

## **Assessment of Air Quality and Air Pollutant Impacts in Isle Royale National Park and Voyageurs National Park**

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Prepared for the US National Park Service

September 1, 2004

## EXECUTIVE SUMMARY

This report presents the concentrations, trends, and impacts of air pollutants in two national parks in the north central Midwest: Isle Royale National Park and Voyageurs National Park. Although far from major urban and industrial centers, these two parks are still subject to air pollution that may have negative impacts. In this report, we evaluate the major air pollutants that affect, or potentially affect, the parks; the major mechanisms by which air pollutants can cause harm; the regional characteristics of the parks that may cause vulnerabilities; and current data on air pollutants and their effects. The following represent major findings.

The air pollutants that are of most concern in Isle Royale and Voyageurs include mercury and persistent organic pollutants. Human and ecosystem exposure to these chemicals through fish consumption may be significant. Long range atmospheric transport of mercury and persistent organic pollutants (POPs) such as dioxins, polychlorinated biphenyls (PCBs), chlorinated pesticides, fluorinated compounds, and brominated flame retardants is the major source of these compounds in fish and other organisms in the waters of Isle Royale and Voyageurs. Exposure to many of these compounds has been positively linked to various reproductive, neurological, and developmental problems in humans and laboratory animals. For these reasons, the wildlife of Isle Royale and Voyageurs National Parks is at risk.

Preliminary data from the U.S. Environmental Protection Agency's National Fish Tissue Study show that the highest levels of dioxins and furans (PCDD/Fs) and PCBs in any fish from Minnesota were found in a fish collected in Voyageurs. These persistent organic compounds reach aquatic foodwebs through long-range atmospheric transport and subsequent deposition. Neither natural geological processes nor local anthropogenic point sources are major contributors to these compounds in fish from the two parks.

Unusually high concentrations of monomethyl mercury have also been reported in fish from Voyageurs. Like persistent organic pollutants, inputs of mercury to lakes in Voyageurs and Isle Royale are dominated by atmospheric sources. Mercury is deposited as or converted to monomethyl mercury and can accumulate to levels that

may be hazardous to humans and wildlife. Current concentrations of mercury in fish collected in or near Isle Royale and Voyageurs range from less than 100 ng/g d.w. to more than 1000 ng/g d.w. The highest concentrations are often found in older fish and top predators, although watershed characteristics may also cause elevated concentrations of mercury in fish.

The relationship between atmospheric concentrations of pollutants and fish burdens is not straightforward. That is, even though high concentrations of persistent organic pollutants and mercury have been found in fish from Voyageurs, it does not mean that atmospheric deposition is elevated in Voyageurs compared to the region. Accumulation of these compounds in fish is a result of one or both of two processes: food web dynamics that result in biomagnification of the pollutants in some fish; and water chemistry that influences the availability of the pollutants.

Food web dynamics have a major impact on the accumulation of atmospheric pollutants such as mercury and persistent organic pollutants. Fish that eat other fish will accumulate more of these compounds than fish that eat phytoplankton or aquatic plants. Interpretation of results is often confounded because the same fish species in different lakes do not necessarily have the same diet. The age of the fish also plays a role: older fish usually have higher concentrations of these compounds than do younger fish. The high concentration of PCDD/Fs and PCBs in a fish from Voyageurs may be a result of the age of the fish compared to the average age in the sample set.

Water chemistry can affect the transformation and availability of these chemicals. Recent data gathered by the Minnesota Pollution Control Agency found that high concentrations of monomethyl mercury in fish collected in Voyageurs correlate positively with dissolved organic carbon in the lake water. Researchers have tentatively concluded that water chemistry in some wetlands influences mercury accumulation in fish.

Air pollutants other than persistent organic pollutants and mercury are of less immediate concern, but may be used as indicators of long term trends in overall air quality. For example, tropospheric ozone concentrations are increasing in Voyageurs National Park, although the concentrations are much lower than in most regions of the United States, and there is no evidence for damage or negative impacts. Ozone

production in the region is limited by the concentration of nitrogen oxides in the area and efforts to reduce ozone should focus on reduction of nitrogen oxides. A major source of nitrogen oxides to Voyageurs are two pulp and paper plants immediately west of the park in International Falls, Minnesota and Fort Francis, Ontario.

Significant in-park sources of air pollutants exist at Voyageurs and include emissions of particulate matter, volatile organic compounds, and carbon monoxide. In-park sources include snowmobiles and outboard marine motors. Although concentrations are low and emissions data are limited, in-park sources of these pollutants may dominate total sources of some of these pollutants to the park. In any case, these emissions are typical for the region and there are no adverse impacts that clearly indicate that these sources should be reduced.

Major regional sources of air pollutants arriving at Voyageurs and Isle Royale originate south and southwest of the parks. Mining and ore processing are large sources of particulate matter, sulfur dioxide, and nitrogen oxides. Coal-fired power plants, including industrial and municipal utilities, are major sources of sulfur dioxides. Sulfur dioxides are a major cause of acid rain, although there is little indication of this problem at Voyageurs and Isle Royale. Sulfur dioxide emissions also contribute significantly to visibility impairment at Voyageurs National Park and at other sites in the region.

This report makes the following recommendations for improved monitoring and research in the two parks. With respect to monitoring, we summarize our recommendations as follows.

- 1) A trend monitoring program for contaminants of concern in fish and wildlife is needed. Concentrations of many air pollutants are not well estimated for either park due to lack of data for the region. In particular, concentrations of persistent, bioaccumulating organic compounds such as PCBs and monomethyl mercury are of concern. These compounds are accumulated in fish at levels that pose risk to humans and animals in the parks. Therefore, we recommend regular monitoring of mercury and a select set of organic contaminants in fish from the lakes that have already been identified as having elevated concentrations in fish. Monitoring of fish-eating birds such as loons is also warranted. Organic contaminants of concern include PCBs,

PCDD/PCDF, PBDEs, PFOS, and chlorinated pesticides. Such a program will only be successful if there are standardized procedures established for the collection, compositing, and analyses of samples. In order to link the mercury concentrations in fish to atmospheric deposition processes, monitoring of wet deposition of mercury is recommended (wet deposition dominates all atmospheric sources for mercury). The details of such a monitoring program (when, where, how often, using what methods, etc.) should be done with expert consultation both inside and external to the NPS, and with as much partnering with other agencies as possible.

2) Ongoing efforts to count and evaluate the number and activities of visitors to Voyageurs National Park are important. Snowmobile activity, in particular, should be monitored. Snowmobile use at Voyageurs is second only to Yellowstone in annual visits to a National Park. However, the trends and patterns of snowmobile use at Voyageurs are poorly understood, largely because there is no regularly monitored and uniform entry or permit system for snowmobile access to Voyageurs.

With respect to research, we also see several important areas that deserve attention and coordination.

1) Research is needed to compare the impact of local sources to more distant sources and their relative importance to air quality in the park. A modeling research study is recommended, with focus on ozone precursors, mercury, polycyclic aromatic hydrocarbons (PAHs) and current use pesticides. These pollutants have adequate emission inventories available to allow a successful modeling outcome. Modeling of deposition and accumulation of PCBs, PCDD/Fs, PBDEs and PFOS is also needed, but because the emission inventories have significant uncertainties, the outcome would not be identification of sources and source distance but should focus on trend assessment, food web dynamics, and potential for accumulation at harmful levels.

2) Research is also needed to identify the ecological risks associated with accumulated toxics in fish and fish-eating animals. Concentrations of mercury and POPs in fish are known for some lakes and some species, but the potential effects of these contaminants should be assessed. Research on birds of prey should continue and expansion of these studies to mammals should be considered. Research on the

mechanisms and endpoints of endocrine disruption in fish and wildlife need considerable study, with a focus on reproduction, growth, and development.

3) There is a need to better understand the processes of mercury cycling and bioaccumulation. We recommend that research on the relationships and linkages between atmospheric deposition, watershed characteristics and processes, methylation and de-methylation, and transfer up the foodweb. The composition and structure of the foodweb and their impacts on foodweb accumulation need further study. Isle Royale and Voyageurs are both ideally suited for research studies on these topics, as they have a variety of lakes with different characteristics that can be studied.

3) Improved estimates of emissions of organic contaminants from snowmobiles, marine engines, and other in-park activities are needed. Research is also needed to map the pathway between emissions, atmospheric sources and ecosystem impacts of many other pollutants. For example, it is not clear if accumulated PAHs, particulate matter, and hydrocarbons in snowpack are efficiently transferred to the lakes after snowmelt. In Voyageurs, this is an important question, due to the heavy use of snowmobiles and outboard marine engines.

Although excellent research has been conducted by the National Park Service and by universities and cooperating agencies, better coordination of research efforts and findings is needed. Regular reporting of park research in the peer reviewed literature and at national and international meetings is necessary to meet the goal of preserving the precious natural resources in Isle Royale National Park and Voyageurs National Park.

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## LIST OF ACRONYMS AND UNITS

### ACRONYMS

Al	Aluminum
As	Arsenic
B	Boron
$b_{\text{ext}}$	Light extinction coefficient
CAA	US Clean Air Act
CIRA	Cooperative Institute for Research in the Atmosphere
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
Cr	Chromium
Cu	Copper
EPA	Environmental Protection Agency
Fe	Iron
FLMs	Federal Land Managers
GLI	Great Lakes Initiative/Final Water Quality Guidance
Hg	Mercury
HgS	Cinnabar
H <sub>2</sub> S	Hydrogen sulfide
HAPs	Hazardous air pollutants
HC	Hydrocarbons
HCCP	High concentration conditional probability
HSCF	High concentration source contribution function
Hv	Sunlight
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory Model
IADN	Integrated Atmospheric Deposition Network
IMPROVE	Interagency <u>M</u> onitoring of <u>P</u> rotected <u>V</u> isual <u>E</u> nvironments Program
K	Potassium
LADCO	Lake Michigan Air Directors Consortium
MMHg	Monomethylmercury

N	Nitrogen
Ni	Nickel
NAAQS	National Ambient Air Quality Standards
NADP	National Atmospheric Deposition Program
NO <sub>x</sub>	Nitrogen oxides
NO <sub>2</sub>	Nitrogen dioxide
NP	National Park
NPS	National Park Service
NRC	National Research Council
P	Phosphorus
PAHs	Polycyclic aromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDD/F	Polychlorinated dibenzo-p-dioxin and dibenzofurans
PFOS	Perfluorooctane sulfonate
PM	Particulate matter
POPs	Persistent organic pollutants
PSD	Prevention of Significant Deterioration
RGM	Reactive gaseous mercury
RPO	Regional Planning Organization
RAQPs	Regional Air Quality Partnerships
S	Sulfur
SIPs	State Implementation Plans
SO <sub>x</sub>	Sulfur oxides
SO <sub>2</sub>	Sulfur dioxide
UP	Upper Peninsula of Michigan
USGS	US Geological Survey
VOC	Volatile organic compounds
VR	Visual range

## UNITS

dv	deciview
d.w.	dry weight
kg	kilogram
km <sup>-1</sup>	inverse kilometers
Mm <sup>-1</sup>	inverse megameters
ng	nanograms
pg	picograms
ppbv	parts per billion by volume
ppmv	parts per million by volume
µg	micrograms
µm	micrometers
µS	microsiemens

## ACKNOWLEDGEMENTS

The authors acknowledge the assistance of many National Park Service employees in providing data used in this document. In particular, the authors wish to thank Roger Andrascik and Jim Schaberl, both formerly at Voyageurs National Park, and Jack Oelfke, formerly at Isle Royale National Park.

Assistance with emissions data and figures was provided by David Joseph, Air Resources Division of the National Park Service. For assistance with snowmobile emissions, we thank Howard Haines at the Montana Department of Natural Resources and Conservation. Interviews with the following people added significantly to our knowledge of current research activities in the parks: Dr. Ed Swain and Dr. Bruce Monson, Minnesota Pollution Control Agency; Dr. Jeff Jeremiason, Gustavus Adolphus College; Dr. Jim Wiener and Dr. Mark Sandheinrich, University of Wisconsin-LaCrosse; Dr. Dan Engstrom, St. Croix Watershed Research Station of the Science Museum of Minnesota; Dr. David Krabbenhoft and Dr. Laurel Woodruff, US Geological Survey; and Dr. Bill Bowerman, Clemson University.

Visibility Sections were contributed by Air Resource Specialists, Inc., under Task Order 03 of NPS Contract C2350010850 by Kristi Savig (ARS) and Dee Morse (NPS).

Diana Thrift was our technical editor and we appreciate her constructive comments and suggestions.

This work was funded by the National Park Service, Tonnie Maniero, project director. We appreciate Tonnie's support and assistance with the extensive peer review and subsequent revision of this document. We also thank Jerrilyn Thompson for administering the grant through the Cooperative Park Studies Unit at the University of Minnesota.

## I. INTRODUCTION

### A. OBJECTIVES

This document serves as an overview of the air quality at two National Park Service units: Voyageurs National Park in northern Minnesota, and Isle Royale National Park in Lake Superior within the boundaries of the state of Michigan (See Figure I-1). Throughout this document the parks will be referred to as Voyageurs and Isle Royale. The overall air quality of the parks has been assessed with respect to concentrations, trends in concentrations, and trends in deposition of atmospheric compounds within the park. Deposition is a major consideration as it affects vegetation, biological ecosystems, and human health. We were able to make these assessments using the large volume of data collected by the NPS personnel and other researchers at the parks and in the region.

The focus is on several *criteria pollutants, visibility and hazardous air pollutants*. Criteria pollutants are those regulated under the US Clean Air Act (CAA) through National Ambient Air Quality Standards (NAAQS), and include nitrogen and sulfur oxides, ozone, lead, carbon monoxide, and particulate matter. Since ozone is a result of reactions of nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs), these compounds are assessed in this report as well. Visibility impacts in remote areas are primarily the result of fine particulate matter. Therefore, this report will focus on sources and effects of particulate matter in and near the two parks. Although 188 air pollutants are regulated as hazardous air pollutants by the CAA, this report will focus on those pollutants of greatest concern in the region—mercury, PCBs, and other bioaccumulating and persistent compounds. Many of these compounds are known to accumulate in fish at levels unsafe for human consumption.



Figure I-1. Map of the upper Midwestern US and Great Lakes regions, indicating locations of Voyageurs and Isle Royale

## **B. SCOPE AND ORGANIZATION**

In assessing the air quality of these two national parks, we have limited the scope of this report to the pollutants mentioned above. This document comprises four main sections, with Section II presenting an overview of the two parks.

Section III provides background information on the pollutants. We review the compounds of interest, including the major characteristics of the pollutants, their potential impacts on ecosystems and human health, and the mechanisms by which they cause their adverse effects. Because both Voyageurs and Isle Royale are water-based parks, the impact of these pollutants on water and aquatic life is of prime importance. Thus, we discuss the process by which the compounds are deposited and accumulated in water and aquatic organisms. Both terrestrial and aquatic receptors are considered, and potential and known impacts to these systems are discussed in some detail. Section III also includes a review of federal, state, and local regulations that apply to the pollutants discussed.

In Section IV, we review the regional characteristics of the upper midwest and Great Lakes states, and focus on known sources of air pollutants emitted in the region. Section IV also emphasizes major point sources within 250 km of the parks, as well as the potential for long-range transport to the region.

Section V describes monitoring and research activities in each of the parks, and gives concentrations, trends, and deposition of the pollutants. In this section, we describe and discuss relevant data collected in or near the parks, and compare the concentrations and effects of air pollutants at Voyageurs to that apparent in Isle Royale. Finally, the vulnerabilities or unique characteristics of the two units are considered and assessed based on the findings above.

The final sections, VI and VII, provide the appendices and literature citations.

## II. GENERAL DESCRIPTION AND HISTORY OF PARKS

### A. ISLE ROYALE NATIONAL PARK

#### 1. Description

Isle Royale National Park is an archipelago of more than 400 islands, the largest and most dominant being Isle Royale itself (see Figure II-1). The main island is comprised of glaciated basaltic rock lying from southwest to northeast in northwestern Lake Superior (48N latitude, 89W longitude). It is approximately 35 miles from Thunder Bay, Ontario, and 22 miles from Grand Portage, Minnesota. The entire park covers 571,700 acres and 99% of the 133,000 acre land base is designated as wilderness.

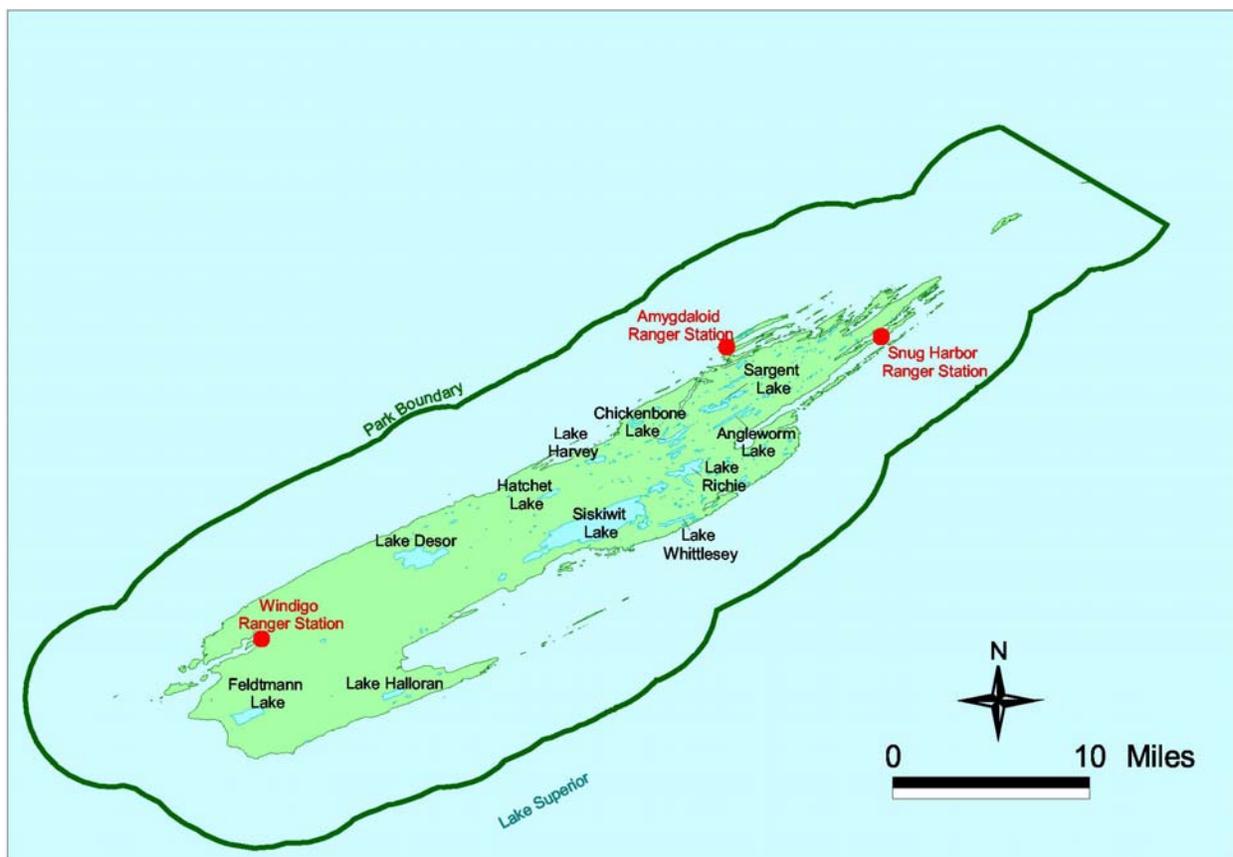


Figure II-1. Isle Royale National Park, in Lake Superior, MI, US.

Isle Royale is 45 miles long and 9 miles wide, and has 42 named inland lakes. Visitors come to Isle Royale for wilderness backpacking and hiking, wildlife observation, fishing, canoeing, kayaking, and boating. It has 165 miles of hiking trails and 36 campgrounds, which contain 244 campsites, of which 88 are shelters. There is one public lodge on the island located at Rock Harbor. Visitors reach the park by one of two ferries operated by the park contractor (Copper Harbor, MI, or Grand Portage, MN). Visitors can also arrive on the Park Service vessel, the Ranger III out of Houghton, MI. Approximately 15-20% of the visitors arrive by private boat. Generally, 15,000-18,000 people visit Isle Royale during its open season that runs from mid-April through October, and in FY2001 the island logged 15,306 visitors.

Isle Royale is currently covered by coniferous and northern hardwood forest at different stages of succession. White (*Betula papyrifera*) and yellow birch (*Betula lutea*) and aspen (*Populus tremuloides*) are the dominant species along the ridges, while balsam fir (*Abies balsama*) and white (*Picea glauca*) and black spruce (*Picea mariana*) are found along the lakes' shores and in valleys. Bogs and wetland areas contain white cedar (*Thuja occidentalis*). Its "north country" appearance is aided by the significant presence of mosses and lichens.

The island was first used by native North Americans who fished its productive waters and mined its rich copper deposits. Evidence for this use extends back at least 4500 years to 2500 B.C. European explorers identified Isle Royale in the early 1600s, and the island was initially used by fur traders. Commercial mining for copper (Cu) took place during three different periods in the 1800s, followed by logging and commercial fishing of the adjacent Lake Superior waters in the late 1800s through early 1900s. The first visitors to the islands for purely recreational purposes came in the early 1900s.

Isle Royale became official US territory as a result of the Treaty of LaPointe in 1842 and subsequent Compact of 1844 between the US government and the Ojibwa (Chippewa) Nation (Magnaghi 1977).

The US Congress voted to add Isle Royale to the list of National Parks on March 3, 1931. However, it was not until 1940 that all of the land for the park was acquired by the National Park Service. Approximately 20 private summer residents were granted

life leases, a few of which remain in effect today. There are still two family-run commercial fisheries permitted by the State of Michigan, and the National Park Service also maintains a demonstration commercial fishery for historical and educational purposes. The park was designated on April 3, 1940, but was not officially dedicated until 1946 following the end of WWII. In October 1976, the Congress designated that 98% of the park be maintained as wilderness; later acquisitions brought this value to 99%. This directs the NPS to manage the land “without permanent improvements or human habitation.” The park was designated a Class I air quality area in 1977. In 1980, Isle Royale was dedicated as an International Biosphere Reserve by the UN Educational Scientific and Cultural Organization—one of only 43 such designated places in the US. This designation is to preserve a classic boreal forest ecosystem. Although this park is one of the least accessible in the National Park system, it has the highest overnight backcountry use per acre of any national park.

The natural resources of particular significance in Isle Royale include its diverse and abundant natural fisheries, both that of the inland lakes and in the adjacent Lake Superior waters. For instance, the lake trout population around Isle Royale contains a number of wild strains that are extinct elsewhere in Lake Superior and the Great Lakes. The inland lakes are also valued for their inherent unspoiled beauty, and use by canoeists and kayakers. The wilderness itself is a highly valued resource, and it contains significant wildlife populations of moose, gray wolf, red fox, beaver, snowshoe hare, red squirrel, and deer mice, as well as selected species of reptiles and amphibians. The flora of the island includes species typical of northern Michigan, Wisconsin, and Minnesota. Its small diversity of wildlife species presents fairly simplified terrestrial foodchains, and has allowed scientists to study predator-prey relationships in ways that are not possible elsewhere. The most famous example of this is the more than 40 years of research into the moose-wolf relationship on the island, and its contribution to our understanding of keystone predators and how predation and food availability play their roles in controlling population size over time.

## B. VOYAGEURS NATIONAL PARK

### 1. Description

Voyageurs National Park consists of lakes, extensive waterways, forested woodlands, and more than 1,000 islands (see Figure II-2). The entire park covers 218,054 acres, of which ~84,000 acres are water. The main landmass, the Kabetogama Peninsula, is nearly surrounded by waterways, including Rainy Lake, Kabetogama Lake, and Namakan Lake and numerous small rivers, streams, and waterways. The peninsula is ~ 7.5 miles wide by ~ 26 miles long, and is primarily southern boreal forest, shaped by glaciation typical of Canadian Shield topography. The park was named for the French-Canadian voyageurs who used the waterways as part of the “transcontinental highway” for exploration and trade in the 18<sup>th</sup> and early 19<sup>th</sup> century.

