| Total | 266 | 65 | 201 | 144 | 122 | 126 | 18 | 81 | 41 |
| Percentage (based on 266 fish)[b] | 100 | 24 | 76 | 54 | 46 | 47 | 7 | 30 | 15 |

[a] Data from Minnesota Department of Natural Resources (1978). Mercury levels in eleven northeastern lakes, 1977. Spec. Publ., Ecol. Serv. Sect. (mimeo). 34 p.

[b] Of 122 fish 21 in. and over, 34% contained 0.5 ppm Hg and over and 66% contained under 0.5 ppm Hg. Of 144 fish under 21 in., 12.5% contained 0.5 ppm Hg and over and 87.5% contained under 0.5 ppm Hg.

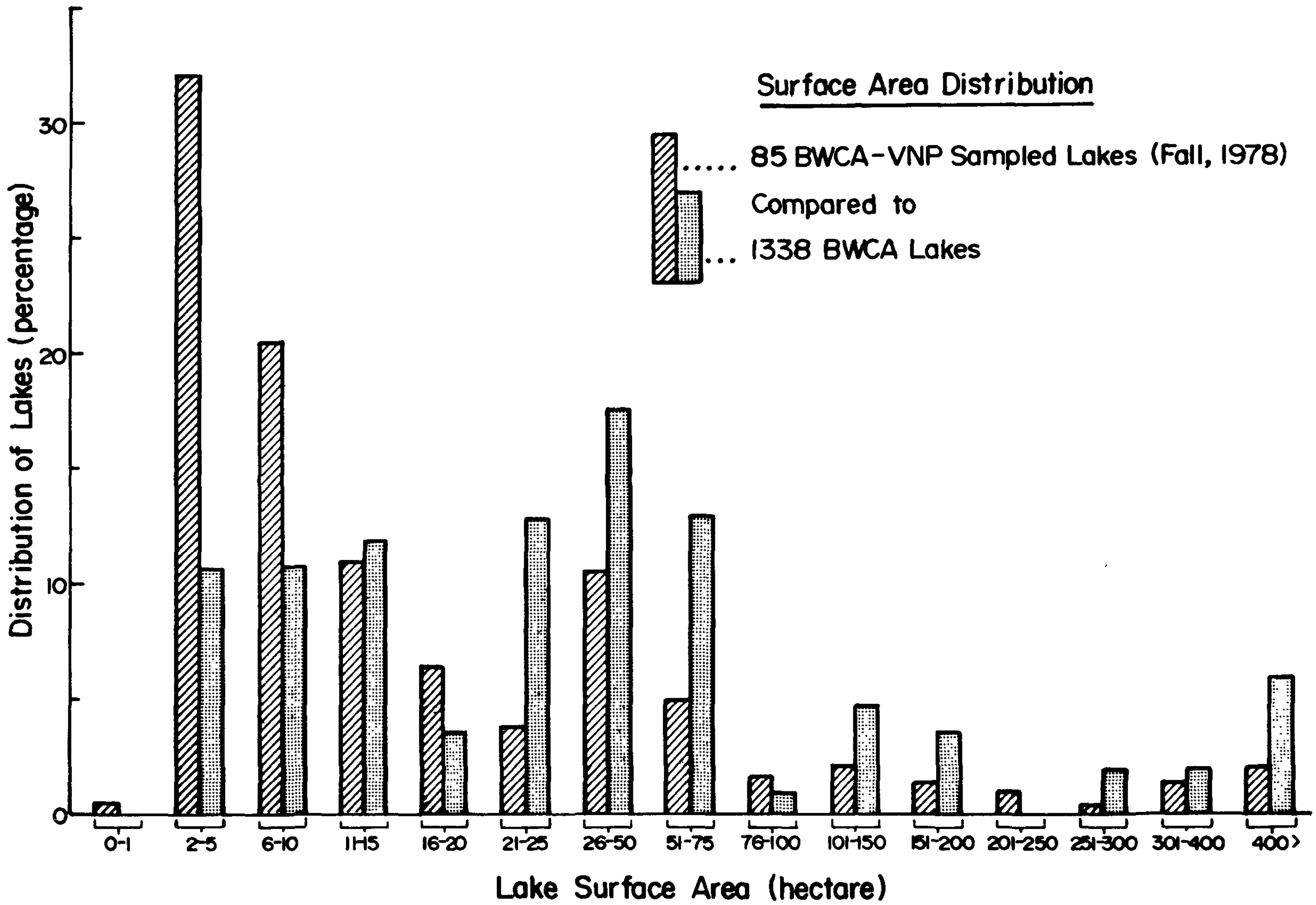


Figure D-1. Distribution of lake surface areas for BWCA and VNP Fall 1978 sampling.

| TECHNICAL REPORT DATA<br>*(Please read Instructions on the reverse before completing)* | | |
|---|---|---|
| 1. REPORT NO.<br>EPA-600/3-80-044 | 2. | 3. RECIPIENT'S ACCESSION NO. |
| 4. TITLE AND SUBTITLE<br>Impacts of Airborne Pollutants on Wilderness Areas Along the Minnesota-Ontario Border | | 5. REPORT DATE<br>May 1980 issuing date<br>6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S)<br>Gary E. Glass<br>Orie L. Loucks | | 8. PERFORMING ORGANIZATION REPORT NO. |
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| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Environmental Research Laboratory - Duluth, MN<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Duluth, Minnesota 55804 | | 13. TYPE OF REPORT AND PERIOD COVERED<br>14. SPONSORING AGENCY CODE<br>EPA/600/03 |
| 15. SUPPLEMENTARY NOTES | | |

16. ABSTRACT

The goal of this study was to examine previously unanswered questions concerning potential effects of the proposed Atikokan, Ontario power plant on ecosystems in the Boundary Waters Canoe Area Wilderness (BWCA) and Voyageurs National Park (VNP) of Minnesota by using the most relevant data and analytical methods. The principal steps were to focus on: (1) the ultimate deposition of emissions from the plant (rather than only on pollutant concentrations), (2) the use of a time-varying grid model with provision for atmospheric transformations, and (3) a detailed review of all available data from the region on atmospheric deposition of pollutants, water quality, and effects. The results are considered in relation to a review of responses by terrestrial and aquatic organisms to changes in the chemistry of this environment.

The sensitive aquatic and terrestrial receptors in the BWCA-VNP region are described quantitatively, and this information is assessed in terms of what is currently known about the impacts of atmospheric pollutants. Specific conclusions based on factual information, probable consequences, and possible impacts of the proposed coal-fired power generating station at Atikokan are presented.

The study supports, in part, the conclusions reached previously concerning the predicted air concentrations of sulfur dioxide, but differs significantly with the conclusions concerning the significance of future impacts. When the total emissions from the proposed power plant are considered, the increased loadings of sulfuric and nitric acids, fly ash, and mercury as an addition over and above other regional sources will, with high probability, have significant consequences for the sensitive receptors in the BWCA-VNP region, especially for the future of sport fisheries and other aquatic resources.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|---|
| Air pollution<br>Water pollution<br>Acid rain<br>Investigations<br>Documentation<br>Modeling | Wilderness areas<br>Park areas<br>Plumes<br>Power Plants | Northern Minnesota<br>BWCA,<br>Boundary Waters Canoe Area Wilderness<br>Atikokan (Ontario)<br>Power Plant | 1313 06F<br>06T, 06P, 06S<br>08L08F |

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