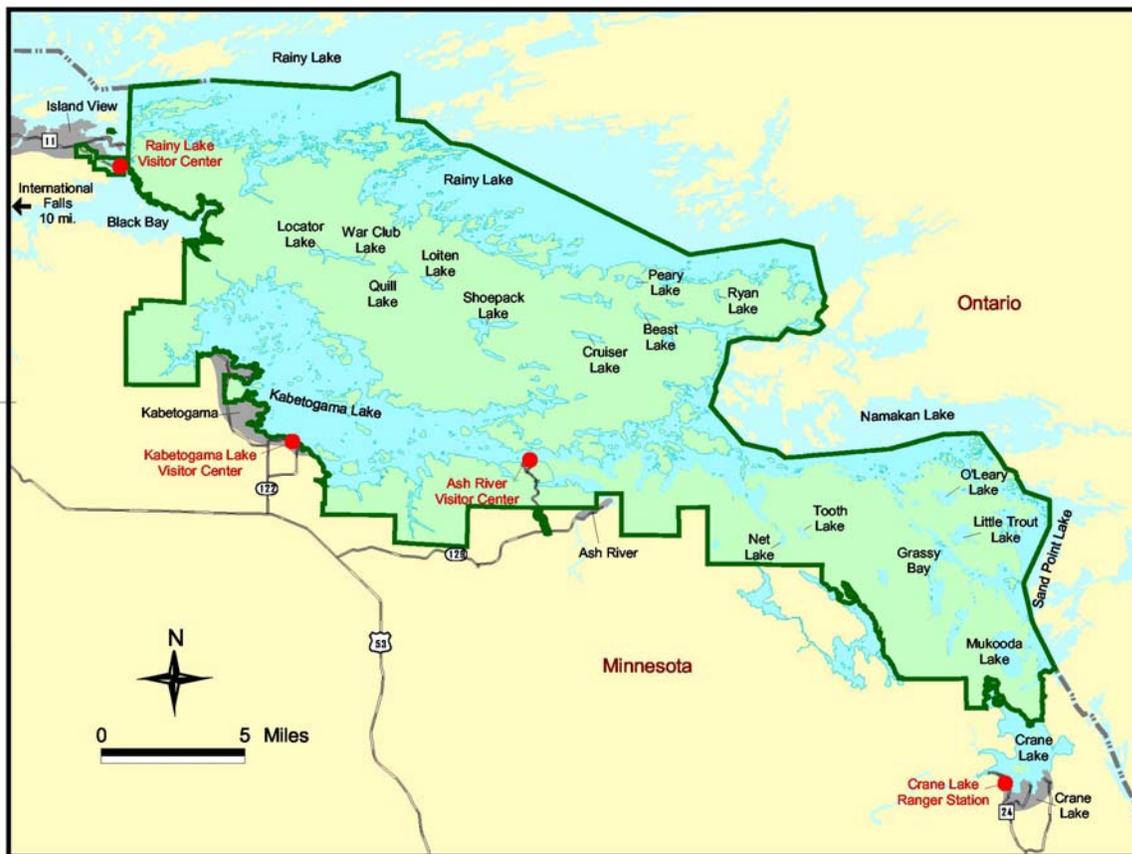


Figure II-2. Voyageurs National Park, MN, US.  
[http://www.lib.utexas.edu/maps/national\\_parks/](http://www.lib.utexas.edu/maps/national_parks/).

Wildlife populating the park includes river otter, Eastern timber wolf, bald eagles, black bears and moose. Activity by beavers has had significant impact on the waterways of the park—primarily from numerous beaver dams and resulting ponds.

The park was authorized in 1971 and established in 1975. The park was designated a Class I air quality area in 1977. Voyageurs does not contain designated wilderness, although a portion (58%—most of the terrestrial area) of the park was proposed as wilderness in 1992. The designation continues to await action from the Congress, and has been slowed in part due to protests from the local community of regular park users. Motorized vehicles are allowed in the park, and recreational uses of the park include motorized boats and snowmobiles.

The park is located in Northern Minnesota and shares a border with the Canadian province of Ontario. The closest cities, International Falls, MN and Fort Frances, Ontario, are approximately 12 miles away. Two other natural areas are nearby: Quetico Provincial Park in Ontario and the Boundary Waters Canoe Area Wilderness in Minnesota. Visitors arrive at the park by various means and through many access points. The four main roads to the park bring visitors to the three visitor centers and the ranger station. In the winter, only the visitor center at Rainy Lake, at the far west point of the park, remains open. However, groomed snowmobile trails in the winter encourage entrances at 4–5 central points. At all times of the year, visitors may enter the park at all other points. Estimates of park use are primarily determined using aerial surveys of boats, augmented by visitor surveys of number of fish caught and number of people per boat (creel surveys). A 1992 correlation based on the number of visitors counted at the visitor centers is also used in determining park use. Aerial surveys of snowmobiles in the park are less reliable and a more accurate counting method is currently in development. A February 2000 NPS report estimated that ~35,000 snowmobile visits occur each winter (National Park Service Air Resources Division, 2000a). In total, the existing estimates suggest that ~250,000 visits are made to the park each year.

Recreational opportunities at the park include motorboating, houseboating (79 current overnight houseboat sites, increasing to 108 in 2004), water skiing, canoeing, fishing, and hiking in the summer. In the winter, the park maintains 110 miles of

groomed snowmobile trails, 5 miles of snowshoeing trails, 7 miles of ice road through water ways, and about 20 miles of groomed cross country skiing trails. The Final General Management Plan \ Environmental Impact Statement contains an excellent description of park uses and proposed management plans and can be referred to for additional information and data on park use (National Park Service, 2001).

### **C. VULNERABLE ECOSYSTEMS**

The isolation and uniqueness that makes both of these parks valuable and significant also contributes to making them vulnerable to external disturbances. These disturbances range from natural occurrences to direct and indirect human activities. Natural disturbances, which include fires and blowdowns, are part of nature and thus part of the inherent legacy of a national park. Direct human activity and impacts, such as too many visitors in an area, can be monitored and controlled by management policies. The indirect human impacts—air pollution being a major concern—are much more difficult to evaluate and control. One of the current threats to the parks' ecosystems is that posed by air pollution.

Another vulnerable part of these ecosystems includes the water resources, made up of both inland lakes at both parks and Lake Superior at Isle Royale. The fact that a high proportion of the parks' surface areas are aquatic makes the parks susceptible to atmospheric deposition of a wide variety of pollutants, particularly those carried by long-range transport such as persistent organic pollutants (POPs) and mercury (Hg). The deposition of these pollutants leads to bioaccumulation of persistent compounds in the aquatic foodweb, leading to risks to the parks' fisheries and to animals and humans that consume fish. Some of the aquatic resources, particularly the inland lakes along the northeastern shore of Isle Royale, may be especially sensitive to acid precipitation because their small drainages and shallow surrounding soils offer little buffering capacity.

Isle Royale's flora and fauna are at particular risk from this threat due to the park's remoteness (impacted populations cannot be replenished by migration of new individuals into the park), and its harsh climate (plants grow slowly in long cold winters). The soil ecosystem is also potentially vulnerable, as the soil covering the Precambrian bedrock is shallow, and has a low cation exchange capacity. Acid precipitation could be

a major stress to this ecosystem, as excess acidity leaches nutrients from the soil, and adversely affects the microbial community (Moore and Moore, 1976). Mercury released by coal-burning power plants can also be transported to Isle Royale and end up in fish and wildlife.

Isle Royale has additional vulnerabilities due to its isolation from other land. It is a unique and fragile ecosystem, having low biodiversity and less complex terrestrial foodwebs. For example, the plant communities on Isle Royale are very vulnerable to stress as they have a narrow community structure, and because they may take up sulfur dioxide (SO<sub>2</sub>) and dissolved metals such as aluminum. SO<sub>2</sub> and acid precipitation can affect stomate and cuticle health, and lead to plant death at sufficient concentrations (Tamm and Cowling, 1976). Lichens are a critical part of the boreal forest ecosystem, due to their major role in nutrient cycling (Uliczka, 1999). Stress on the plant community translates to stress on the moose population, due to their high dependence on saplings and lichens for food. Stress on the moose population eventually leads to stress on the wolf population. Thus, changes to the plant community can have a domino effect on the terrestrial animal community composition and function.

Direct impact of air pollutants on vegetation is of relatively low risk at Isle Royale and Voyageurs, primarily as a result of the remote location and low air pollutant concentrations. A statistical analysis of the vulnerability of all flora at twenty-two midwestern parks (including Isle Royale and Voyageurs) shows the low risk from air pollution (Bennett and Banerjee, 1995). Vulnerability was defined in this study as a function of species sensitivity and species abundance. Air pollution was limited to impacts from sulfate (SO<sub>4</sub>), ozone and SO<sub>2</sub>.

This section has outlined ecosystem components that are potentially vulnerable to air pollutants. Their actual vulnerability would depend on the exposure concentrations and pathways of the pollutants of concern. Section II.B describes specific receptors and sensitive resources, and Section V.F addresses the known or likely vulnerabilities in the parks from specific airborne stressors.

#### **D. RISKS TO HUMAN HEALTH**

The primary health risks to humans are from atmospherically deposited contaminants that accumulate in the aquatic foodweb. Humans are the top predator of that foodweb, and may receive significant doses of POPs and mercury from consuming contaminated fish, even though the air concentrations leading to this contamination are low. This process of bioaccumulation results in chemical concentrations in fish tissue that are between 10,000 and 10,000,000 greater than the surrounding water, depending on the chemical. The US EPA and the departments of health for some states develop guidelines for the consumption of fish that are contaminated with environmental pollutants. The states and federal government use different strategies for determining their advisories, but in general they estimate how much fish can be consumed before there is an increased risk of a given health effect. Based on an estimate of an acceptable level of intake of chemical and known concentrations of contaminants in fish tissue, the guidelines recommend appropriate limits on fish consumption that would be protective of human health.

The Minnesota Department of Health (MDH) issues general guidance for consumption based on the species of fish (predators have higher concentrations than fish lower on the foodchain) and its size (older and larger fish have more contaminants) (MDH, 2003). The MDH also issues site-specific guidance that applies to a given lake (different lakes have different concentrations of contaminants) (MDH, 2003). Furthermore, the guidance stresses more stringent consumption limits on children and women of childbearing age, as these populations are considered to be more sensitive to the effects of POPs and mercury. For example, the Minnesota Department of Health advises against eating a meal of lake trout from Lake Superior that are greater than 34" in length more than once every 2 months. Their general guidance advises that no one consume any walleye greater than 30" in length from any Minnesota waters, including Lake Superior. The Michigan Department of Community Health advises that no one should eat walleye of any size caught in Michigan more than once per week, and that children and women of childbearing age should not eat them more than once per month.

The advisories for consumption of fish from inland lakes are driven by concentrations of Hg, while the advisories for consumption of fish from Lake Superior are driven by POPs, mostly PCBs. These contaminants are stored in the body, and can cross the placenta and impact fetal development. Mercury is a neurotoxin that affects the central nervous system, and is a developmental toxicant (Weihe, 1996; Grandjean et al., 1997; Grandjean and White, 1999; Mahaffey, 2000; NRC, 2000; Clarkson, 2002). The concerns from PCB exposures are primarily developmental, behavioral, and intellectual deficits in children born to women who consume fish during or before pregnancy (Jacobson, 1985; Jacobson et al., 1990b, a; Jacobson et al., 1992; Jacobson and Jacobson, 1993, 1996).

### **III. BACKGROUND**

The compounds considered in this report include nitrogen and sulfur compounds, ozone, hydrocarbons, mercury and lead, and persistent organic compounds. For these compounds, the chemistry, effects, deposition to vulnerable receptors, and current regulations are considered. Visibility impairment is reviewed in a similar fashion.

#### **A. COMPOUNDS / ISSUES OF INTEREST**

##### **1. Nitrogen and sulfur compounds**

Nitrogen (N) and sulfur (S) compounds are of concern in Voyageurs and Isle Royale because of their direct impacts on vegetation, their contribution to acid deposition and visibility impairment, and for nitrogen oxide's role in ozone production. Nitrogen in the atmosphere is found in the following forms: gaseous molecular  $N_2$ , which is ~80% of the tropospheric atmosphere and not a pollutant; gaseous and dissolved nitrogen oxides  $NO$ ,  $NO_2$  and  $NO_3$ ; dissolved organic nitrogen; and gaseous and dissolved ammonia. Nitrogen oxides ( $NO_x$ ) are produced and released from combustion processes, especially under lean fuel/air conditions and high temperatures. Although there are natural sources of  $NO_x$ , including lightning, chemical reactions in the upper atmosphere, and bacterial action in soil, anthropogenic sources tend to be more important at the near surface troposphere.  $NO_x$  can be an eye irritant, but its major impacts in the rural upper Midwest are its contribution to ozone formation and to reduced visibility. These impacts are further discussed below. Nitrogen is deposited as inorganic nitrogen (ammonia, nitrite, and nitrate) and organic nitrogen dissolved in rain (Seitzinger and Sanders, 1999). Both forms of dissolved nitrogen are of anthropogenic origin and can contribute to eutrophication of surface waters.

Sulfur oxides ( $SO_x$ ), especially  $SO_2$ , are the primary forms of sulfurous air pollutants. Coal combustion is a major source of  $SO_x$ , although diesel combustion, fuel oil combustion, and natural sources can be important contributors. Another form of atmospheric sulfur, hydrogen sulfide ( $H_2S$ ), can be found near sources of anaerobic decay of organic materials. Sources of  $H_2S$  in the upper Midwest include animal

manure and wastewater treatment, as well as natural release from swamps, bogs, and fens. At high concentrations, H<sub>2</sub>S can cause asthma-like symptoms and has an unpleasant odor. H<sub>2</sub>S does not travel far, as it is quickly oxidized. It is not considered an air pollutant of concern at Voyageurs and Isle Royale. Volcano eruption is a major global source of atmospheric sulfur, but is not considered in detail here.

One of the main concerns associated with NO<sub>x</sub> and SO<sub>x</sub> emissions is that they can form nitric and sulfuric acids, the dominant components of “acid rain.” The acidic nitrogen and sulfur species are mostly formed in the atmosphere, and then are transferred by precipitation events (rain, snow, fog) to surface waters, soils, and plant surfaces. These acids lower the pH of the receiving porewater, or surface waters, once the buffering capacity is used up, and can cause a wide range of adverse ecological effects. One of the primary effects is their toxicity to certain species of fishes and aquatic invertebrates. Sensitive species are affected at a pH of about 5.0, and as the pH decreases, more and more of the aquatic life begins to show the effects. In the soil and sediment environments, low pH is associated with increased leaching of metals (Cronan and Schofield, 1990) and nutrients, caused in part by the loss of cation exchange capacity (Stumm and Morgan, 1981). For example, increasing dissolved Al<sup>3+</sup> concentrations can cause root death in plants and aluminum accumulation in the gills of fish (Spry and Wiener, 1991). Nutrients loosely bound to the soil where they are available for uptake by plants are leached away, causing nutrient deficiencies. Gaseous SO<sub>2</sub> can also be taken up by plants through their stomata, causing leaf damage and dieback in understory plants and tree species.

## **2. Ozone**

Ozone (O<sub>3</sub>) is produced by a series of complex chemical reactions of nitrogen oxides and volatile organic compounds (VOCs) in the presence of light. These reactions have been extensively studied in order to reduce or control ozone concentrations, primarily in urban areas. Control of ozone by reductions in NO<sub>x</sub> and VOCs depends on the relative concentrations of the two precursors (NRC, 1992b). In urban areas, emissions of NO<sub>x</sub> from gasoline and diesel vehicles are high and therefore the areas are considered VOC-limited (Figure III-1). Reduction of ozone in urban areas

generally focuses on reduction of VOCs. In Voyageurs and Isle Royale, emissions of nitrogen oxides are low, but VOCs, which have important natural as well as anthropogenic sources (NRC, 1992b), are sufficiently high to support ozone formation. Any reduction of ozone at Voyageurs and Isle Royale is likely to require reductions of available  $\text{NO}_x$ .

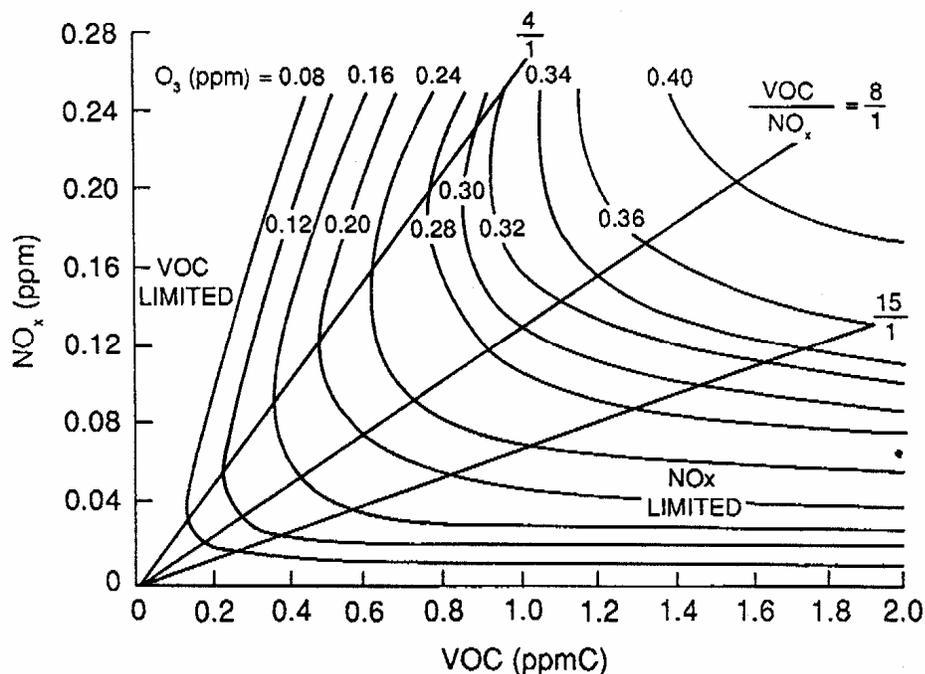


Figure III-1. Typical ozone isopleths used in U.S. EPA Empirical Kinetic Modeling Approach (EKMA). The  $\text{NO}_x$ -limited region is typical of locations downwind of urban and suburban areas, whereas the VOC-limited region is typical of highly polluted urban areas. Reproduced from Committee on Tropospheric Ozone, National Research Council, 1992 (NRC, 1992a).

Ozone exposure causes injury to human and ecological health. Human health impacts include lung and eye irritation, aggravation of asthma, and reduced lung capacity (Desqueyroux and Momas, 1999; Levy et al., 2001). In forests, ozone can damage vegetation through uptake and by passive diffusion through the plant cuticle or stomata. Effects include reduced growth not only of seedlings, but also of mature trees (McLaughlin and Downing, 1995; Sandermann, 1996; Samuelson and Kelly, 2001). Ozone has been identified as a cause for conspicuous needle necrosis in eastern pine trees, but evidence is not conclusive (it is conclusive for western pines) (Sanchini, 1990a; Bennett et al., 1994; Wenner and Merrill, 1998). In fact, studies of the effects of artificially supplied high ozone exposure indicate that some species acquire genetic resistance to ozone damage (Berrang et al., 1986; Karnosky and Berrang, 1986). In any event, adverse ozone effects have not been observed in vegetation at or near Isle Royale or Voyageurs (Wetmore, 1985; Kromroy et al., 1990; Sanchini, 1990b). Ozone concentrations, however, have been identified as being on an increasing trend in Voyageurs (National Park Service, 2001).

### **3. Visibility**

Visitors come to national parks in part to experience the breathtaking views of mountains, valleys, clear skies, and unique geologic features. Air pollution interferes with this experience to some degree in all national parks, particularly in the eastern US. The National Park Service monitors visibility conditions and supports studies to determine the causes of visibility impairment (haze) at many parks and wilderness areas nationwide. The purpose of this monitoring is to characterize current visibility conditions, identify the specific pollutants and their sources that contribute to visibility impairment, and document long-term trends to assess the effects of changes in pollutant emissions. The NPS cooperates and shares resources with other federal land management agencies, states, and the US EPA in the Interagency Monitoring of Protected Visual Environments (IMPROVE) Program, which is further described in Section IV.C.

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#### a. Visibility Impairment

Visibility impairment under the CAA visibility protection regulations is defined as “any humanly perceptible change in visibility.” In this document, visibility impairment is discussed using the CAA definition. Visibility can be altered by a variety of naturally occurring events, such as inclement weather, wildfires, or blowing dust, although visibility impairment as considered here excludes the effects of weather. Visibility impairment results from the scattering and absorption of visible light by gases and particles in the atmosphere. If there are no suspended particles in the air, the limit of natural visibility is determined by the amount of light scattered by “air molecules.” Scattering of visible light from “air molecules” is referred to as Rayleigh scattering, which means that the light is scattered evenly in both the forward and backward direction with a preferential scattering of shorter wavelengths (blue light); this scattering is responsible for the blueness of the sky. Rayleigh scattering is a function of air density and elevation.

Particles in the atmosphere, both naturally occurring and human-made, also scatter light. The amount of particle light scattering depends on the size and concentration of the particles, which in turn is affected by their physical and chemical properties. Fine particles (particles less than 2.5 micrometers [ $\mu\text{m}$ ] in diameter) have a greater scattering efficiency, on a per mass basis, than coarse particles (particles between 2.5 and 10.0  $\mu\text{m}$  in diameter). Particles with sizes near the wavelength of visible light (0.4  $\mu\text{m}$  to 0.7  $\mu\text{m}$ ) scatter more efficiently.

Chemical composition of particles (aerosols) also plays a role in their relative scattering efficiencies. Categories generally used to differentiate between fine particle chemical species that scatter light include sulfates, nitrates, organics, and soil. Sulfate and nitrate aerosols are hygroscopic, that is, they absorb water at higher relative humidity conditions. Growth of these aerosols at higher relative humidity conditions can dramatically enhance their effect on scattering. Coarse particles are generally not speciated and are generally lumped together in terms of their scattering efficiency.

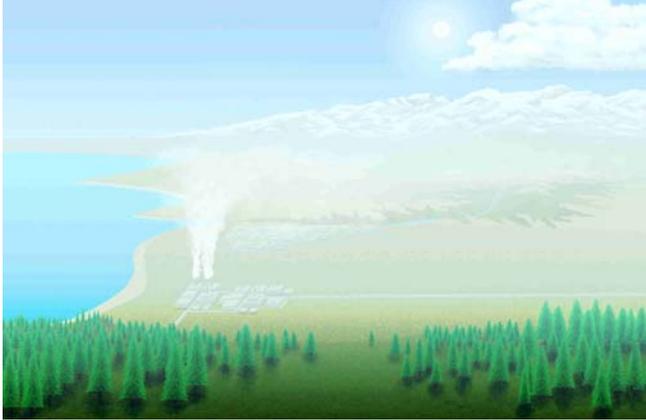
Some gases and particles can also absorb light. Nitrogen dioxide ( $\text{NO}_2$ ) is the only major visible light-absorbing gas in the lower atmosphere. It usually does not occur

in sufficient concentration in remote areas to make a major contribution to absorption. Elemental carbon (soot) is the dominant light-absorbing particle in the lower atmosphere.

#### b. Types of Visibility Impairment

Visibility impairment from atmospheric pollutants can generally be classified as 1) a uniform haze, 2) a layered haze, or 3) a plume. A uniform haze causes a general obscuration in the appearance of landscape features or the sky, causes changes in the color or the contrast among landscape features, or causes features of a view to disappear altogether. Pollutants suspended in a section of the atmosphere cause layered haze or plume(s) which become visible by the contrast or color difference between a layer or plume and a viewed background, such as a landscape feature or the sky. The view through a layered haze or plume will be altered in similar fashion to a uniform haze, but layered hazes and plumes are distinguished by a discernable boundary between the haze layer or plume and the cleaner atmosphere.

Pollutants mixed through the lower atmosphere cause uniform hazes. This mixing typically occurs over several diurnal cycles and the resulting haze can extend for hundreds of kilometers. This condition is shown schematically in Figure III-2a. Pollutants observed far from an emission source typically appear as elevated haze layers. Pollutants observed near the source of emissions often cause plume impacts (Figure III-2b). Plumes can occur under any wind and stability conditions, but are usually most severe with light wind speeds and stable thermal stratification. When plumes are emitted from elevated sources into a stable layer aloft, they can be transported for long distances with little vertical dispersion. Pollutants emitted into a stable layer at the earth's surface can form a ground-based layered haze (Figure III-2c). Layered hazes are usually associated with emissions that are more local in nature as opposed to pollutants that are transported over hundreds of kilometers. An observer positioned within a layered haze may perceive it as a uniform haze because layered haze boundaries can only be observed from an elevated position.



a. Uniform Haze: Air pollution uniformly obscures a scenic vista



b. Coherent Plume: A clearly defined source plume obscures a scenic vista.



c. Layered Haze: A pollutant layer can obscure part of a scenic vista.

Figure III-2abc. Effects of Air Pollution on a Scenic Vista.

### c. Visibility Scales/Metrics

To quantify visibility conditions and estimate the degree of impairment, several visibility scales/metrics can be employed. Depending on the application, several metrics may be used: contrast and color difference index, light extinction coefficient, visual range, or, degree of haziness.

For uniform haze circumstances as depicted in Figure III-2a where the pollutant loading becomes visible by contrast or color difference between the plume and the viewed background, contrast or color difference metrics are generally used.

Light extinction coefficient ( $b_{\text{ext}}$ ) represents the attenuation of light per unit distance of travel in some medium, such as air, and is measured in inverse length (e.g., inverse kilometers [ $\text{km}^{-1}$ ] or inverse mega meters [ $\text{Mm}^{-1}$ ]). In the atmosphere, the light extinction coefficient comprises attenuation of light due to scattering and absorption of light by particles and gases in the air (an aerosol).

Visual range (VR) is simply the greatest distance that a large, black object can be seen against a viewing background and is expressed as a distance (e.g., kilometers or miles). Though easily understood and valuable for airport safety considerations, visual range does not relate well to the perceived visual quality of a scene. A related metric is the Standard Visual Range. This metric is indexed to Rayleigh conditions at 1800 meters elevation rather than actual Rayleigh conditions at a specific location.

Visual range and the light extinction coefficient are inversely related (as visual range decreases, light extinction increases) for certain assumed viewing conditions; a VR of 391 km signifies the best possible visibility (particle free air, or Rayleigh conditions) and corresponds to a  $b_{\text{ext}}$  of  $10 \text{ Mm}^{-1}$ . These two metrics are usually used to quantify the level of impairment associated with uniform or ground-based layered hazes (Figures III-2a and c).

Neither visual range nor light extinction coefficient is linear with respect to increases or decreases in perceived visual air quality. For example, a 15 km change in visual range can result in a scene change either unnoticeably small or very apparent depending on the baseline visibility conditions. Therefore, another visibility metric, the haziness index (expressed as deciview [ $\text{dv}$ ]), was defined to index a constant fractional

change in extinction coefficient to visual perception (Pitchford and Malm, 1993). The advantage of this characterization is that equal changes in deciview are equally perceptible across different baseline conditions. Higher deciview values signify poorer visibility. A zero deciview corresponds to Rayleigh scattering (clean air), a visual range of 391 km or a  $b_{ext}$  of  $10 \text{ Mm}^{-1}$ . Figure III-3 below compares the three visibility metrics; extinction, visual range, and deciview (Malm 1999).

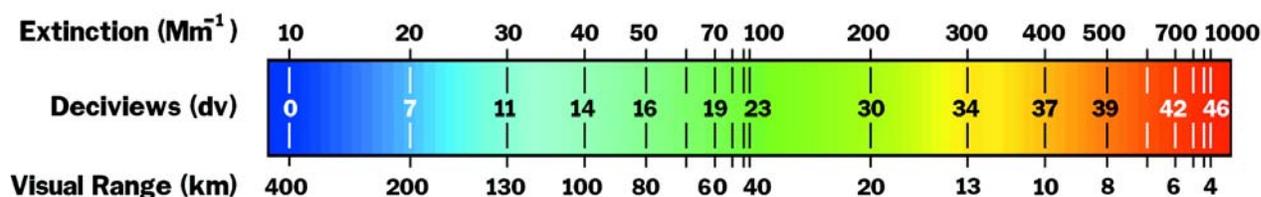


Figure III-3. Scale of Visibility Metrics.

Of the three visibility metrics, the light extinction coefficient ( $b_{ext}$ , commonly called extinction) is the characterization most used by scientists concerned with the assessment of the causes of visibility impairment. Extinction can be directly calculated from light transmittance measurements (measured extinction) or derived from measured particle concentrations using derived, analytic relationships between the concentrations of particles and gases and their contribution to the extinction coefficient (calculated extinction). Understanding these relationships provides a method of estimating how visibility would change with changes in the concentrations of these atmospheric constituents. This methodology, known as “extinction budget analysis,” is important for assessing the visibility consequences of proposed pollutant emission sources, or for determining the extent of pollution control required to meet a desired visibility condition. Calculated extinction is the primary visibility characterization provided in this report. The functional relationship among the three scales/metrics can be found in the Appendix.

#### 4. Carbon Monoxide

Carbon monoxide (CO) is a product of incomplete combustion of fuel. It is produced primarily as a result of insufficient oxygen content during combustion. Major

sources of CO include vehicle exhaust, and coal and other fossil fuel combustion. Natural sources include soil microbes, vegetation, lightning, and biomass burning—the latter being the largest natural source of CO. These natural sources are influenced by human activities, especially agricultural, that have led to significant changes in the magnitude and distribution of natural emissions in the past two centuries.

In the National Parks, hazards to animals and humans associated with non-forest fire-related CO have come from heavy vehicle use. For example, CO from snowmobiles has reached hazardous levels at some entrances to Yellowstone National Park. Although acute exposure to CO can cause death, chronic exposure is associated with headaches, fatigue, and reduced lung function. CO is not considered to cause significant direct damage to plants, although its role as a greenhouse gas could have indirect consequences for plant communities.

## **5. Volatile Organic Compounds**

Volatile organic compounds (VOCs) is a term used to describe the entire group of gas-phase organic compounds, excluding CO and carbon dioxide. VOCs can contain other elements in addition to hydrogen and carbon, and hence gas-phase hydrocarbons (HC) are considered a subset of VOCs. Motor vehicles are considered a major source of VOC emissions in the United States. During and after use, vehicles release VOCs through evaporative loss and exhaust. Exhaust emissions include incomplete combustion products, release of unburned fuel, and release of partially combusted or uncombusted lubrication oils from exhaust systems and leaks in the engine. Evaporative losses result from spills and vapor displacement during fueling, vaporization of fuel during cool down and during operation, and leaks in the engine or fuel tank. Gasoline and oil are major sources of alkane and aromatic emissions (Seinfeld and Pandis, 1998).

Hydrocarbons are an important component in the production of smog and have many natural and anthropogenic sources. Classes of HC most commonly found in the troposphere include alkanes, alkenes, alkynes, aromatics, aldehydes, ketones, acids, and alcohols. Table III-1 lists the major compounds in each class and typical sources and sinks.

Class	Compound	Typical Source	Sink
Alkanes	Methane	Microbial processes, natural gas	OH
	Ethane	Motor vehicles	OH
	Hexane	Motor vehicles	OH
Alkenes	Ethene	Motor vehicles, microbial processes	OH, O <sub>3</sub>
	Propene	Motor vehicles	OH, O <sub>3</sub>
	Isoprene	Vegetation	OH, O <sub>3</sub>
Alkynes	Acetylene	Motor vehicles	OH
Aromatics	Benzene	Motor vehicles	OH
	Toluene	Motor vehicles	OH
Aldehydes	Formaldehyde	Motor vehicles	<i>Hv (sunlight)</i> , OH
	Acetaldehyde	Motor vehicles	<i>Hv</i> , OH
	Acrolein		<i>Hv</i> , OH
Ketones	Acetone		<i>Hv</i> , OH
Acids	Formic Acid		Rain
	Acetic Acid		Rain
Alcohols	Methanol		OH

Adapted from Seinfeld and Pandis (1998), p78.

## 6. Mercury and Lead

Mercury (Hg) and lead (Pb) are heavy metal pollutants that are naturally occurring elements, but that have been mobilized by anthropogenic activities that have contaminated the environment. Historically, the major source of lead in the atmosphere was the burning of gasoline containing tetraethyl lead as an anti-knocking compound. In the US, leaded gasoline has been banned since 1976 and the concentrations of lead in the atmosphere have declined more than 90% (<http://www.epa.gov/oar>). There are still point sources of lead from industrial activities such as lead smelters, but lead contamination in remote areas such as Voyageurs and Isle Royale is not a concern (there are only 3 nonattainment sites for lead in the entire U.S., located in Missouri and Montana --<http://www.epa.gov/oar/oaqps/greenbk/lindex.html>).

Mercury is a global pollutant that has been mobilized into the atmosphere from many activities (Schroeder and Munthe, 1998). These include combustion sources, such as the burning of municipal trash and medical waste, burning of sulfur-containing coal in coal-fired power plants (coal contains HgS, or cinnabar), utility and industrial boilers, smelting, chlor-alkali plants, and gold extraction, as well as from uses of fungicides containing mercury in latex paints and the paper and pulp industry. Atmospheric mercury deposition in urbanized and industrial areas of North America and Europe peaked in the 1960s and 70s, while at the same time global deposition rates have continued to increase (Engstrom and Swain, 1997; Kamman and Engstrom, 2002). In the US, there have been significant attempts to reduce mercury emissions, from the banning of certain secondary uses (such as its use in latex paints, which was banned in the early 1990s) to imposing strict emission limits on hazardous and medical incinerators in 2002 ([http://www.epa.gov/grtlakes/bnsdocs/mercsrce/merc\\_srce.html](http://www.epa.gov/grtlakes/bnsdocs/mercsrce/merc_srce.html)). It has been estimated that human activities contribute 70–80% of the total annual mercury to the atmosphere (Fitzgerald, 1995) and that >95% of the atmospheric mercury in the vapor phase exists as elemental Hg. Numerous sediment core studies throughout the US and Europe have shown modern mercury deposition to range from 2.3 to 3.4 times greater than the deposition that occurred prior to industrialization (more than 150 years ago) (Lockhart et al., 1995; Fitzgerald and Steuer, 1997; Bindler et al., 2001a; Bindler et al., 2001b; Lamborg et al., 2002). Ice core samples from the Upper Fremont Glacier in Wyoming indicate that North America underwent a 20 percent increase in Hg deposition over the same period (Schuster et al., 2002).

There is a very dynamic redox cycle and exchange between the oceans and atmosphere (Mason and Sullivan, 1997). The remaining balance of the mercury exists as oxidized reactive gaseous mercury (RGM), particulate complexes of divalent mercury, and as monomethyl mercury (MMHg) (Stratton and Lindberg, 1995a, b). The total mass of mercury in the atmosphere has been estimated to be between 5000-6000 metric tons (Fitzgerald and Watras, 1989), with approximately half due to anthropogenic sources (Lindqvist et al., 1991).

Mercury in its elemental state has low reactivity and a long atmospheric residence time, thus allowing it to be mixed in the atmosphere on a global scale. The

oxidized forms are removed by wet deposition and dry deposition (Fogg and Fitzgerald, 1979; Mason et al., 1994). RGM is very soluble in water, and thus is effectively scavenged by wet deposition. Particulate forms are removed by dry deposition (Keeler et al., 1995). Once removed from the atmosphere, much of the deposited mercury ends up in aquatic systems due to direct deposition and transfer from the terrestrial ecosystem to aquatic ones (Mierle and Ingram, 1991).

Mercury effects on fish, and birds and mammals that eat contaminated fish, are of significant concern (Wiener et al., 2003). Our public health and wildlife concerns about mercury stem from exposure to the monomethylated form, MMHg. In anaerobic environments such as lake sediments, mercury is transformed to MMHg by microbial action, most notably by sulfur-reducing bacteria (Gilmour and Henry, 1991; Gilmour et al., 1992; Watras et al., 1995; Benoit et al., 2001a, b; King et al., 2001). A quantitative understanding of the factors that control the rate of mercury methylation is currently the subject of intense study. Methylation is controlled by the amount of mercury deposited to the watershed (Marvin-DiPasquale et al., 2000), its speciation (Benoit et al., 1999), the geomorphology of the watershed (St. Louis et al., 1994; St. Louis et al., 1996; Krabbenhoft et al., 1998; Marvin-DiPasquale et al., 2000), dissolved organic carbon (Miskimmin et al., 1992), the sulfate and acid loading to the watershed (Winfrey and Rudd, 1990; Gilmour and Henry, 1991; Branfireun et al., 1999; Branfireun et al., 2001; Kelly et al., 2003), and the bacteria community structure (King et al., 2000; King et al., 2001). Geomorphologic influences include the presence of wetlands, the size of the lake littoral area, and the total area of the watershed. The presence of fringing wetlands and littoral zones around a lake play an important role, as their sediments are the site of significant recycling of sulfur and thus sites where methylation can occur.

The largest field study ever conducted on mercury recycling is being conducted in the Experimental Lakes Area in northwestern Ontario, Canada. This multi-investigator, whole-ecosystem program named the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States, or METAALICUS, is adding 3 stable (non-radioactive) isotopic forms of mercury over a three year period to a lake, and monitoring the fate of the three mercury forms in an effort to better understand the fate and transport of mercury, and the factors that control its methylation to the toxic

MMHg form ([http://www.biology.ualberta.ca/old\\_site/metaallicus/metaallicus.htm](http://www.biology.ualberta.ca/old_site/metaallicus/metaallicus.htm)) (Gilmour et al., 2002; Hintelmann et al., 2002; Babiarz et al., 2003). A second large-scale field study is being conducted in the Marcel Experimental Forest located in the Chippewa National Forest in Minnesota, and is evaluating the effect of sulfate additions to wetlands and its role in stimulating mercury methylation.

The MMHg is soluble, and diffuses into the water column from sediments where it can be taken up by fish, accumulating in their muscle tissue by binding to thiol groups. MMHg is the most toxic form of mercury, and causes neurological, liver and kidney damage in animals and humans, as well as neurodevelopmental effects in children (Grandjean et al., 1997; Davidson et al., 2000; Mahaffey, 2000; NRC, 2000; Clarkson, 2002). Reproductive effects have also been documented in fish and fish-eating wildlife (Scheuhammer, 1991; Hammerschmidt et al., 2002). In 2002, 45 states in the US advised the public against unlimited consumption of freshwater fish due to their MMHg levels (<http://www.epa.gov/waterscience/fish/advisories/factsheet.pdf>). In addition, the US EPA has issued a mercury-based national fish consumption advisory for five species of oceanic fish. The EPA considers the maximum allowable no-effects dose of mercury in humans to be 0.1 ug/kg body weight/day, and this was recently supported by an independent study of the National Academy of Sciences (NRC, 2000). This reference dose was used by the EPA to derive a health-based MMHg criterion of 0.3 mg/kg in fish tissue that should not be exceeded to protect the health of consumers of noncommercial freshwater and estuarine fish. Approximately 8% of women in a 1999-2000 nationwide survey were found to have blood mercury levels above the EPA reference dose of 5.8 µg/L (Schober et al., 2003).

## **7. Persistent Organic Pollutants**

Persistent organic pollutants (POPs) include a wide variety of environmental chemical contaminants that share certain characteristics and properties. In general, POPs include those toxic chemicals that are known to be widely distributed in the environment. The common characteristic of “persistence” results from the pollutant’s tremendously slow degradation via chemical or biological means, and its relative unreactivity. These compounds are often toxic to animals and humans, as these same

properties often correlate with toxicity. POPs are semi-volatile and thus are found in the atmosphere, where their persistence allows them to be subject to long-range transport and global dispersion. Their semi-volatile nature also results in their being condensed at colder latitudes and readily exchanged between the atmosphere and oceans (Wania and Mackay, 1995). Thus, POPs are ubiquitous, and found from the Arctic to the Antarctic, far from their sources of origin.

Two broad categories of POPs are polyhalogenated organic compounds, and polycyclic aromatic hydrocarbons (PAHs). The polyhalogenated organic compounds include those banned by the Stockholm Convention of the United Nations Environment Programme (<http://www.pops.int>), including polychlorinated biphenyls (PCBs), DDT, dieldrin, aldrin, endrin, chlordane, toxaphene, hexachlorobenzene, heptachlor, and mirex, as well as other globally distributed POPs such as hexachlorocyclohexanes, polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/Fs), and polybrominated diphenyl ethers (PBDEs). The PAH family includes naphthalene (2 rings), anthracene (3 rings), phenanthrene (3 rings), pyrene (4 rings), chrysene (4 rings), fluoranthene (4 rings), benzo[a]pyrene (5 rings), benzo[e]pyrene (5 rings), perylene (5 rings), benzo[g,h,i]perylene (6 rings), and coronene (7 rings) (Harvey, 1991).

The POPs that have received the most attention are those that are hydrophobic and persistent, and thus bioaccumulate in foodwebs (Lipnick and Muir, 2001). Thus, even though these chemicals may occur in the environment in trace amounts, human and animal exposures may be substantial due to consumption of fish and other food that has accumulated these chemicals by several orders of magnitude (Connell, 1990).

Most POPs are completely anthropogenic in origin (Lipnick and Muir, 2001). Many of them are synthetic organic compounds produced for industrial purposes, such as PCBs, PBDEs, and hexachlorobenzene. Many are pesticides, such as DDT, toxaphene, chlordane, heptachlor, dieldrin, aldrin, endrin, and mirex. Others were never manufactured intentionally, but are by-products of industrial or combustion processes, such as the PCDD/Fs. The only class of POPs that has some natural sources includes the PAHs, which form from burning wood (e.g. forest fires) as well as from the combustion of fossil fuels.

In the context of Isle Royale and Voyageurs, the POPS of concern include PCBs, PCDD/Fs, DDT, toxaphene, and PAHs. In addition, reports of PBDEs in Great Lakes fish (Manchester-Neesvig et al., 2001; Stoner et al., 2003) have increased concerns and awareness regarding these chemicals. More background on these compounds and compound classes is provided below. All of these compounds are subject to long-range transport, and atmospheric removal by wet and dry deposition and gas sorption into water.

PCBs. This class of compounds contains 209 different possible structures or congeners, of which 110 are found in the environment (Swackhamer et al., 1996). They were manufactured in this country almost exclusively by Monsanto Chemical from 1929–76, and used in a wide variety of applications (National Research Council, 1979). Their principal use was as heat insulating fluids in capacitors and transformers, as PCBs are resistant to both thermal and biological degradation. They found additional uses as cutting fluids, hydraulic fluids, paint additives, ink carrier fluids, and as additives to construction materials. Their global distribution and toxicity led to their restriction and ban in the US in the mid-1970s. Exposure to PCBs can cause developmental and behavioral effects, cancer, malformations, neurotoxicity, and reproductive failure through a number of different mechanisms (Jacobson and Jacobson, 2001; Landrigan, 2001; Safe, 2003).

PCDD/Fs. This family of compounds forms during the combustion of organic materials and chlorine, such as in the burning of municipal waste containing chlorinated plastics (Safe, 1990; Safe, 1991). They are also formed during the kraft bleaching process used by many pulp and paper mills, and in the manufacture of pentachlorophenol. There are 75 possible congeners each of chlorinated dioxins and furans, although far fewer congeners end up in the environment (Fiedler, 2003). The dominant PCDD in air is octachlorodioxin, while the furans are dominated by several penta and hexachlorinated congeners. PCDFs are also trace contaminants in PCBs, and can be formed in much greater quantities when PCBs are burned, such as in an electrical fire. These compounds exert their toxic effects by binding to the aryl hydrocarbon hydroxylase (AHH) receptor (Safe, 1990). They are considered to be reproductive and developmental toxins, teratogens, carcinogens, and liver toxins (Safe,

1990). Accumulation of PCBs and PCDD/Fs in Great Lakes trout is likely the reason that this species is not self-sustaining in most areas of the Great Lakes (Cook et al., 2003) (Guiney et al., 1996).

*DDT and Toxaphene.* DDT has been used world-wide to control mosquitoes as vectors of infectious diseases, and for pest control in agriculture. In the 1960s, it was discovered that it and its stable degradation products (DDD, DDE) were ubiquitous environmental pollutants, and that DDT was causing certain raptor, colonial water bird, and song bird populations to plummet due to egg-shell thinning (De Rosa et al., 2002; Zitko, 2003). It was banned in the US in 1972, but was replaced for agricultural use by toxaphene, which became the most widely-used organochlorine pesticide in US history. Toxaphene is a complex mixture of more than 600 compounds (possibly thousands) and causes adverse effects in the lungs, liver, nervous system, and kidneys (Coelhan and Parlar, 1998; De Geus et al., 1999). It is mutagenic and a likely human carcinogen. It can interfere with calcium transport and bone formation. Toxaphene was restricted in 1982, and banned several years later (USEPA, 1982; Swackhamer et al., 1998).

*PAHs.* This class of compounds includes fused-ring structures having from 1-5 rings, and includes the substituted structures as well. Their major source to the environment is from energy production involving the combustion of fossil fuels, including gasoline, oil, diesel, wood, coal, etc (Harvey, 1991). They are known carcinogens, with benzo-(a)-pyrene being the most potent. This compound is the dominant carcinogen in cigarette smoke (Harvey, 1991). PAHs are found throughout the globe, but are not considered bioaccumulative. Fish and mammals have enzyme systems that are capable of metabolizing certain PAHs, thus limiting the total amount that accumulates in lipids as the parent form (Penning, 1993; Ingersoll et al., 1995).

*PBDEs.* PBDEs are flame retardants currently used in polyurethane and in coatings on fabrics and furniture. There are three technical mixtures: penta, octa and deca. Each mixture contains several congeners with the majority of them being penta, octa or deca, respectively. PBDE mixtures, containing approximately 12 congeners, are not as complex as PCB mixtures. In 1992, 40,000 metric tons of PBDE were produced. In 1999, 67,000 metric tons were produced worldwide with the Americas accounting for approximately 50% (BSEF, 2000). The deca mixture accounts for approximately 80% of

total PDBE production. There are three manufacturers of PBDEs worldwide, with two located in the US and one in Israel. PBDEs are known to have dioxin-like toxicity, affecting the liver and thyroid (Darnerud et al., 2001; McDonald, 2002); however, they are currently unregulated in the US. The penta technical mixture of BDE was banned in the European Union starting July 1, 2003. A recent Swedish study of human breast milk shows PBDEs exponentially increasing with a doubling time of 5 years (Meironyte et al., 1999; Noren and Meironyte, 2000).

## **8. Other Hazardous Air Pollutants**

The US EPA has classified 188 compounds as Hazardous Air Pollutants (HAPs). This list includes many of those discussed above, including many volatile organic compounds, hydrocarbons, and persistent organic compounds. Many of these hazardous air pollutants have never been measured in the regions surrounding Voyageurs and Isle Royale and are not expected to cause adverse impacts in the park. Therefore, discussion of these compounds is not included in this report. More information on the sources of these compounds is detailed on the Great Lakes Commission's most recent Inventory of Toxic Air Emissions (<http://www.glc.org>).

## **B. RECEPTORS**

Degradation of air quality can result in many possible effects, including human health effects and "welfare" effects, as described in the Clean Air Act. While effects on human health are of concern (e.g. respiratory distress due to ozone), receptors such as plants and wildlife may be more sensitive than humans to air pollutants. Given the NPS mandate to protect park natural resources, it is the welfare effects that here should be given the most attention. For the upper Great Lakes parks, air quality issues of concern include deposition and accumulation of organic contaminants and mercury in plants, fish, and wildlife; acid deposition and its effects on both aquatic and terrestrial communities; visibility impairment due to regional air quality degradation; heavy metal accumulation in plants; and nitrogen deposition to aquatic and terrestrial ecosystems. As discussed in more detail below, the more sensitive resources in these parks are the

fish and aquatic ecosystems because they are so vulnerable to atmospheric deposits of toxic chemicals and acid rain.

## **1. Importance of Foodweb Dynamics**

Although the concentrations of the POPs and mercury in the aquatic resources of the parks are not extremely high, they are capable of exerting a significant impact on top predators in the ecosystem due to amplification of their concentrations within the foodweb. While both POPs and MMHg can bioaccumulate, the mechanisms of how this happens differ between them. The mechanism by which POPs bioaccumulate in the foodweb is best understood as an imbalance in the rate of uptake of the compound relative to the rate at which the organism can eliminate the compound. POPs are hydrophobic and bind to phytoplankton, the base of the foodweb. Grazers pass on the POPs to their predators. Predators readily take in the compounds through respiration (bioconcentration) and from their prey (biomagnification), but because of their strong lipid solubility and resistance to degradation, the compounds are not readily eliminated. The rate of uptake can be 1,000 to 100,000 times as fast as the rate at which the compound is metabolized or excreted. Since this imbalance occurs at each trophic level, the concentrations of POPs increase by factors of approximately 2–4 with each increasing trophic level (Kidd et al., 1995). Predators at the top of the aquatic foodweb such as walleye or pike can have concentrations of POPs that are 1,000,000 to 10,000,000 times as great as the concentrations in the lake water (Kucklick et al., 1996). Wildlife and humans who consume these fish thus receive a substantial dose of these toxic chemicals. The exact risks depend on the chemical, the dose, and what percentage of the diet is fish.

Inorganic divalent mercury is converted to an organic form, monomethylmercury or MMHg. The MMHg binds to protein rather than solubilizing in lipids, and thus accumulates in muscle tissue in fish, wildlife, and humans. Concentrations in fish are typically 100,000 to 10,000,000 times greater than in the water in which the fish are living. MMHg is the most toxic form of mercury, and is a potent neurotoxin, and liver and kidney toxin. It also crosses the placenta, and may cause developmental problems in mammalian fetuses (Ramirez et al., 2000).

## **2. Sensitive Resources**

The biomagnification of POPs and mercury results in the conversion of small levels of these compounds in the environment to much greater concentrations in the aquatic foodweb. This poses a risk to animals who rely on this foodweb for prey, as well as to humans who eat the fish. Thus, the top consumers of the aquatic foodweb are particularly sensitive receptors in both National Parks. These include top predator fish, fish-eating birds such as eagles and loons, fish-eating wildlife such as otters and mink, and humans. Given that wetlands can lead to greater mercury methylation rates, Isle Royale, and especially Voyageurs, may be more sensitive to the impacts of monomethyl mercury than other areas receiving similar mercury deposition due the prevalence of wetlands in these aquatic parks.

In addition, Isle Royale has a simple terrestrial foodweb with wolves as the sole top predator, and few species of large mammals. This foodweb is precarious due to geographic isolation, small numbers of individuals, and harsh conditions. Thus, any additional stress from pollution could have severe consequences.

The upper Midwest of the United States historically has had, and still has, precipitation of lowered pH; thus, the soil and plant communities and inland lakes of both parks may be sensitive receptors to acid rain. These biocommunities are an integral part of the ecology of the parks, particularly at Isle Royale.

Finally, the plant communities and human populations that use Voyageurs are receptors for tropospheric ozone formed in or near the park.

## **3. Indicators**

To assess the impacts of air pollutants on natural resources, it is not practical or even feasible to measure the concentrations of every chemical in every possible receptor. Thus indicators of exposure and effects of pollutants have been developed that are sensitive and can be monitored or studied more efficiently. Examples of indicators include measurements of POPs in sediments from the inland lakes in Isle Royale and Voyageurs (which can be used to infer the exposure concentrations of contaminants over time), to measurements of metals and elements in lichens (which can be used to infer the impacts due to acid deposition). Few of these indicators are

standardized, and even fewer are integrated to reveal a more indepth picture of the ecosystem. Thus, there has been no systematic assessment of the health of the ecological systems within the National Parks due to the difficulty of conducting such a holistic assessment. Indicator measurements that have been made are included in the discussions in the sections below.

The table below presents a summary of the pollutants, their receptors, and generic indicators of exposure/effects.

Table III-2. Pollutants of interest in this report, their common receptors, and common indicators of exposure or effects on plants, fish, and wildlife.			
Pollutant of Concern	Receptor	Indicator of Exposure	Indicator of Effect
NO <sub>x</sub>	Soils	Increased soil [NO <sub>3</sub> ] and fertilization, decreased pH	Shift in species composition
	Surface water	Increased aqueous [NO <sub>3</sub> ]	Shift in species composition
SO <sub>x</sub>	Plant surfaces	Increased air [SO <sub>x</sub> ]	Leaf damage, forest decline
	Soils	Decreased pH	Increased Al <sup>3+</sup> leaching
	Surface water	Decreased pH	Loss of aquatic life
Ozone	Plants	Leaf or needle loss, damage	Leaf stipple or burn
	Humans		Loss of visibility, respiratory effects
CO	Wildlife	Increased air [CO]	Lower blood [O <sub>2</sub> ]
	Humans	Increased air [CO]	Lower blood [O <sub>2</sub> ] Headaches, decreased mental acuity
Hg and Pb	Soils	Increased soil concentrations	Fish consumption advisories Measures of Hg poisoning (liver & kidney damage, reproductive problems)
	Surface water	Increased water conc's	
	Sediments	Increased sediment conc's	
	Fish	Increased tissue conc's	
	Wildlife	Increased tissue conc's	
POPs	Soils	Increased soil conc's	Reproduction/recruitment problems, MFO activity Deformities; reproduction problems; MFO activity
	Surface water	Increased water conc's	
	Sediments	Increased sediment conc's	
	Fish	Increased tissue conc's	
	Wildlife	Increased tissue conc's	

## **E. REGULATIONS**

Understanding the context of this report requires some knowledge of the regulations that describe the responsibilities of the NPS, as well as the state and federal legislation that regulates the management of air quality and water resources. We discuss these regulations and guidelines below.

### **1. NPS Organic Act**

The National Park Service was established by the US Congress in 1916 by enactment of the National Park Service Organic Act. This legislation required the new agency “to conserve the scenery and natural and historic objects and the wild life therein and to provide for the enjoyment of the same in such a manner and by such means as will leave them unimpaired for the enjoyment of future generations.” This directive created two potentially opposing objectives that challenge the NPS to this day: to preserve park resources, while allowing visitors to enjoy these same resources. In some cases, the threat to the resource may come from outside the park boundaries, which creates an even more difficult situation for park managers. This is often the case in air quality issues, where the pollutants are generated far from the park and are transported long distances to impact the park’s environment.

### **2. Clean Air Act and Amendments**

The first federal legislative initiative pertaining to air quality protection was the Air Pollution Control Act of 1955, which focused on research and state program support. In 1963, Congress passed the Clean Air Act (CAA), which was the nation’s first comprehensive environmental legislation. Among other things, it provided for federal responsibility for mitigating vehicle and SO<sub>x</sub> pollution, and it required the development of non-mandatory air pollution criteria to protect public health and welfare.

The CAA was amended slightly in 1965 with the passing of the Motor Vehicle Air Pollution Control Act. The CAA was amended again in 1967, and required states to designate air quality control regions, adopt ambient air quality standards, and develop plans to achieve those standards. Major changes in the CAA occurred in 1970, when the responsibility for regulating air pollution was transferred to the newly created

Environmental Protection Agency (EPA). Whereas air pollution control had been a low priority in the former agency of Health, Education and Welfare (HEW), it would receive high priority at EPA. The biggest change to the CAA was that it federalized air pollution control, providing significant enforcement authority to the Federal government. It also established a strict timetable for EPA to follow. The 1970 amendments included a number of key changes. The amendments:

- provided for the development of uniform National Ambient Air Quality Standards (NAAQS);
- immediately designated Air Quality Regions, which were both intra- and interstate regions, and acknowledged that air pollution is a regional phenomenon that doesn't follow political boundaries;
- required the states to develop State Implementation Plans (SIPs) to achieve the NAAQS. The SIPs included plans for implementation, enforcement, and maintenance for each criteria pollutant, and response plans for emergency air pollution episodes;
- established stringent new automobile standards;
- established emission standards for new or modified sources, and for hazardous air pollutants (HAPs);
- established the right of citizens to bring suit against polluters;
- provided the Federal government full authority in the case of air pollution emergencies and violations; and
- defined new source performance standards (NSPS) that applied to new, or modification of existing, sources. The standards required best available technology to minimize emissions, and were based on source type and pollutant type (including non-criteria pollutants).

Mid-course corrections to the 1970 amendments occurred with the 1977 CAA Amendments. Congress postponed the compliance deadlines for primary NAAQS and auto emission standards. Another major provision of the amendments was of great significance to the NPS. In response to the 1974 Supreme Court decision on *Sierra Club v. EPA*, the Congress included provisions in the law for Prevention of Significant

Deterioration (PSD). The law was to ensure that the air quality of pristine areas such as national parks not be allowed to degrade to the level of the allowable standards set by the CAA. Under the PSD program, Congress established three area classifications. Class I areas (e.g., National Parks) were allowed the least deterioration, Class II areas were allowed moderate deterioration, and Class III areas were allowed the greatest deterioration. Class I areas were defined as those national parks greater than 6,000 acres, national wilderness areas greater than 5,000 acres, and international parks, that were in existence on August 7, 1977. Federal Land Managers (FLMs, designated as the Secretaries of Interior and Agriculture) had direct responsibility to protect “air quality related values” in the parks and wilderness areas from adverse impacts of air pollution. The NPS defines air quality related values as “visibility and those scenic, cultural, biological, and recreational resources of an area that are affected by air quality” (43 Fed Reg 15016). The CAA Amendments of 1977 also required states to incorporate measures in SIPs that would meet the goals of PSD.

The Clean Air Act came up for reauthorization in 1990, and was revised substantially in the 1990 Clean Air Act Amendments. The 1990 Clean Air Act Amendments included the concept of market-based regulation and tradable emission credits for controlling SO<sub>2</sub> emissions. Standards for the regulation of hazardous air pollutants were changed from a risk-based determination method to a technology-based determination that focused on maximum achievable control technology (MACT). Enforcement authority by EPA was enhanced significantly.

### **3. Changes to Particulate Matter (PM) and Ozone Standards**

The CAA requires that the criteria pollutant NAAQS be reviewed every five years. In keeping with the spirit of this requirement, the US EPA reviewed the standards for PM<sub>10</sub> and ozone in the mid-1990s and issued revised NAAQS in 1997. The primary and secondary ozone standards were lowered from 0.12 ppm (1 hour averaging time) to 0.08 ppm (8 hour averaging time), and the PM<sub>10</sub> standard was revised to include PM<sub>2.5</sub> criteria of 15 ug/m<sup>3</sup> for the annual arithmetic mean, and 65 ug/m<sup>3</sup> for a 24 hour averaging time. These standards were challenged in the courts, and a recent US

Supreme Court ruling will permit the EPA to proceed with their implementation. The current NAAQS are shown in Table III-3.

Table III-3. Current National Ambient Air Quality Standards (NAAQS). Standards, other than those based on the annual average, are generally not to be exceeded more than once a year.			
Pollutant	Averaging Time	Primary Standard	Secondary Standard
Carbon Monoxide	8 hr	10 mg/m <sup>3</sup> (9 ppm)	Same
	1 hr	40 mg/m <sup>3</sup> (35 ppm)	Same
Nitrogen dioxide	Annual average	100 µg/m <sup>3</sup> (0.05 ppm)	Same
Sulfur dioxide	Annual average	80 µg/m <sup>3</sup> (0.03 ppm)	
	24 hr	365 µg/m <sup>3</sup> (0.14 ppm)	
	3 hr		1300 µg/m <sup>3</sup> (0.5 ppm)
PM <sub>10</sub> (≤ 10 µm)	Annual arithmetic mean	50 µg/m <sup>3</sup>	Same
PM <sub>2.5</sub>	Annual arithmetic mean	15 µg/m <sup>3</sup>	
PM <sub>10</sub> (≤ 10 µm)	24 hr	150 µg/m <sup>3</sup>	Same
	24 hr	65 µg/m <sup>3</sup>	Same
Ozone	8 hr	157 µg/m <sup>3</sup> (0.08 ppm)	Same
Lead	3 mo average	1.5 µg/m <sup>3</sup>	Same

#### **4. EPA Regional Haze Regulations**

A recent action by US EPA relates directly to the NPS air quality goals. The US EPA promulgated the Regional Haze Regulations in 1999 to implement section 169A of the CAA (64 FR 35714). These regulations require the states to develop regional haze rules that provide for goals and emission reduction strategies for improving visibility due to haze in all federally designated Class I areas. Because of the regional (rather than state) nature of the problem, EPA is encouraging a collaborative approach to this problem by establishing five regional planning organizations (RPOs). Isle Royale falls under the Midwest RPO, which includes the states of Ohio, Michigan, Wisconsin, Illinois, and Indiana. The role of the Midwest RPO is to provide a forum for a regional planning process, which includes assessing visibility impairment and effects, and developing and implementing air quality protection plans. Voyageurs falls under the Central States Regional Air Planning Association, which includes the states of Arkansas, Iowa, Kansas, Louisiana, Minnesota, Missouri, Nebraska, Oklahoma and Texas and has a similar goal as the Midwest RPO. While the FLMs and EPA participate in RPO activities, the decision-making responsibility lies with the states.

#### **5. State and Local Regulations**

Isle Royale is an example where there is a dove-tailing of state and federal regulations. The park is considered to be within the boundaries of the state of Michigan. The inland waters are wholly contained within the park, and are managed by the NPS. However, the Lake Superior waters within the park boundaries are regulated by the state of Michigan. Nevertheless, the state of Michigan issues fish consumption advisories for fish caught in all park waters. A Michigan fishing license is required to fish in Lake Superior waters within the park, while in inland waters, a state license is not required. However, state regulations regarding open seasons, size, and possession limits apply, with the exception of park-specific restrictions for coaster brook trout.

Voyageurs is contained wholly within the boundaries of the state of Minnesota. The state is responsible for issuing air and water discharge permits for any regulated sources within the park (although there are no such sources). The Minnesota Department of Health issues fish consumption advisories for fish caught from lakes

within the park, and the Minnesota Department of Natural Resources regulates fishing within the park. A Minnesota fishing license is required to fish within the park, and state and federal boating regulations apply.

## **6. Annex I of the Great Lakes Water Quality Agreement**

The Great Lakes are governed by the 1909 Boundary Waters Treaty, which established the International Joint Commission (IJC) of the US and Canada to oversee the Treaty and jointly manage this important resource. In 1972 the Great Lakes Water Quality Agreement was signed, and subsequently amended in 1978 and 1987 to address concerns over toxic substances. The 1987 amendment included several annexes to the Agreement, the first of which specified the toxic substances to be covered under the Agreement and stated the specific objectives for those compounds that would protect the most sensitive use of the water and be protective of aquatic life. The Annex I Specific Objectives include maximum allowable concentrations in water (and in some cases fish tissue) for 12 groups of organic compounds, 10 metals, and a range of other non-persistent compounds. The Lake Superior waters surrounding Isle Royale are subject to these Specific Objectives.

## **7. Great Lakes Water Quality Guidance (GLI)**

In 1995, the US EPA and the eight Great Lakes states agreed to implement a regional, comprehensive approach that would restore the integrity of the Great Lakes. The agreement, Final Water Quality Guidance for the Great Lakes System, is most commonly referred to as the Great Lakes Initiative or GLI. The agreement establishes common criteria for all Great Lakes states to use for establishing regulatory limits for 29 toxic substances in water, including bioaccumulative chemicals. Isle Royale is subject to Michigan's implementation of the GLI.

## **8. Voluntary Programs**

In the spirit of approaching air quality issues with a regional view, the NPS cooperated with other FLM agencies (US Fish and Wildlife Service, Bureau of Land Management, National Forest Service), states, EPA and Canadian officials to develop Regional Air Quality Partnerships (RAQPs). This voluntary association of agencies

organized around a specific region or set of similar resources, and shared monitoring, research, permit review, and other activities to avoid duplication of effort, increase efficiency, and increase consistency in strategies and views. Several areas around the country organized RAQPs, including the establishment in 1997 of the Great Lakes Regional Partnership for Air Quality Concerns, which included Isle Royale and Voyageurs. The Great Lakes Regional Partnership has not been active for several years.

## IV. REGIONAL CHARACTERISTICS

### A. ENVIRONMENTAL SETTING

Both Isle Royale and Voyageurs are part of the National Park Service Midwest Region, which includes a total of 60 parks, monuments, lakeshores, recreational areas, historical sites, etc. Of these 60 sites, 11 areas are associated with the Great Lakes (see Table IV-1).

Table IV-1. Eleven National Park Service areas of the Midwest region that are associated with the Great Lakes.		
Name	Location	Area (Hectares)
Voyageurs National Park	MN	89,130
Grand Portage National Monument	MN	287
Isle Royale National Park	MI	230,000
Apostle Islands National Lakeshore	WI	17,010
St. Croix National Scenic Riverway	MN & WI	25,380
Pictured Rocks National Lakeshore	MI	28,910
Sleeping Bear Dunes National Lakeshore	MI	28,800
Indiana Dunes National Lakeshore	IN	5,100
Perry's Victory National Monument	OH	10
Cuyahoga Valley National Recreational Area	OH	12,900
Mississippi National River and Recreation Area	MN	21762

These parks are dominated by the upper Great Lakes, but they represent a huge diversity of ecological regions, from sand dunes to boreal forests. Isle Royale is totally contained within Lake Superior in the Great Lakes, and both Isle Royale and Voyageurs are considered to be water-based parks. They are both imbedded in the vast Canadian shield of granite bedrock that runs along the eastern half of the US-Canadian border. Of all the parks in this region, Voyageurs is the only one that is considered to be in the transitional southern boreal forest. The rock outcrops of Isle Royale support both a spruce-fire boreal forest and a northern hardwoods-conifer forest. Both parks have a cool northern climate. The extreme high and low temperatures felt at Voyageurs are moderated at Isle Royale by the presence of Lake Superior.

Voyageurs and Isle Royale are the two most remote parks in this region, and due to their large surface areas of water, they are particularly sensitive to the effects of air

pollutants that are atmospherically deposited following regional and long-range transport. Thus, although they are both far from large urban and industrial areas, they are vulnerable to certain kinds of air pollutants.

Armentano and Loucks (1983) reviewed the potential threats to air quality to 10 national parks, monuments, and lakeshores in the Great Lakes region. Their assessment included threats posed by the criteria pollutants, and included reduction in visibility, photochemical smog formation, and effects caused by acid deposition. They concluded that the plant communities of both Voyageurs and Isle Royale were potentially at risk to damage caused by excess ozone, their aquatic resources were potentially threatened by acid deposition, and that visibility reductions could occur in both parks, with impairment of scenic vistas affecting Isle Royale in particular. Their report stated that none of the pollutants of concern came from local or regional sources, but were mostly the result of long-range transport from the industrial Midwest and Ohio Valley.

A more recent study done by Bennett and Banerjee (1995) assessed the relative vulnerabilities to air pollutants of 22 NPS areas within the Midwest Region. The assessment first used a vulnerability analysis that combined the abundances of all plant species in a park with their sensitivities to ozone. The vulnerability score of a given park was calculated as the mean of the product of species sensitivity and species abundance. Concentration data for ozone, sulfur dioxide, and sulfate were obtained from the US EPA and extrapolated to park areas using a kriging algorithm. Cluster analysis of the pollutant data and the vulnerability scores were used to assign risk. Of the 22 parks considered in the analysis, Isle Royale had a low vulnerability score for its flora (ranked 19<sup>th</sup>) while Voyageurs was considered to be moderately vulnerable and was ranked 7<sup>th</sup>. The cluster analysis placed both Isle Royale and Voyageurs in the lowest risk group, with low concentrations of all three air pollutants combined with moderate vulnerability.

## **B. EMISSION INVENTORIES**

Emissions of air pollutants in the region include PM, sulfur dioxide, carbon monoxide, nitrogen oxides, lead and hazardous air pollutants (188 compounds including VOCs and POPs).

For criteria pollutants, a major source is defined under the Clean Air Act Title V as any stationary source or any group of stationary sources located within a contiguous area and under common control that has the potential to emit 100 tons per year. In this section, we report major US sources of nitrogen oxides, volatile organic compounds (both ozone precursors), particulate matter, sulfur dioxide, and carbon monoxide within 250 km of either Voyageurs or Isle Royale. Figures showing the distribution of these sources and tables listing the facilities responsible for the emissions follow brief discussion of the nature of these sources (Figures IV-1 through IV-10; Tables IV-2 through IV-4).

Emissions of hazardous air pollutants are important for the two parks, especially with respect to accumulation in fish and in transfer to the human and non-human food chain. Mercury is a hazardous air pollutant of particular concern. A discussion of regional sources of mercury is provided at the end of this section. A report of current emissions of POPs and other toxic compounds has recently been released by the Great Lakes Commission (<http://www.glc.org>). This extensive report covers 213 individual toxic air pollutants emitted by 674 point and area source categories and 1,597 different processes. A separate report covers emissions from mobile sources. This emissions inventory cannot be used to compare sources between states or countries or between in-park and outside park sources. The reporting procedures are nonstandard and therefore do not allow such comparisons. Assessment of air toxics releases within the region remains an important research issue requiring additional sampling and analysis beyond the scope of this report.

## **1. Point Source Emissions from Outside the Parks**

### **a. Ozone Precursors**

Ozone is a result of a series of complex chemical reactions between nitrogen oxides ( $\text{NO}_x$ ) and volatile organic compounds (VOCs) in the presence of light. Nitrogen oxides result primarily from anthropogenic (human) sources. Volcanoes, bacteria, and lightning can contribute, but these are considered minor sources in this area. VOCs are the major hydrocarbon contributors to ozone production, and have significant

anthropogenic and natural sources. The ratio of VOCs to  $\text{NO}_x$  has been well studied with the goal of reducing ozone in urban areas. Reduction of ozone in the remote areas of Voyageurs and Isle Royale is likely to depend on reduction of local and regional sources of  $\text{NO}_x$ , since natural sources of VOCs (e.g., isoprene from trees, methane from wetlands) are likely to be significant and uncontrollable in the region. In the following sections, major anthropogenic sources of  $\text{NO}_x$  and VOCs are outlined by facility type and location. While transport from regions outside Minnesota, Wisconsin, Michigan, and Canada is possible, it is expected to be a much smaller contribution due to the small number of large sources west (upwind) of these two parks. More detailed determination of the relative magnitude of those long-range sources is beyond the scope of this report. In addition, although Canadian sources of  $\text{NO}_x$  and VOCs are present, the emissions data, by facility, are not readily available from the Ontario Province.

Major sources of  $\text{NO}_x$  are found in northern St. Louis County in the Minnesota Iron Range near the towns of Hibbing and Virginia. The highest emissions result from taconite (low grade iron ore) mining and processing. Sources of nitrogen oxides in Koochiching County are exclusively in the International Falls area, with the Boise-Cascade pulp mill dominating. (Presumably, a similar plant on the Canadian side in Fort Frances has similar emissions but no data are available). Total emissions of  $\text{NO}_x$  from facilities in the Michigan Upper Peninsula (UP) is similar to the amount emitted in northern Minnesota, except that emissions from the pulp and paper industry are greater. Emissions from the UP are dominated by three general sectors: utilities and natural gas handling; mining (primarily copper and iron); and the paper and wood products industry. Emissions from the lower peninsula may also contribute, but are not detailed here. Emissions from Northern Wisconsin counties bordering Lake Superior are smaller than the totals from northern Minnesota and UP Michigan but the emissions are from the same classes of industry: utilities and fuel handling, paper and wood processing, and mining.

Anthropogenic VOCs released to the air in the UP are about 1,200 tons/year. The paper and wood processing industry contributes the majority of this, at ~900 tons/year. This includes not only the paper and pulp industry, but also various wood

processing plants, including those that manufacture hardwood furniture. About 1,300 tons per year of VOCs are emitted by point sources in the northern counties of Wisconsin. In this region, the VOC sources are dominated by fuel processing, with the petroleum refinery as the largest source. It is not possible to determine if local sources of either NO<sub>x</sub> or VOCs are the major cause of the ozone increase at Voyageurs. Nor is it possible to assess if natural sources of VOCs are sufficient to support the development of tropospheric ozone in combination with the anthropogenic nitrogen oxides discussed above. We recommend further work be done to trace sources of ozone precursors to Voyageurs and Isle Royale. Sufficient information is available to make a modeling study of the impact of these very low, but increasing, levels both feasible and reliable.

Anthropogenic sources of VOCs are not expected to be major contributors to the ozone measured in northern Minnesota, Wisconsin, and Michigan. Northern Minnesota has the lowest VOC emissions from the three areas examined, at ~700 tons/year. The sources of VOCs from human activity that have similar spatial distribution as that described for NO<sub>x</sub> are primarily in the Hibbing-Virginia area of the Minnesota Iron Range, and in International Falls. The Boise-Cascade pulp mill near International Falls is the only reported source of VOCs in Koochiching County.

#### b. Particulate Matter

The largest sources of particulate matter are from iron and mining facilities, especially in northern Minnesota. These facilities contribute to reduced visibility in the parks. Particulate matter can also act as a vector for transport of other compounds, including polycyclic aromatic hydrocarbons, dioxins, and other persistent organic pollutants. See section V.F for further discussion of these pollutants.

#### c. Sulfur Dioxide and Carbon Monoxide

Sulfur dioxide sources are primarily related to coal combustion processes, of which there are several major sources near the parks. In Voyageurs and Isle Royale, the most significant issue related to emissions of sulfur dioxides is the contribution to haze and visibility degradation through the formation of ammonium sulfate particles.

Sulfur dioxide is converted to sulfuric acid and contributes to acid rain. Inhalation of high concentrations of sulfur dioxide causes lung irritation. However, neither acid rain nor inhalation issues are currently major problems in either park. Visibility impacts are a more immediate concern. There is a significant source of SO<sub>2</sub> at the western border of Voyageurs. Boise-Cascade reports 561 tons/year of SO<sub>2</sub> are emitted from their plant in International Falls. There are larger point sources within the 250 km radius, but they are not expected to be as important due to the relative proximity of the Boise-Cascade facility to the park.

Carbon monoxide also is emitted as a result of coal burning; however, many other activities result in release of this product of incomplete combustion. CO sources encompass a wide range of activities, including mining and iron processing, and hence have a wider distribution near the parks.

#### d. Emissions Data for Point Sources

Figures IV-1 through IV-5 and Tables IV-2 through IV-4 describe the spatial distribution and magnitude of US point sources of NO<sub>x</sub>, VOCs, PM<sub>10</sub>, SO<sub>2</sub>, and CO within 250 km of the parks.

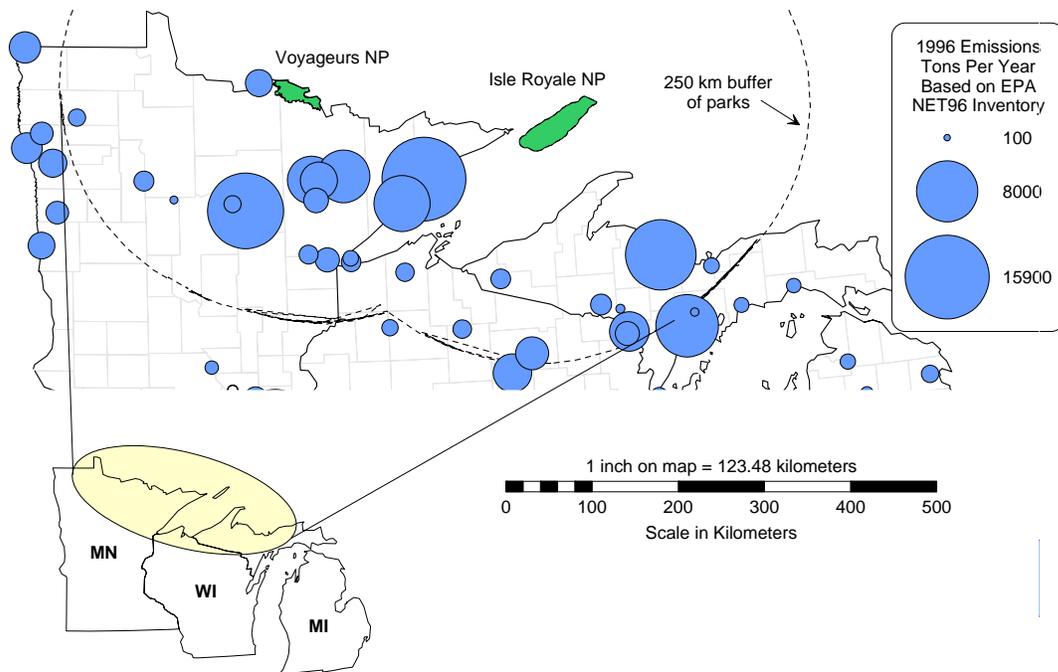


Figure IV-1. US nitrogen oxide point sources with 1996 annual emissions  $\geq$  100 tons per year.

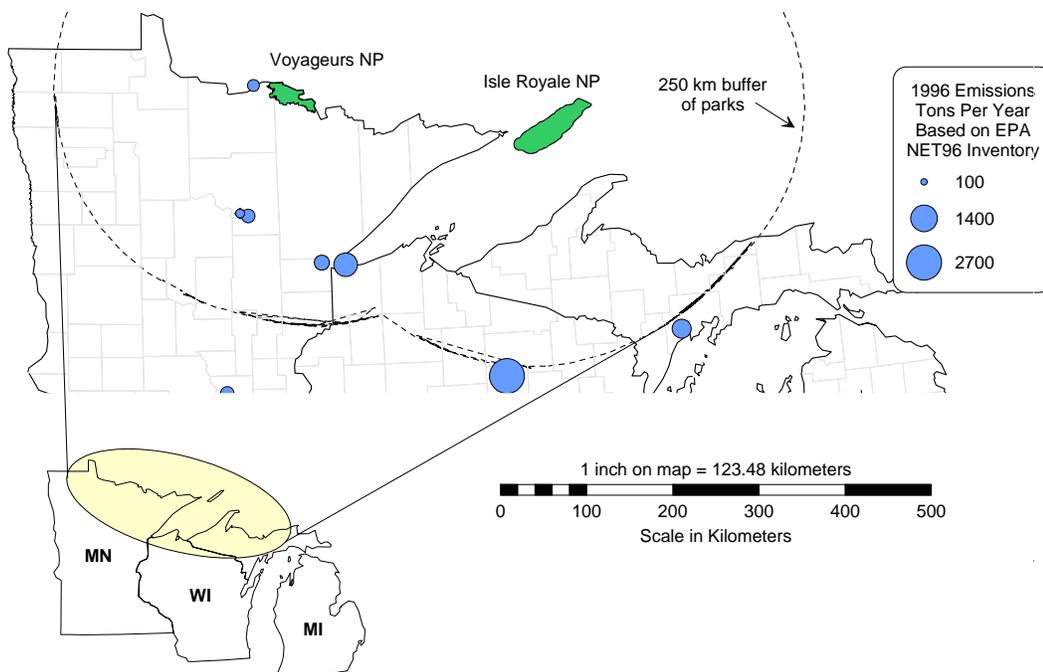


Figure IV-2. US volatile organic compounds point sources with 1996 annual emissions  $\geq$  100 tons per year.

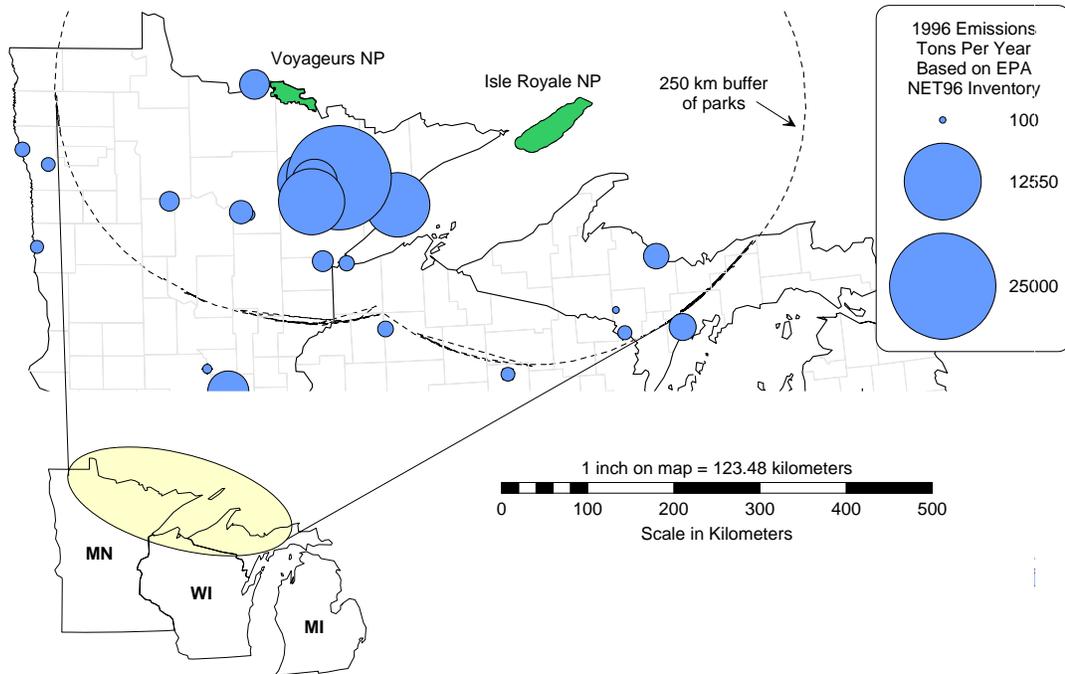


Figure IV-3. US PM<sub>10</sub> point sources with 1996 annual emissions  $\geq$  100 tons per year.

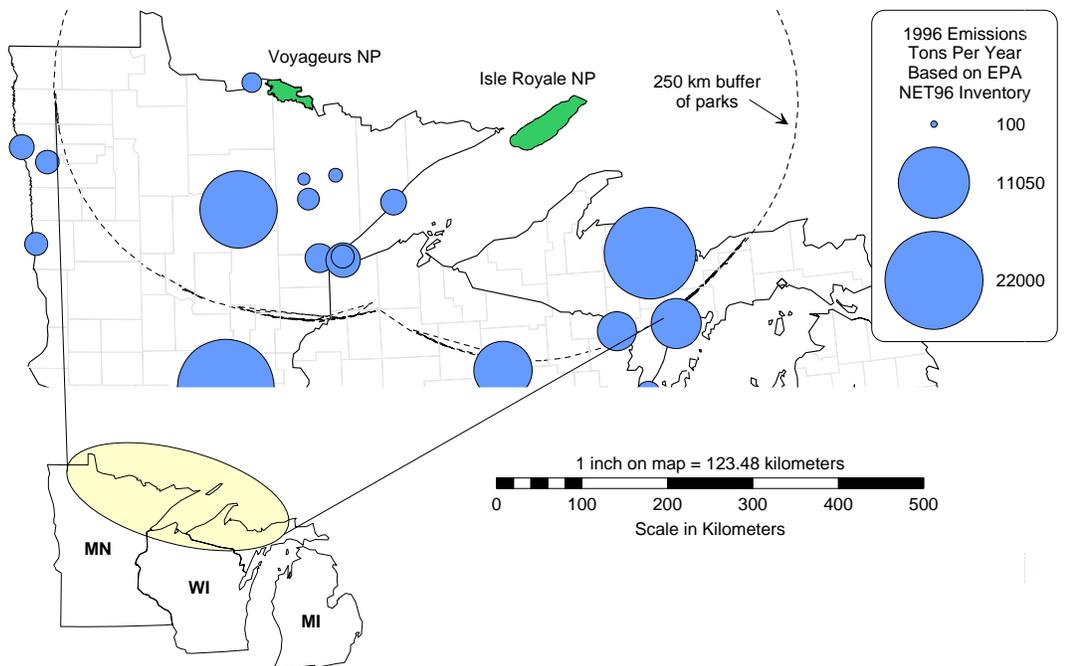


Figure IV-4. US sulfur dioxide point sources with 1996 annual emissions  $\geq$  100 tons per year.

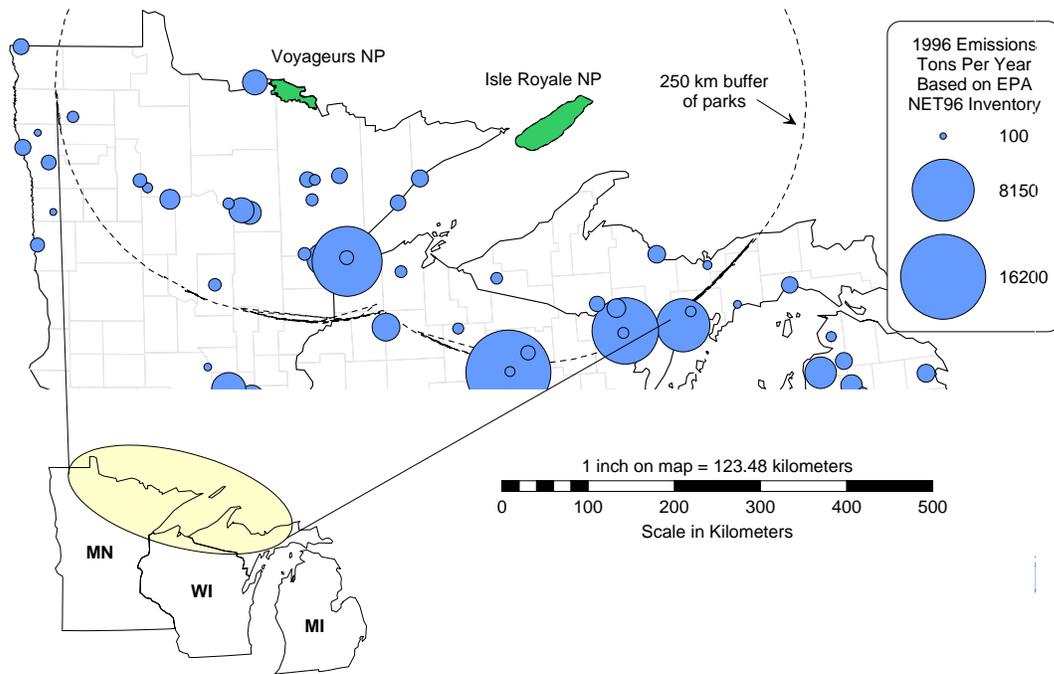


Figure IV-5. US carbon monoxide point sources with 1996 annual emissions  $\geq$  100 tons per year.

Table IV-2. Michigan point sources with 1996 emissions greater than or equal to 100 tons per year and located within 250 km of either Isle Royale NP or Voyageurs NP (1996 emissions based on US EPA NET96 Emissions Inventory).

County	Plant Name	EPA Point Source ID #	SIC Code	Distance to Isle Royale NP (km)	Distance to Voyageurs NP (km)	Latitude deg	Longitude deg	CO ton/y	NO <sub>x</sub> ton/y	PM <sub>10</sub> ton/y	SO <sub>2</sub> ton/y	VOC ton/y
Alger	KIMBERLY CLARK CORP	260030001	2621	234.5	501.7	46.4086	-86.6461	117	326		763	
Dickinson	CHAMPION INTERNATIONAL CORP	260430014	2611	246.4	458.5	45.7950	-87.9586	9512	2991	245	665	
Dickinson	LOUISIANA PACIFIC CORP	260430030	2493	218.9	435.6	46.0400	-88.0650	495	118	101		
Gogebic	GREAT LAKES GAS TRANSMISSION	260530028	4922	183.9	309.8	46.4389	-89.8275	173	569			
Iron	GREAT LAKES GAS TRANSMISSION	260710022	4922	208.3	415.2	46.0997	-88.3481	310	658			
Marquette	EMPIRE IRON MINING PTNRSHP	261030003	1011	190.5	438.5	46.4453	-87.6028		6159	449	365	
Marquette	SHIRAS	261030004	4911	190.4	436.4	46.4300	-87.6500		498		363	
Marquette	PRESQUE ISLE	261030010	4911	186.9	445.0	46.5694	-87.3933	426	10898	1010	19056	
Marquette	TILDEN MINING CO LC	261030011	1011	189.5	435.8	46.4386	-87.6522		10609	1637	782	
Ontonagon	STONE CONTAINER CORP	261310001	2611	127.8	307.8	46.8689	-89.3211		2239		3054	447
Ontonagon	BHP WHITE PINE REFINERY INC	261310002	1021	144.4	299.9	46.7644	-89.5733		381		895	

Table IV-3. Wisconsin point sources with 1996 emissions greater than or equal to 100 tons per year and located within 250 km of either Isle Royale NP or Voyageurs NP (1996 emissions based on US EPA NET96 Emissions Inventory).

County	Plant Name	EPA Point Source ID #	SIC Code	Distance to Isle Royale NP (km)	Distance to Voyageurs NP (km)	Latitude deg	Longitude deg	CO ton/y	NO <sub>x</sub> ton/y	PM <sub>10</sub> ton/y	SO <sub>2</sub> ton/y	VOC ton/y
	NORTHERN STATES											
Ashland	POWER CO-BAY FRONT GEN S	550030333	4931	214.8	247.7	46.5853	-90.8986		728		362	
Bayfield	GREAT LAKES GAS TRANSMISSION-COMP STATIO	550070418	4922	236.1	235.9	46.5608	-91.2647	178	479			
Douglas	BURLINGTON NORTHERN-ORE FACILITY	550310089	4789	272.9	202.3	46.6811	-92.0258			553		
Douglas	GEORGIA PACIFIC CORP.	550310091	2493	273.3	195.8	46.7339	-92.0800					157
Douglas	MURPHY OIL USA MIDWEST ENERGY	550310095	2911	275.2	200.3	46.6917	-92.0714	10637	553	296	2158	1035
Douglas	RESOURCES CO. C L M CORPORATION-	550310133	5052	275.2	194.7	46.7378	-92.1139			393		
Douglas	SUPERIOR	550310364	3274	273.3	196.2	46.7303	-92.0761	245	325		821	
Marinette	CONSOLIDATED PAPERS, INC. NIAGARA DIVISI	550750393	2621	247.9	458.2	45.7750	-87.9903	154	919		2891	

Table IV-4. Minnesota point sources with 1996 emissions greater than or equal to 100 tons per year and located within 250 km of either Isle Royale NP or Voyageurs NP (1996 emissions based on US EPA NET96 Emissions Inventory).

County	Plant Name	EPA Point Source ID #	SIC Code	Distance to Isle Royale NP (km)	Distance to Voyageurs NP (km)	Latitude deg	Longitude deg	CO ton/y	NO <sub>x</sub> ton/y	PM <sub>10</sub> ton/y	SO <sub>2</sub> ton/y	VOC ton/y
Beltrami	GEORGIA PACIFIC - BEMIDJI HARDBOARD	270070004	2493	440.0	182.6	47.4630	-94.8669			259		491
Beltrami	NORTHWOOD PANELBOARD	270070019	2499	455.0	192.7	47.5080	-95.0863	133				429
Carlton	POTLATCH - CLOQUET	270170002	2611	296.3	191.5	46.7220	-92.4308	1859	934	627	1419	336
Carlton	DIAMOND BRANDS INC	270170003	3999	297.1	191.5	46.7210	-92.4425			123		
Carlton	USG INTERIORS - CLOQUET	270170006	2493	298.6	190.8	46.7250	-92.4700		164	198		
Carlton	NORTHERN NATURAL GAS - CARLTON	270170019	4922	318.9	203.4	46.5933	-92.6778		147			
Clearwater	GREAT LAKES GAS TRANS - SHEVLIN	270290004	4922	462.0	195.4	47.5860	-95.2025	233	583			
Cook	LTV STEEL MINING - TACONITE HARBOR	270310001	4911	158.8	172.2	47.5310	-90.9102	393	15880		14800	
Crow Wing	POTLATCH - BRAINERD (NW PAPER DIVISION)	270350002	2621	428.0	246.3	46.3780	-94.1805		401			
Crow Wing	TRUS JOIST MACMILLAN - DEERWOOD PLANT	270350031	2493	416.3	233.2	46.4808	-94.0771	199		240		198
Hubbard	POTLATCH - BEMIDJI (MN WOOD PRODUCTS)	270570005	2493	432.8	181.1	47.3850	-94.7450	577	106	545		730
Hubbard	LAMB WESTON - RDO FROZEN FOODS	270570006	2099	467.4	233.0	46.9130	-95.0591				323	
Itasca	BLANDIN PAPER	270610001	2621	350.4	143.4	47.2320	-93.5297	831	967	163	233	261
Itasca	MN POWER & LIGHT - CLAY BOSWELL	270610004	4911	358.3	144.0	47.2600	-93.6530	999	12793	815	13210	120
Itasca	POTLATCH - GRAND RAPIDS	270610010	2493	350.6	143.8	47.2290	-93.5322					115
Itasca	GREAT LAKES GAS TRANS - DEER RIVER	270610011	4922	370.3	143.5	47.3330	-93.8497	160	401			
Koochiching	BOISE CASCADE - PAPER	270710002	2611	333.2	42.5	48.6060	-93.4055	988	1231	1458	561	193
Lake	NORTHSHORE MINING CO	270750003	1011	192.6	171.6	47.2850	-91.2625	315	6597	8567	1090	
Lake	LOUISIANA PACIFIC	270750019	2493	230.9	175.8	47.0460	-91.6744			166		190
Marshall	GREAT LAKES GAS TRANS - THIEF RIVER FALL	270890012	4922	531.7	244.0	48.2550	-96.2369	165	412			

Table IV-4. cont.

County	Plant Name	EPA Point Source ID #	SIC Code	Distance to Isle Royale NP (km)	Distance to Voyageurs NP (km)	Latitude deg	Longitude deg	CO ton/y	NO <sub>x</sub> ton/y	PM <sub>10</sub> ton/y	SO <sub>2</sub> ton/y	VOC ton/y
Pennington	ARCTCO MARVIN WINDOWS & DOORS	271130014	3799	528.8	243.3	48.1090	-96.1936					125
Roseau	DOORS	271350002	2431	472.8	182.5	48.9140	-95.3244					392
Roseau	POLARIS INDUSTRIES LP	271350008	3799	500.3	209.1	48.7694	-95.7481					102
St. Louis	USS - MN ORE OPERATION	271370005	1011	278.6	99.7	47.5660	-92.6330	315	4679	6936	188	
St. Louis	LTV STEEL MINING - HOYT LAKES TACONITE	271370009	1011	243.1	107.8	47.5950	-92.1408	328	5748	24141	245	
St. Louis	MN POWER & LIGHT - SYL LASKIN	271370013	4911	246.0	113.3	47.5310	-92.1616		1247	164	1889	
St. Louis	MN POWER & LIGHT - ML HIBBARD	271370015	4961	277.9	194.3	46.7350	-92.1530		331		153	
St. Louis	DULUTH STEAM COOP ASSN	271370022	4961	271.8	190.7	46.7800	-92.0961		422		237	
St. Louis	HIBBING PUBLIC UTILITIES COMMISSION	271370027	4931	303.1	113.5	47.4290	-92.9336		744		765	
St. Louis	VIRGINIA DEPT OF PUBLIC UTILITIES	271370028	4931	273.1	105.5	47.5220	-92.5416		941		743	
St. Louis	HILL WOOD PRODUCTS	271370030	2421	277.9	67.7	47.8620	-92.6844			224		
St. Louis	GEORGIA PACIFIC CORP	271370031	2493	273.3	191.3	46.7710	-92.1119			111	121	140
St. Louis	NORTHSHORE MINING CO	271370032	1011	223.3	111.3	47.6670	-91.8838			624		
St. Louis	HIBBING TACONITE	271370061	1011	304.3	108.3	47.4790	-92.9680		1109	2242		
St. Louis	INLAND STEEL MINING	271370062	1011	270.7	101.8	47.5600	-92.5200	149	2570	3910		
St. Louis	NATIONAL STEEL PELLET GREAT LAKES GAS TRANS	271370063	1011	312.7	115.6	47.4190	-93.0663		1709	1683	264	
St. Louis	- CLOQUET	271370066	4922	311.4	182.8	46.7840	-92.7116	206	515			
St. Louis	ME INTERNATIONAL NORTHERN CASTINGS	271370073	3325	271.9	189.0	46.7940	-92.1102					321
St. Louis	CORP	271370082	3321	304.2	114.4	47.4210	-92.9469					120
St. Louis	POTLATCH - COOK	271370083	2493	276.7	74.9	47.7970	-92.6580			263		293
St. Louis	PHILLIPS PIPE LINE	271370094	5171	287.6	194.8	46.7090	-92.2844					201
St. Louis	WLSSD PLANT	271370112	4952	274.8	192.3	46.7590	-92.1252			152	152	
St. Louis	EVELETH MINES - FAIRLANE PLANT	271370113	1011	279.8	123.2	47.3510	-92.5722	184	972	9037	721	
Total Emissions within 250 km, ton/y								30283	100052	67332	69288	6395

#### e. Canadian Emissions

Canadian sources of air pollutants near Voyageurs and Isle Royale are focused in the area around Thunder Bay and Fort Frances, Ontario ([www.ec.gc.ca/pdb/ape/cape\\_home\\_e.cfm](http://www.ec.gc.ca/pdb/ape/cape_home_e.cfm)). Thunder Bay is the closest city to Isle Royale and Fort Frances is just north of International Falls, MN, near Voyageurs. Because Canada does not have comparable air pollution emission reporting requirements, it is not possible to obtain detailed emissions information from Canadian facilities. Environment Canada reports emissions of these pollutants on an area basis (2,500 km<sup>2</sup> resolution). For rough comparison with the US reported emissions units, the magnitude of the Thunder Bay SO<sub>2</sub> source is 250 to 1,000 kg/km<sup>2</sup>/year or 690 to 2,760 tons/year. This is similar to the SO<sub>2</sub> emissions of 561 tons/year reported for International Falls. Surprisingly, no significant emissions of SO<sub>2</sub> are reported from Fort Frances. The most significant regional emissions of CO are reported for Thunder Bay and Fort Frances. Emissions of CO from the Fort Frances region are 500 to 5,000 kg/km<sup>2</sup> or 1,380 to 13,800 tons/year. This range is greater than that reported for International Falls at 988 tons of CO per year. Emissions of CO from the Thunder Bay region are 5,000 to 50,000 kg/km<sup>2</sup> or 13,800 to 138,000 tons/year.

Although the reporting mechanisms in Canada and the US are not the same, it appears that emissions of CO and SO<sub>2</sub> are similar in magnitude for the major point sources of the respective compounds in western Ontario and northern Minnesota. Neither CO nor SO<sub>2</sub> are recognized as major problems in these two parks and so their emissions are not addressed further in this report. However, sulfate is a product of atmospheric reactions of SO<sub>2</sub> and can contribute to visibility reduction and acid deposition.

## 2. County-wide Emissions from Point, Area, and Mobile Sources

Area and mobile sources also contribute to pollutants released in the region surrounding Voyageurs and Isle Royale. Figures IV-6 through IV-10 illustrate the US distribution of these sources on a county-wide basis.

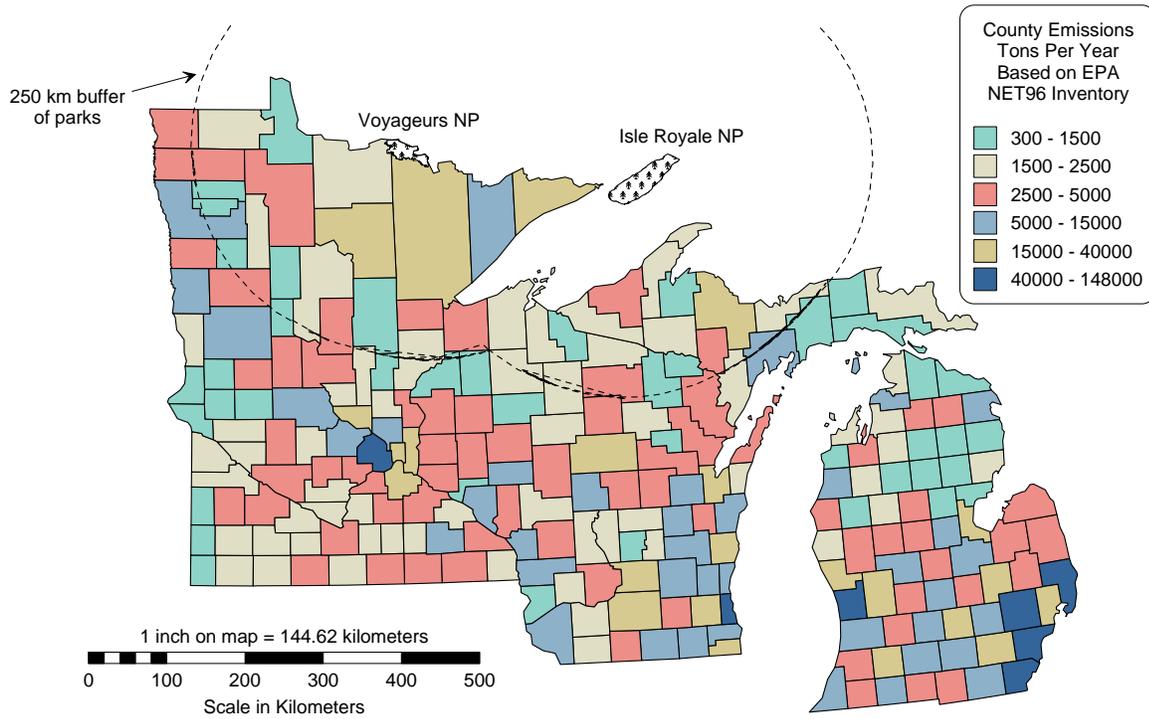


Figure IV-6. US nitrogen oxide point + area + mobile sources in Michigan, Wisconsin, and Minnesota.

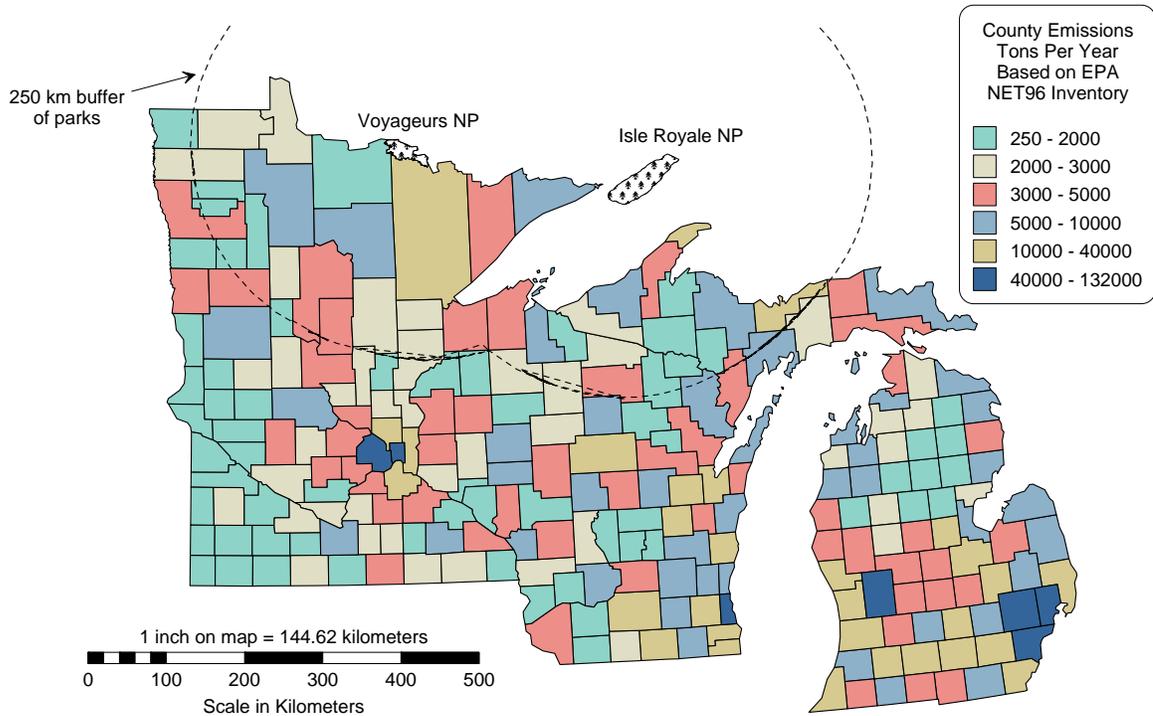


Figure IV-7. US volatile organic compounds point + area+ mobile sources in Michigan, Wisconsin, and Minnesota.

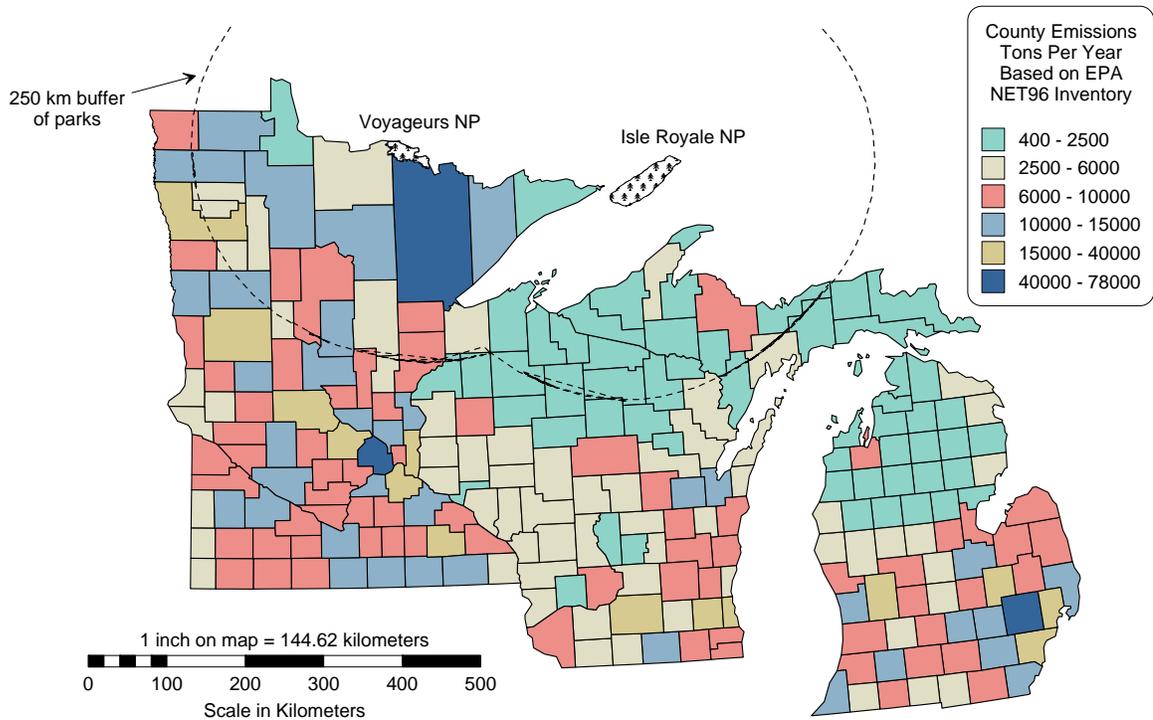


Figure IV-8. US PM<sub>10</sub> point + area+ mobile sources in Michigan, Wisconsin, and Minnesota.

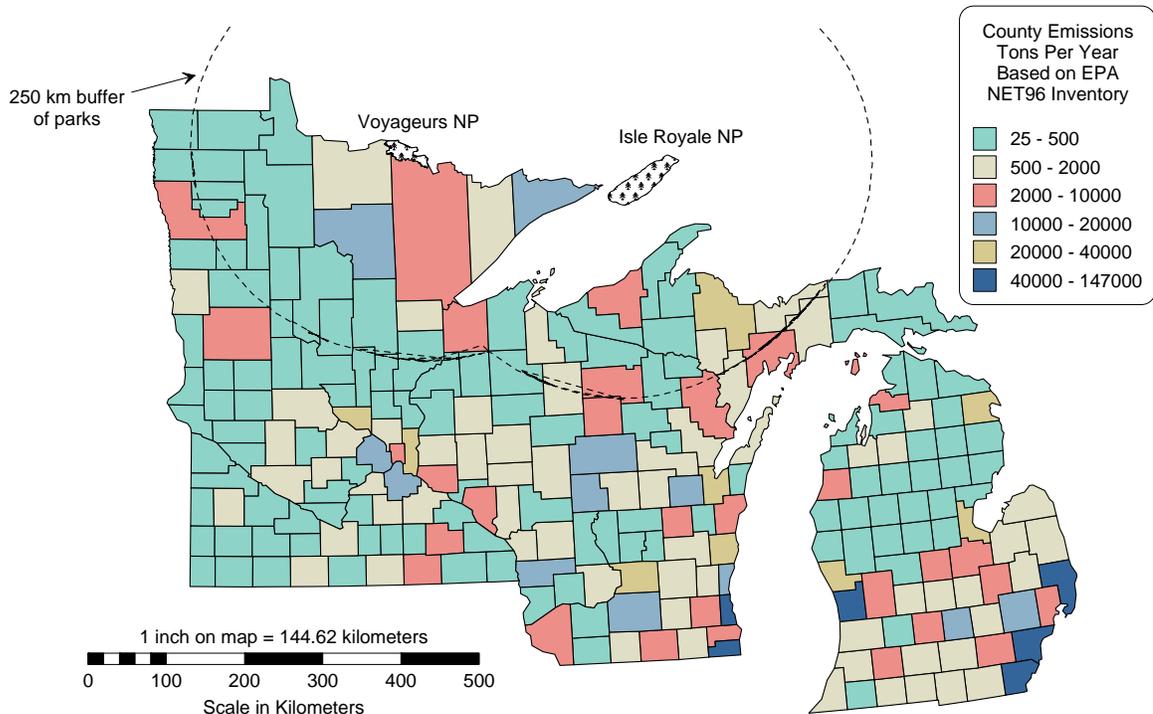


Figure IV-9. US sulfur dioxide point + area+ mobile sources in Michigan, Wisconsin, and Minnesota.

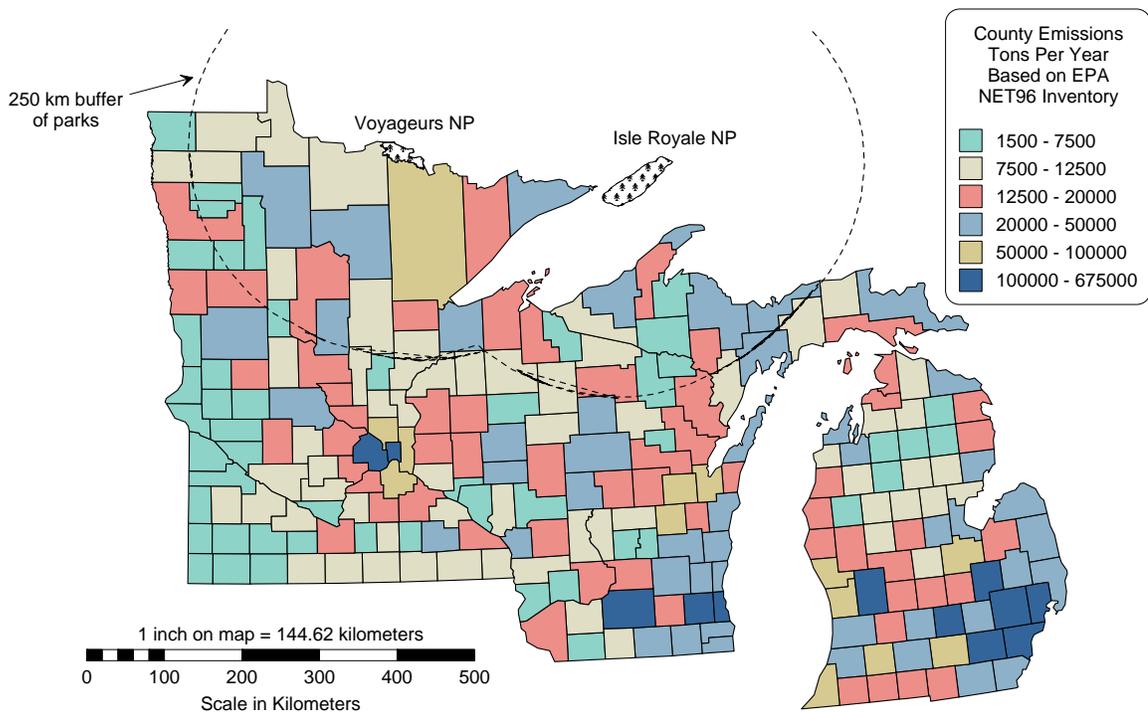


Figure IV-10. US carbon monoxide point + area+ mobile sources in Michigan, Wisconsin, and Minnesota

### 3. In-Park Sources

Sources of major air pollutants (NO<sub>x</sub>, VOCs, CO, and PM) within both parks include park vehicles, recreational marine engines, snowmobiles (Voyageurs only) and campfires. Emissions from recreational boating discharge directly into the water, both during normal use and by evaporation from fuel tanks and lines during storage. While important in busier waters and where outboard engines are stored, these sources to the air are small within either park and insignificant compared to major point sources in the region. There is, however, significant uncertainty about the magnitude of emissions directly to water from recreational boating. Although this source may be an important contributor of toxic metals and organic compounds to these high quality waters, the subject is outside the scope of this report on air pollutants.

#### a. Snowmobile Sources

Snowmobiles are not permitted in Isle Royale except for minimal administrative use by NPS staff, so the following discussion of snowmobile emissions applies only to Voyageurs. Emissions from snowmobiles are expected to be the largest in-park source category in Voyageurs.

Snowmobiles emit air pollutants at a rate significantly greater than automobiles. This is primarily a result of the operation of two-stroke (snowmobile) versus four-stroke (auto) engines. Two-stroke engines are less fuel efficient and release more of the uncombusted fuel. As a result, a snowmobile operating for four hours can emit between 10 and 70 times more CO, and between 45 and 250 times more HC than will an automobile driven 100 miles. HC includes those compounds with only hydrogen and carbon atoms (some VOCs and some POPs are also HC). When compared as a function of fuel consumed, Bishop et al. (Bishop et al., 1999) found that snowmobiles emit HC and CO at rates that are respectively 80 and 7 times higher than for autos. Snowmobiles account for a large portion of the mobile source emissions in Yellowstone: 68% to 90% of HC; 35% to 68% of CO; 2% of NO<sub>x</sub>; and 39% of PM (National Park Service Air Resources Division, 2000a). It is likely that this is true for Voyageurs as well.

A review of air pollutant emissions from snowmobiles was produced by the National Park Service (National Park Service Air Resources Division, 2000a). The report summarizes snowmobile use rates in NPS areas, compiles emission factors for snowmobiles, and reports a comparison between the two-stroke engines used in most snowmobiles and the four-stroke engines used in autos. The report compares emissions from several popular snowmobile models, and calculates total emissions of hydrocarbons, carbon monoxide, nitrogen oxides, and particulate matter in Yellowstone National Park. This comprehensive report was used to support the (now modified) NPS decision to phase out the operation of snowmobiles in Yellowstone starting in 2002 (Special Regulations, Areas of the National Park System, 2001). Yellowstone currently supports the highest rate of snowmobile use of all the national parks, with 63,000 snowmobile visits per year. However, of the 42 units of the National Park system that allow snowmobile use, Voyageurs has the second largest use rate, estimated at 35,410 snowmobile visits per year, primarily during the months of January, February, and March.

Fuel consumption rates for snowmobiles range from 8 to 15 mpg. In Yellowstone, the most common engine was the 488 cm<sup>3</sup> displacement size, although the snowmobiles range from 349 cm<sup>3</sup> to 1L triple cylinder engines. Although snowmobiles used at higher elevation are tuned for that environment, it is expected that fuel use at Voyageurs would be more efficient. There is insufficient data available to estimate this difference, however. The 488 cm<sup>3</sup> engines tested in Yellowstone were reported to have a mean fuel economy of 13 mpg (Bishop et al., 1999) and this is the value used here.

The average length of snowmobile operation in Voyageurs is not known, so a trip time of four hours per day was used to simplify comparison with the Yellowstone data. The engine power is assumed to be 16 hp (average over the trip), and the snowmobiles consume 11.2 gallons or approximately 30 kg of fuel per visit (National Park Service Air Resources Division, 2000a). Table IV-5 summarizes the estimated snowmobile emissions for the 35,410 visits per year to Voyageurs NP.

Table IV-5. Comparison of estimated snowmobile emissions in Voyageurs National Park.			
Pollutant	Emissions, g/visit based on the NPS Air Resources Division Report of 2000 (this study)	Emissions, g/visit based on Bishop et al. (Bishop et al., 2001)	Emissions tons/yr from NPS (2000a) / Bishop (Bishop et al., 2001)
HC	9024	9930	350 / 390
CO	24704	13800	960 / 540
NO <sub>x</sub>	34.56		1
PM	83.2		3

The NPS completed a similar calculation for Voyageurs using a methodology similar to that above (Worstell, 2001). The Worstell estimates are 30% to 50% of the estimates calculated here. This is largely due to the estimate of average length of snowmobile operation at Voyageurs: the NPS report assumed a two-hour visit, while the table above assumes a four-hour visit. The actual average snowmobile visiting time at Voyageurs has not been calculated or measured.

There are major uncertainties in the estimate of emissions from snowmobiles within Voyageurs, especially length and number of snowmobile visits to Voyageurs and the fuel characteristics of snowmobiles used at Voyageurs. However, it appears that the annual emissions of pollutants from snowmobiles at Voyageurs are about one-half of the reported annual emissions for Yellowstone. Since Yellowstone is more than ten times the size of Voyageurs, the potential impact of snowmobiles in Voyageurs may be significantly greater than that observed for Yellowstone. Fortunately, the concentrations of air pollutants released from snowmobiles at Voyageurs are not likely to reach those measured at Yellowstone due to the multiple access points for snowmobiles entering Voyageurs and the lack of stopping points for registration and permitting.

#### b. Persistent Organic Pollutants

Release of organic pollutants to air and indirectly to water within Isle Royale and Voyageurs can be important sources of persistent organic pollutants (POPs) to the park ecosystems. POPs are, as a group, those compounds that tend to bioaccumulate, are semivolatile, and have long half lives in the environment. VOCs and HC are not part of

this group. Polycyclic aromatic hydrocarbons (PAHs) are the only set of POPs that have published and reliable emissions data available. Emissions of other POPs, including PCBs, pesticides, and dioxin-like compounds cannot be estimated. Direct monitoring is required. As described for criteria pollutants, expected sources of PAHs include park vehicles, recreational marine engines, snowmobiles and campfires. In-park sources of PAHs are likely to be more important at Voyageurs than at Isle Royale due to the much greater annual visitation and use of recreational motorized boating and snowmobiles at Voyageurs.

Snowmobile emissions can be estimated for PAHs using the same strategy outlined in the previous section, although the emission factors are difficult to measure. Initial estimates (White et al., 1998) used in the NPS report (2000a) are difficult to substantiate due to insufficient procedural reporting and the NPS appears to have revised their emissions calculations in subsequent reports. It is possible, however, that in-park emissions of PAHs exceed emissions from outside the park, considering the high use of snowmobiles in the winter and outboard marine motors in the summer and the remote location of the park itself. Insufficient data and published methods prevent quantitative review of these sources, unfortunately.

### c. Comparison of Emission Sources Within and Outside the Parks

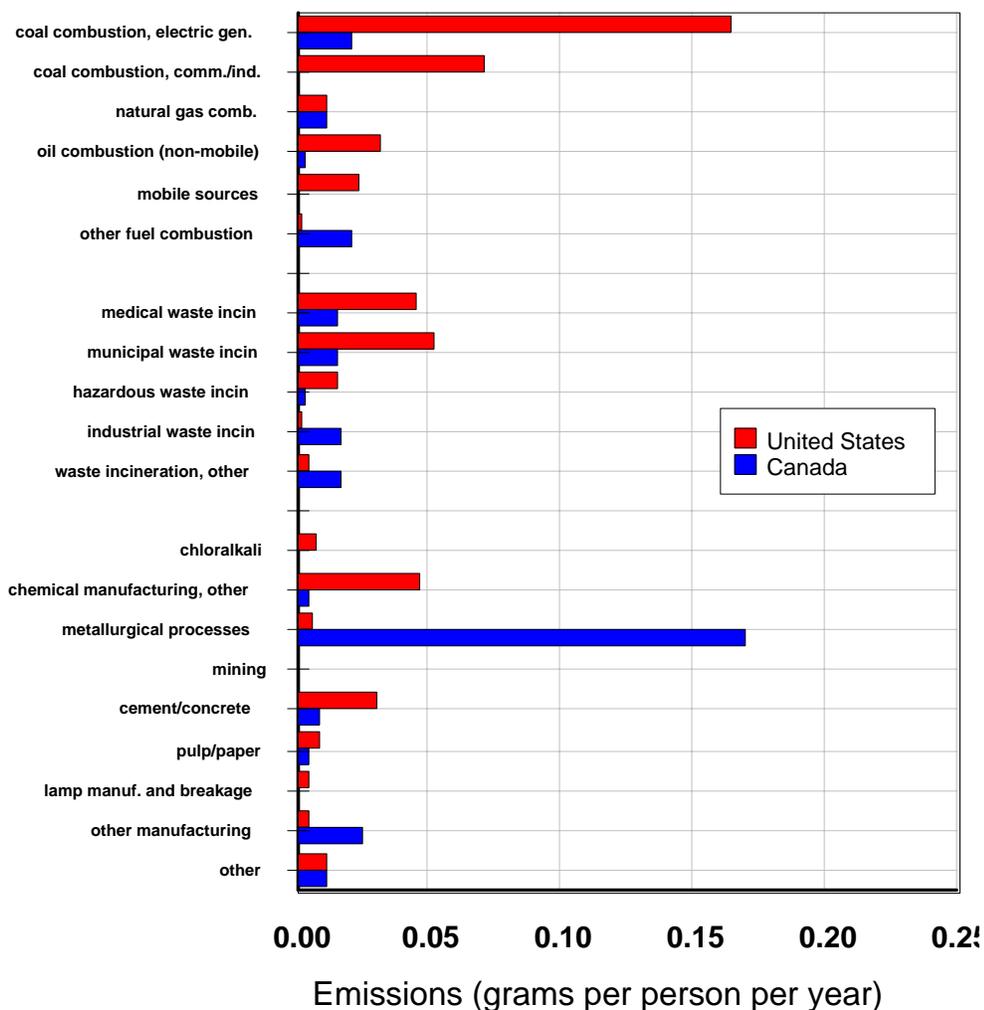
The discussion above is an attempt to quantify sources of air pollutants in the regions most likely to affect Voyageurs and Isle Royale. The discussion is not all-inclusive due to missing or unavailable data. For example, it is not possible at this time to directly compare PAHs or other POPs sources within and outside the park. However, for other pollutants, several conclusions can be made about the magnitude of sources and their potential impacts. Emissions of  $\text{NO}_x$ ,  $\text{PM}_{10}$ , and  $\text{SO}_2$  are dominated by sources outside the park. For example, the Boise Cascade plant, located in International Falls near the western border of Voyageurs, reports emissions of  $\text{NO}_x$ ,  $\text{PM}_{10}$ , and  $\text{SO}_2$  that are two orders of magnitude greater than those estimated to be released from activities within the park. Other very large sources of these compounds are found within 250 km of the parks and are likely to contribute to ozone formation,

visibility reduction, and acid deposition. In-park sources are of minor concern for these compounds.

Contributions of CO and VOCs in the park, on the other hand, are quantitatively similar for sources within and outside Voyageurs. Emissions of CO and VOCs within Voyageurs, primarily from snowmobile use, are similar in magnitude to emissions of these pollutants from major point sources outside the park. For example, in-park sources of CO are estimated to be about 500 to 1,000 tons/year while the Boise Cascade plant in International Falls reports annual emissions of about 1,000 tons. In-park emissions of VOCs were estimated at 300 to 400 tons/year while the Boise Cascade facility reported almost 200 tons/year. In-park sources of CO and VOCs are not unusually high for the region. Many small area, mobile and stationary sources outside the park collectively emit significant amounts of CO and VOCs.

#### **4. Mercury**

Mercury emission estimates have been done by both the US EPA (1996, 1999) and Environment Canada (1995). A global emissions estimate of mercury for 1995 has been constructed (Pacyna and Pacyna, 2002). Below, Figure IV-11 shows the US and Canadian inventories by source category. Energy production from coal and oil combustion accounts for nearly half of the per capita mercury emissions from the US, while metallurgy activities are the dominant source in Canada.



U.S. emissions from a hybrid EPA inventory, representing 1996 for some sources, 1999 for others  
 The Canadian emissions estimates are from an Environment Canada inventory for 1995

Figure IV-11. Per capita mercury emissions for the US (1996) and Canada (1995). From Cohen (2002).

The impact of these emissions has been modeled for the Great Lakes by investigators at the National Oceanic and Atmospheric Administration (NOAA)(Cohen et al., 2002). Using the emissions estimates shown in Figure IV-11 and the NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT), Cohen and co-workers were able to simulate the fate and transport of mercury from the sources, and estimate the depositional flux to each of the Great Lakes. In addition, they were able to estimate the contributions to this deposition from the different source categories.

These results indicate that about 2/3 of the mercury being deposited in Lake Superior comes from sources more than 400 km away from the lake (see Figures IV-12, 13, 14). Thus the mercury deposition in both Isle Royale and Voyageurs is largely due to distant sources.

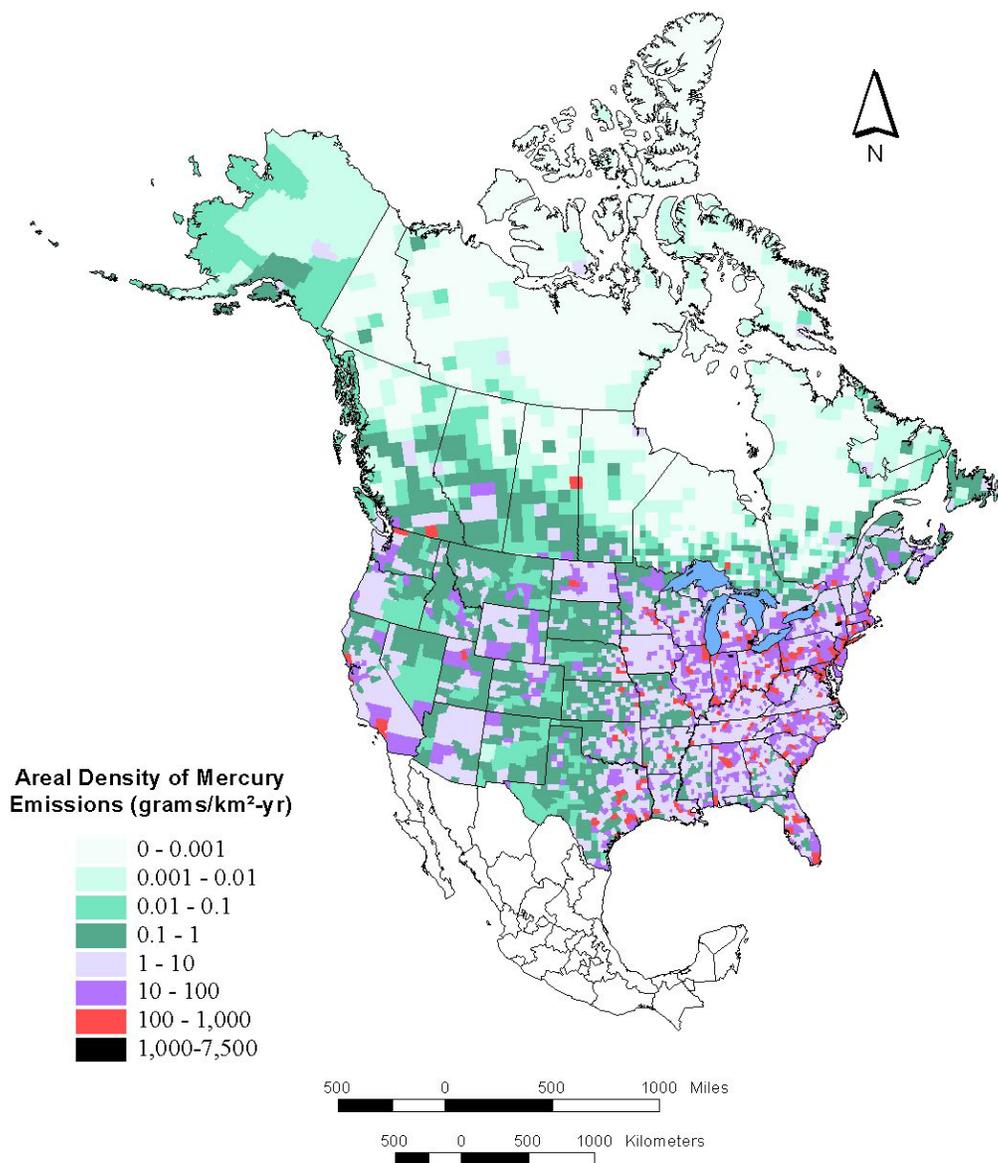


Figure IV-12. Areal density of mercury emissions to North America in g/km<sup>2</sup>-yr. From Cohen (2002). Canadian emissions inventory is for 1995, US inventory is for 1999.

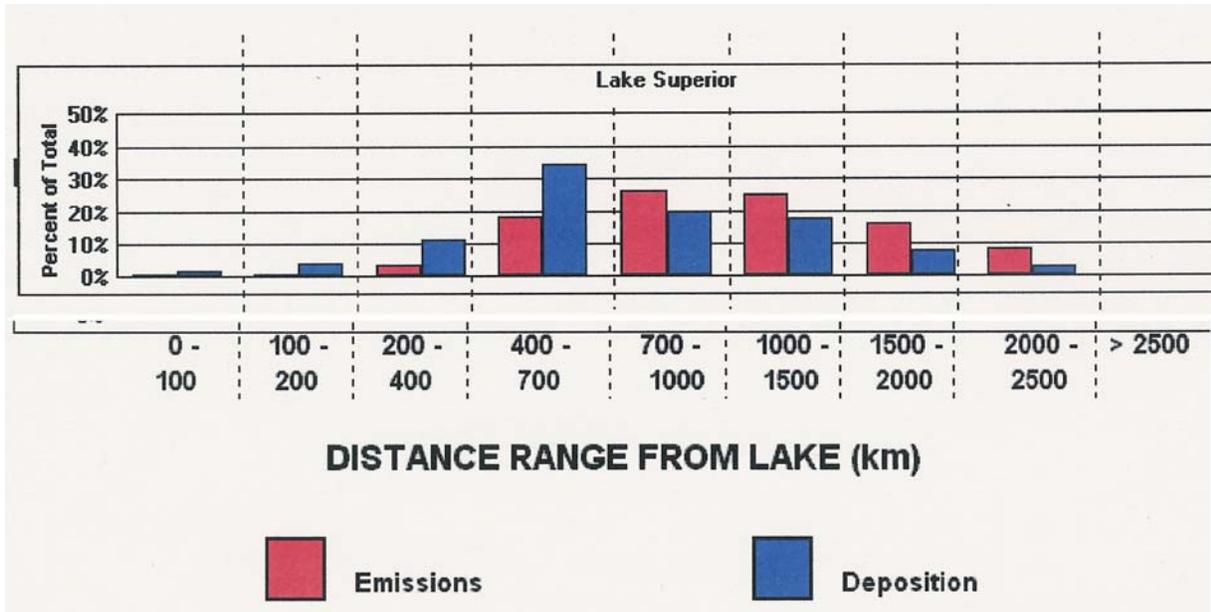


Figure IV-13. Percent of total emissions and deposition of mercury to Lake Superior as a function of distance. Data for sources in the United States (1996, 1999) and sources in Canada (1995): preliminary analysis – Sept 2001. From Cohen (2002).

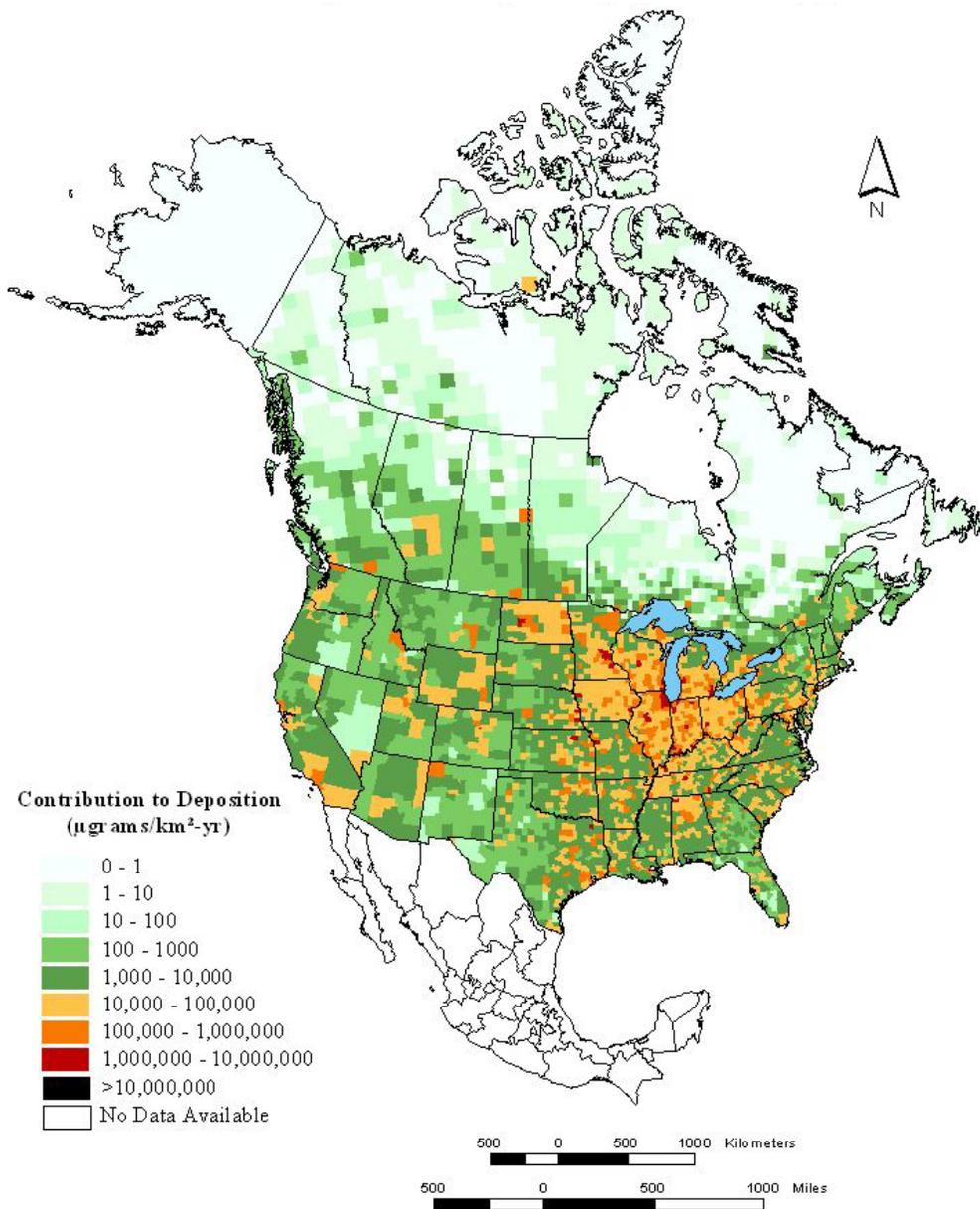


Figure IV-14. Estimated contribution to the atmospheric deposition of mercury to Lake Superior. From Cohen (2002).

## **C. REGIONAL VISIBILITY**

### **1. Background of IMPROVE Monitoring Program**

In 1977 Congress established a national goal of no human-caused visibility impairment in Class I areas, and in 1999 promulgated a rule requiring states to develop and implement plans to make continuous progress toward that goal. The rule directs the states to use the light extinction coefficient as the scale/metric with which to demonstrate their progress. In particular, the states are to use the light extinction coefficient derived from measured particle concentrations and estimated specific extinction efficiencies for relevant particle species (Appendix A). EPA has provided detailed guidance for assessing regional haze using this metric (EPA, 2001a). Clearly, assessment of progress toward the national goal requires long-term particle monitoring on which to base estimates of natural and current visibility conditions. This long-term monitoring is available from the multi-agency IMPROVE Program.

IMPROVE is a cooperative measurement effort governed by a steering committee composed of representatives from federal, regional, and state organizations. The IMPROVE monitoring program was established in 1985 to aid the creation of federal and state implementation plans for the protection of visibility in mandatory Class I areas.

The objectives of IMPROVE are the following:

- to establish current visibility and aerosol conditions in mandatory Class I areas;
- to identify chemical species and emission sources responsible for existing human-caused visibility impairment;
- to document long-term trends for assessing progress toward the national visibility goal; and with the enactment of the Regional Haze Regulations, to provide regional haze monitoring representing all mandatory federal Class I areas.

Ideally, a fully complemented IMPROVE Monitoring Station would include fine and coarse particle monitoring, optical monitoring, and view monitoring with photography.

Particle monitoring provides concentration measurements of atmospheric constituents that contribute to visibility impairment. Four independent IMPROVE sampling modules are used to automatically collect 24-hour samples of suspended particles every Wednesday and Saturday by drawing in air and collecting suspended particles on filters. The filters are then later analyzed to determine the chemical makeup of the suspended particles. Three of the four samplers (modules A, B, and C) collect fine particles with diameters  $<2.5 \mu\text{m}$ . The fourth sampler (module D) collects particles with diameters up to  $10 \mu\text{m}$ . Module A filters are analyzed to determine the gravimetric mass and elemental composition of the collected particles. Module B filters are analyzed specifically for sulfate, nitrate, and chloride ions. Module C filters are analyzed for organic material and light absorbing carbon. The gravimetric mass of coarse particles ( $2.5$  to  $10.0 \mu\text{m}$ ) is determined by subtracting the Module A gravimetric mass from the Module D gravimetric mass.

Version II IMPROVE samplers were deployed throughout the network beginning in the fall of 1999. Although no change in basic sampling methodology over Version I, the new design promotes easier maintenance and servicing, and accommodates the new (2000) EPA one-day-in-three sampling schedule.

Optical monitoring provides a direct quantitative measure of light extinction to represent visibility conditions. Water vapor in combination with suspended particles can affect visibility, so optical stations also record temperature and relative humidity. Optical monitoring uses ambient, long-path transmissometers or ambient nephelometers to collect hourly-averaged data. Transmissometers measure the amount of light (narrow band centered at the  $550 \text{ nm}$  wavelength) transmitted through the atmosphere over a known distance (between  $0.5$  and  $10.0 \text{ km}$ ). The instrument consists of two components; a light source of known intensity (transmitter) and a light measurement device (receiver). The transmission measurements are electronically converted to hourly averaged light extinction ( $b_{\text{ext}}$ , scattering plus absorption). Ambient nephelometers draw air into a chamber and measure the scattering component of light

extinction. Data from both of these instruments are recovered at a central location for storage and analyses. Optical measurements of extinction and scattering include meteorological events such as cloud cover and rain, however, the data are "filtered" by flagging invalid data points with high relative humidities (RH>90%). This filtering process is assumed to remove the effects of weather from the data set. Optical data also fulfill an important need by providing concurrent, independent measurement of extinction to compare with extinction coefficient calculations made using particle data.

Optical monitoring has been conducted for brief periods in the Great Lakes region. However, no NPS optical monitoring sites or optical data records exist at this time.

View monitoring is accomplished with automated 35mm or digital camera systems. Cameras typically take three photographs a day (9:00, 12:00, and 15:00) of selected scenes. The resulting slides are used to facilitate data interpretation, and form a photographic record of characteristic visibility conditions. The goal of view monitoring is to use still-frame or time-lapse imagery to provide a qualitative representation of the visual quality of a scene of interest under a variety of air quality and illumination conditions at different times of day throughout the year. View monitoring images can be used to document how vistas appear under various air quality, meteorological, and seasonal conditions; record the frequency with which various visual conditions occur, provide a quality assurance reference for collocated aerosol or optical measurements, and provide quality media for visually presenting program goals, objectives, and results to decision-makers and the public.

Based on April 1995 recommendations of the IMPROVE Steering Committee, view monitoring has been discontinued at all NPS Class I areas that have a 5-year (or greater) photographic monitoring record. View monitoring has not been conducted at any of the NPS visibility monitoring sites in the Great Lakes region since June 1994.

## **2. Great Lakes Region IMPROVE Data**

Currently there are two NPS IMPROVE Monitoring Stations in Class I areas in the Great Lakes region, Isle Royale and Voyageurs. Additional Class I area IMPROVE Stations have been or are currently operated for the US Forest Service and US Fish

and Wildlife Service. Table IV-6 summarizes the IMPROVE visibility monitoring efforts conducted in the region since 1986.

Site	IMPROVE Visibility Monitoring			
	Particle (Aerosol)		Optical	View
	Version I IMPROVE Sampler	Version II IMPROVE Sampler	Optec Nephelometer	35mm Camera
Boundary Waters Canoe Area Wilderness (MN)	8/91–3/00	3/00–present	5/93–9/97	5/86–9/92
Isle Royale National Park (MI)	3/88–8/91 (seasonal)	11/99–present	--	7/87–10/92
Seney National Wildlife Refuge (MI)	--	11/99–present	1/02–present	--
Voyageurs National Park (MN)	3/88–4/93 (Module A only 5/93 - 6/96)	11/99–present	--	9/86–6/94

At this time, there are insufficient data to summarize regional trends due to the short period of operation and minimal number of sites with overlapping data collection periods. Version II IMPROVE Aerosol Samplers were recently installed at Isle Royale, Voyageurs, Boundary Waters Canoe Area Wilderness, and Seney National Wildlife Refuge. Calculation of regional data summaries and trends may be possible following ongoing data collection through the year 2010. Site-specific data summaries are provided elsewhere in this report.

### 3. Historical Trends in Airport Data

The isopleths of US visual range (75<sup>th</sup> percentile), shown in Figure IV-15, are derived from airport data, from 1950 through 1994 (Schichtel et al., 2001). Winter includes January, February, and March; spring includes April, May, and June; summer includes July, August, and September; and autumn includes October, November, and December. The reference scale shown for each map has been derived using a modified Koschmieder relationship that takes into account site-specific target considerations and human-eye sensitivity (red being worst, blue being best).

The prominent nationwide features are fairly apparent, (i.e., visibility is generally better in the west (southern California excepted) and poorer in the East, and the

summer season provides the worst visibility in the East and the best in the West).

Historical trends for the Great Lakes portion of the country are quite evident in Figure IV-15:

- Seasonally for the Great Lakes states, winter corresponds to the lowest visibility while the summer months have better visibility.
- Over time the maps in Figure IV-15 show the following trends for the US:
  - In the winter, there has been some improvement in visibility in the north-central US from 1950 to 1954 and 1990 to 1994.
  - The spring season shows a general degradation of visibility in the entire eastern US, especially along the Gulf Coast and the south and central East Coast.
  - In the summer, a region of modest visibility in the eastern US during 1950 to 1954 steadily expanded and became worse until the entire eastern US was significantly degraded. There is some evidence of improvement in the early 1990s.
  - The autumn season shows significant improvement in the north-central industrial areas from 1970 to 1974 and 1980 to 1984, with little change in the remainder of the East.

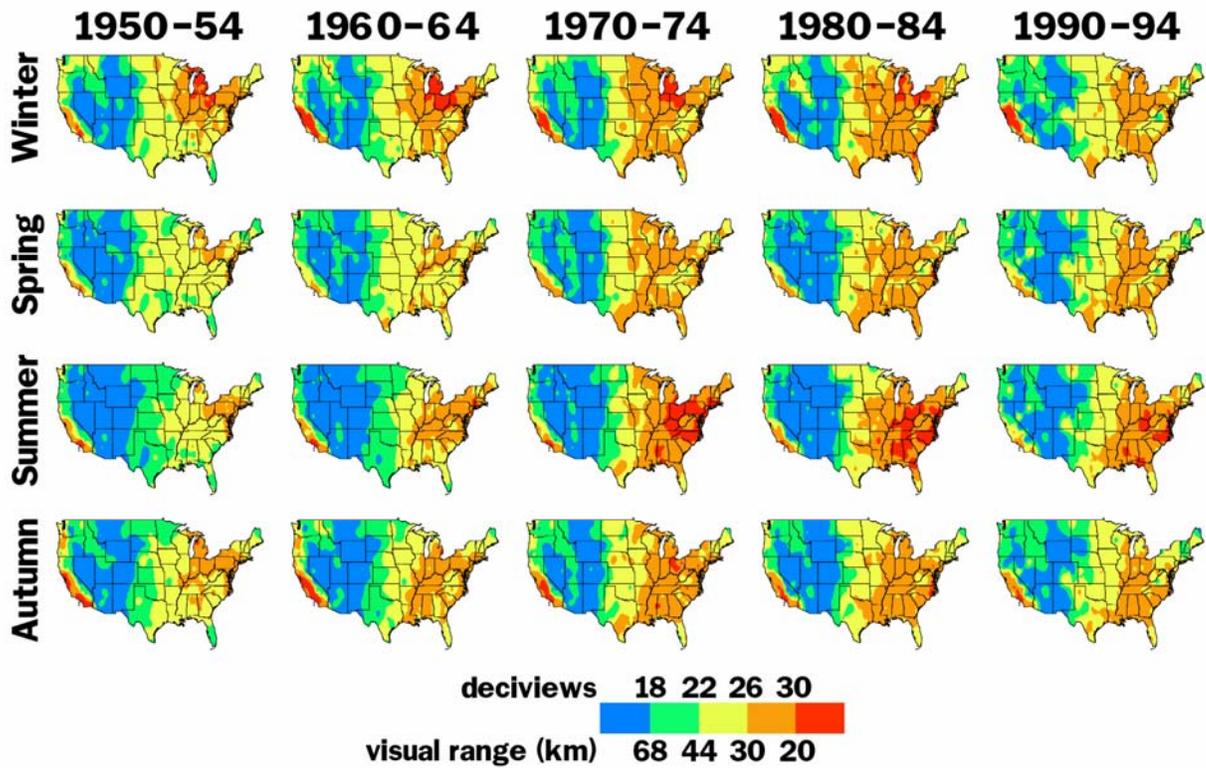


Figure IV-15. Trends in 75<sup>th</sup> percentile visual range over the US from 1950 through 1994. These data have been filtered for weather and adjusted to a relative humidity of 60% (Schichtel, et al., 2001).

#### **4. Midwest Regional Planning Organization**

The States of Illinois, Indiana, Michigan, and Wisconsin established the Lake Michigan Air Directors Consortium (LADCO) in 1990. The purpose of LADCO is to provide technical assessments for and assistance to its member states on problems of air quality. In 1999, the Midwest Regional Planning Organization (RPO) was formed to facilitate regional planning to address the regional haze regulations. The primary responsibility of the Midwest RPO is to assess visibility impairment due to regional haze in the mandatory Federal Class I areas located within the borders of Illinois, Indiana, Michigan, Ohio, and Wisconsin, and the impact of emissions from the five states on mandatory Federal Class I areas outside the borders of those states. LADCO has been designated as the agency to receive Federal grant funds on behalf of the Midwest RPO.

In September of 2001, the Midwest RPO released the report, *Regional Haze and Visibility in the Upper Midwest*. This report was an initial assessment of the regional haze problem in the upper Midwest and was compiled by reviewing existing reports and analyzing available air quality data. The key findings of this initial assessment are summarized in Section V.A.2.g.

## **V. MONITORING AND RESEARCH ACTIVITIES**

### **A. VISIBILITY**

Atmospheric haze and loss of visibility has been an increasing concern in many national parks. In 1993, the National Research Council reported that visibility in the national parks had dropped to half of what it would be in the absence of air emissions (NRC, 1993). Emissions of SO<sub>x</sub> and NO<sub>x</sub> contribute to fine aerosol formation, and these and other small particulates reflect and scatter sunlight. The eastern, western, and southern national parks have had the largest reductions in visibility, while the upper Midwest has had smaller reductions in visibility (Armentano and Loucks, 1983).

#### **1. Isle Royale National Park**

As part of the IMPROVE monitoring network (see Section IV.C above), visual air quality at Isle Royale has been monitored using an aerosol sampler and camera. The aerosol sampler on the island operated intermittently from March 1988 through August 1991. In November 1999, the IMPROVE network installed an IMPROVE Version II aerosol sampler in Eagle Harbor, MI, 45 miles from Isle Royale. Upgrading the IMPROVE site on Isle Royale itself was deemed impractical since the Park has no staff or visitors for 5–6 months of the year. Data are currently being collected 12 months of the year at the Eagle Harbor site. Aerosol data were only collected January to March, and May to October for a short 3-year period, 1988 through 1991, on the island. Therefore, the currently available data are insufficient for aerosol data summaries representative of Isle Royale.

The automatic 35mm camera on the island operated from July 1987 through October 1992. The camera photographed Mount Siskiwit, 14 kilometers to the west-southwest from 1987 through March 1992; in April of 1992 the angle of view was changed to capture Pie Island and Thunder Bay to the west-northwest. Color 35mm slide photographs were taken once per day.

Slides taken by the view monitoring camera document visual conditions and are an effective tool for interpreting the visual effects of measured optical and aerosol parameters. The photographs are also valuable for presenting goals, objectives, and

results of the monitoring program to decision-makers and the public. In Figure V-1, photographs of the Mt. Siskiwit vista are provided to illustrate the range of visibility conditions observed during the period of record.

**Isle Royale National Park**  
on a "Good" day

Estimated Visibility Conditions:  
Visual Range: 260 – 310 km  
 $B_{ext}$ : 15 – 13  $Mm^{-1}$   
Haziness: 4 – 2 dv

(a)



**Isle Royale National Park**  
on an "Average" day

Estimated Visibility Conditions:  
Visual Range: 120 – 140 km  
 $B_{ext}$ : 33 – 28  $Mm^{-1}$   
Haziness: 12 – 10 dv

(b)



**Isle Royale National Park**  
on a "Poor" day

Estimated Visibility Conditions:  
Visual Range: 5 – 15 km  
 $B_{ext}$ : 782 – 261  $Mm^{-1}$   
Haziness: 44 – 33 dv

(c)



Figure V-1. Photographs illustrating visibility conditions at Isle Royale National Park

## 2. Voyageurs National Park

As part of a cooperative agreement with Boise Cascade and the NPS, visual air quality at Voyageurs has been monitored using an aerosol sampler and camera. The aerosol sampler operated at a location northwest of the Rainy Lake Visitor Center from March 1988 through April 1993. In November 1999, the IMPROVE network installed an IMPROVE Version II sampler at a location near the Ash River Visitor Center. An automatic 35mm camera was operated at the Kabetogama Lake Visitor Center from September 1986 through June 1994, viewing Martin Island to the east.

### a. Particle Monitoring - Aerosol Sampler Data

In this report, particle data from the Voyageurs IMPROVE site are summarized to characterize the full range of visibility conditions for the January 1989 through December 1992 period, based on calendar quarters (1<sup>st</sup> quarter: January, February, March; 2<sup>nd</sup> quarter: April, May, June; 3<sup>rd</sup> quarter: July, August, September; and 4<sup>th</sup> quarter: October, November, December) and annual periods (January through December).

The composition and concentration of visibility reducing pollutants are generally quantified by aerosol sampling. Aerosol sampling provides a time-integrated (generally 24-hour average) measurement of the size, concentration, and composition of visibility-related aerosols.

Before the multi-year average was calculated, the following IMPROVE data criteria were applied to the yearly aerosol sampler data:

- No more than 10 samples in a row were missing at any time;
- No more than 50% of the data for a quarter were missing; and
- No fewer than 75% of all possible samples during a year had at least some data available.

In 1996, glycerin was added to the denuders at all IMPROVE sites. At many sites, the nitrate numbers became much less variable and had a drastic change in the number of extremely high values: the average values were also affected. Therefore,

individual daily nitrate values prior to 1996 were replaced with constant 1997 - 99 mean values. Because Voyageurs did not have any post-1996 data, nitrate values could not be adjusted.

b. Observed Concentrations

Table V-1 shows the mass concentrations ( $\mu\text{g}/\text{m}^3$ ) of fine and coarse aerosol, and the chemical composition (mass budgets) of the fine aerosol for Voyageurs, January 1989 through December 1992.

Table V-1. Measured Fine and Coarse Aerosol Mass Concentrations (in  $\mu\text{g}/\text{m}^3$ ) for Voyageurs National Park (January 1989–December 1992).

Quarter	Fine Mass	Ammonium Sulfate	Ammonium Nitrate	Organics	Light Absorbing Carbon	Fine Soil	Coarse Mass
1st	5.1	2.5	1.0	1.2	.2	.2	3.4
2nd	5.1	2.5	.2	1.8	.2	.4	5.5
3rd	5.3	1.9	.1	2.8	.2	.3	8.5
4th	4.6	1.7	1.0	1.5	.2	.2	4.7
Annual	5.0	2.2	.6	1.8	.2	.3	5.6

Fine mass budgets for the mean of the clearest, middle, and haziest 20% of days are presented in Figure V-2. The “clearest” and the “haziest” signify lowest fine mass concentrations and highest fine mass concentrations respectively, with “middle” representing the 20% of days with fine mass concentrations in the middle of the distribution. Each budget includes the standard visual range (km), and deciview (dv) (Pitchford and Malm, 1994).

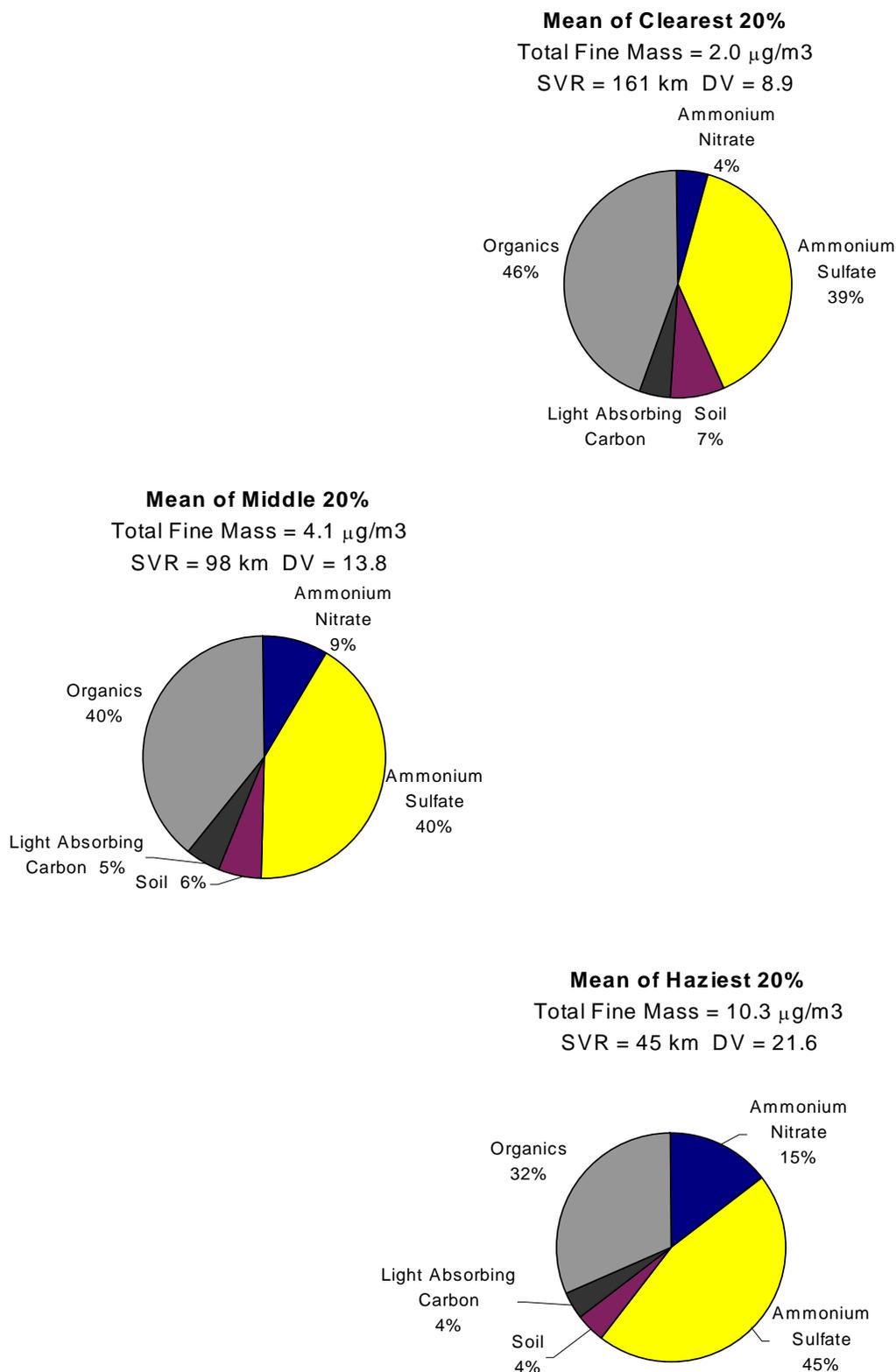


Figure V-2. Fine mass budgets (in percent) for the mean of the clearest, middle, and haziest 20% of days for Voyageurs National Park, January 1989–December 1992.

c. Calculated Light Extinction Coefficients

Atmospheric light extinction coefficient budgets (see Appendix A) generated from aerosol sampler data apportion the extinction at Voyageurs to specific aerosol species: Rayleigh, ammonium sulfate, ammonium nitrate, organics, elemental (light absorbing) carbon, and coarse mass. The sum of these species account for the majority of non-weather related extinctions. Figure V-3 depicts graphically the seasonal and annual variation in extinction budgets for the mean of the clearest, middle, and haziest 20% of days. Definitions are the same as explained above for Figure V-2, plus each budget includes the corresponding extinction coefficient.

The segment at the bottom of each stacked bar in Figure V-3 represents Rayleigh scattering, which is assumed to be a constant  $10 \text{ Mm}^{-1}$  at all sites during all seasons. Rayleigh scattering is the natural scattering of light by atmospheric gases. Higher fractions of extinction due to Rayleigh scattering indicate cleaner conditions.

Ammonium sulfates are the single largest contributor to visibility extinction at Voyageurs, as shown in Figure V-3.

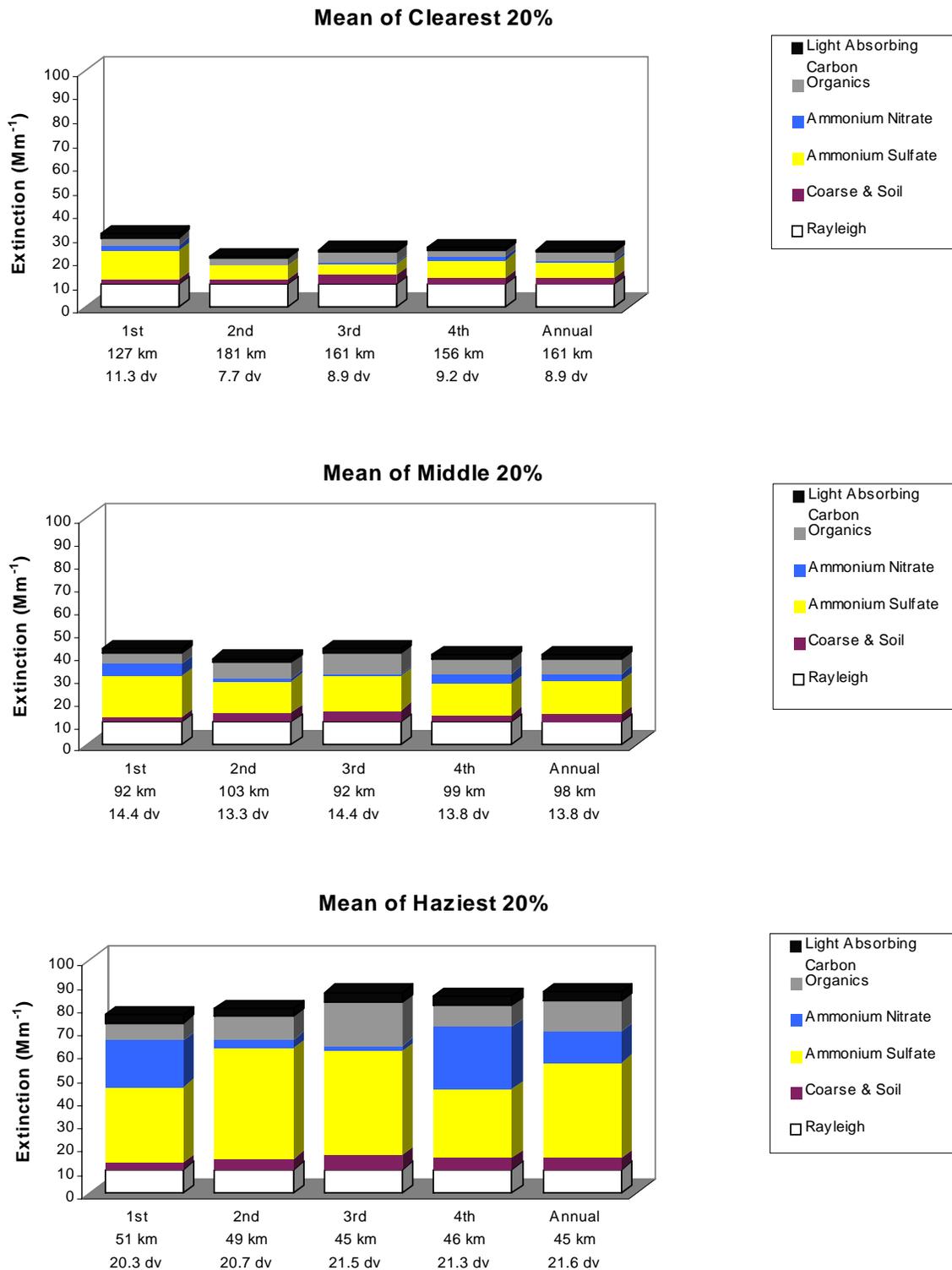


Figure V-3. Calculated extinction coefficient budgets for Voyageurs National Park, January 1989–December 1992.

A tabular summary of average calculated extinction coefficient values by quarter and year for the January 1989 - December 1992 period are provided in Table V-2.

Table V-2. Seasonal and Annual Average Standard Visual Range (km) and Calculated Extinction ( $Mm^{-1}$ ), Voyageurs National Park, January 1989–December 1992.

Year	1st (Jan, Feb, Mar)		2nd (Apr, May, Jun)		3rd (Jul, Aug, Sep)		4th (Oct, Nov, Dec)		Annual (Jan-Dec) <sup>a</sup>	
	SVR (km)	$b_{ext}$ ( $Mm^{-1}$ )	SVR (km)	$b_{ext}$ ( $Mm^{-1}$ )						
1989	82	47.5	103	38.1	61	64.3	86	45.5	77	50.5
1990	90	43.3	100	39.1	83	47.2	68	57.7	84	46.4
1991	85	46.2	84	46.8	93	42.1	107	36.6	91	42.8
1992	82	47.5	103	38.1	61	64.3	86	45.5	82	47.7
Mean <sup>b</sup>	82.3	47.8	92.5	42.7	82.8	48.8	85.5	47.0	83.5	46.9 <sup>c</sup>

<sup>a</sup> Annual period data represent the mean of all data for each January through December annual period.

<sup>b</sup> Combined quarter data represent the mean of all quarterly means for each quarter of the January 1989 through December 1992 period.

<sup>c</sup> Combined annual period data represent the mean of all combined quarterly means.

#### d. Observed Trends

A four-year aerosol data record, January 1989 through December 1992, is insufficient to adequately evaluate observed trends for Voyageurs. Therefore, efforts were made to evaluate whether visibility conditions and data from the nearby IMPROVE station at Boundary Waters Canoe Area could be representative of Voyageurs. Boundary Waters Canoe Area, a wilderness area within the Superior National Forest, is located approximately 89 miles to the east-southeast of Voyageurs National Park. IMPROVE aerosol sampler data have been collected from August 1991 to the present. Minimal differences in seasonal means and average species concentrations have been observed by others in overlapping data sets from the two IMPROVE locations (Miller, 2000). Therefore, the Boundary Waters Canoe Area data were further reviewed and summarized, as shown in Figures V-4 through V-7, to represent regional visibility conditions for Voyageurs and the northern-Minnesota portion of the Great Lakes region.

Particle data from the Boundary Waters Canoe Area IMPROVE site have been summarized for the January 1992 through December 1997 period, based on calendar quarters. Yearly aerosol sampler data were verified to determine whether they met the following IMPROVE data criteria:

- No more than 10 samples in a row were missing at any time;
- No more than 50% of the data for a quarter were missing; and
- No fewer than 75% of all possible samples during a year had at least some data available.

The Boundary Waters Canoe Area data for 1996, 1998, and 1999 did not pass this data verification.

Figure V-4 plots the relative contribution to aerosol light-extinction by the five principal particulate matter constituents for the clearest 20%, middle 20%, and haziest 20% groups at Boundary Waters Canoe Area from 1992 to 1997. This figure shows that ammonium sulfate is also the single largest contributor to visibility extinction at the Boundary Waters Canoe Area.

Figure V-5 shows plots of the trends in annual average calculated light extinction for the clearest 20%, middle 20%, and haziest 20% groups at the Boundary Waters Canoe Area. Extinction is also presented in units of standard visual range (km) and  $dv$ . A slight trend of improvement was observed during the period.

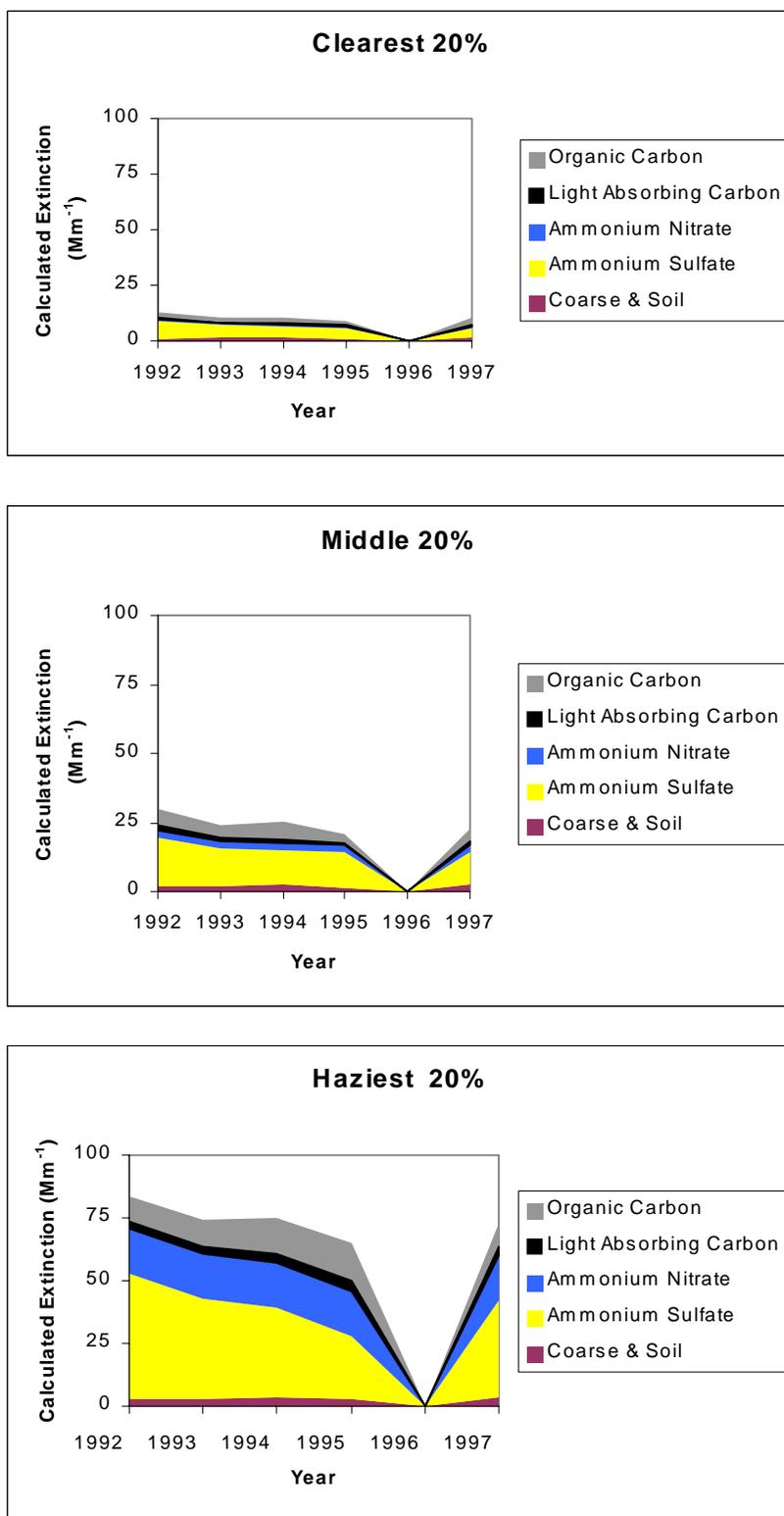


Figure V-4. Calculated aerosol light extinction in the Boundary Waters Canoe Area for the clearest 20%, middle 20%, and haziest 20% of the days in the distribution, January 1992–December 1997. Note: The 1996 data were not used because data did not pass verification for this year.

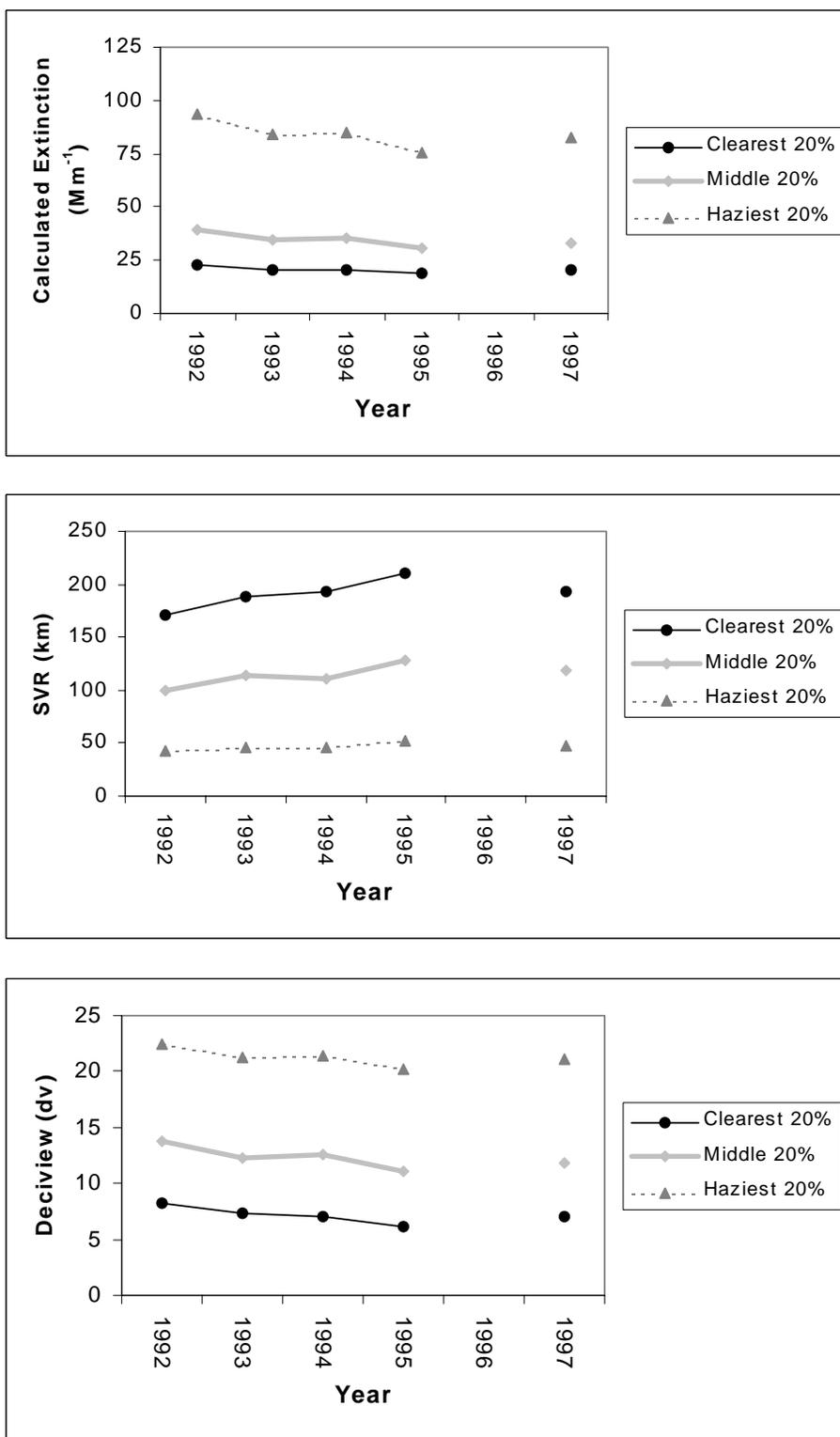


Figure V-5. Trends in annual averages for aerosol extinction ( $Mm^{-1}$ ), SVR (km), and deciview (dv), Boundary Waters Canoe Area, January 1992–December 1997.

e. Additional Analyses

In order to gain further insight into the geographic regions that may be contributing to visibility impairment, the results of additional analyses of conditional probability, source contribution, and back trajectory analyses are presented in the following subsections. The Boundary Waters Canoe Area data analysis is presented because there are insufficient data from Voyageurs to complete a regional analysis. In fact, available data indicate that the wind directions associated with good and bad visibility conditions are dramatically different at Voyageurs from those at the Boundary Waters Canoe Area. Therefore, major source contributions identified for the Boundary Waters Canoe Area may not be representative for Voyageurs.

f. Conditional Probability and Source Contribution Analysis

Two methods have previously been used successfully to determine the source regions and transport pathways associated with high particulate concentrations observed in remote areas of the US (Malm et al., 1990; Gebhart and Malm, 1991). These analyses are high concentration source contribution function (HSCF) and high concentration conditional probability (HCCP). Both analyses are based on examining the transport pathways of air parcels which arrive at the receptor (location of interest) when the concentration of the chemical species of interest meets a pre-defined criteria for being a “low/high” concentration. The Boundary Waters Canoe Area low/high sulfur concentrations for the January 1992 through December 1997 period were compiled by the Cooperative Institute for Research in the Atmosphere (CIRA), for the best and worst concentrations. Best (clearest) concentrations are defined as the 20<sup>th</sup> percentile or lower. Worst (haziest) concentrations are defined as the 80<sup>th</sup> percentile or greater. Sulfur accounted for a majority of extinction during the period.

The conditional probability is the probability that if an air mass arrived at Boundary Waters Canoe Area after passing over a given area, it arrived when the sulfur concentration was at the clearest 20% concentration or lower (lowest concentration, Figure V-6), or at the haziest 20% or greater (highest concentration, Figure V-8). For example, as shown in Figure V-8, if an air mass arrived from northern Illinois, there is a

60-80% chance that the sulfur concentrations would be the highest 20% (worst) of those measured at Boundary Waters Canoe Area during 1992 - 1997. The conditional probability does not take into account how often air masses arrive from a given area, only the probability that if transport from that direction occurs, the sulfur concentration is high.

The HSCF shows areas from which air masses were most likely to arrive when the sulfur concentrations at Boundary Waters Canoe Area were in the lowest (best)/highest (worst) 20%. (See Figures V-7 and V-9 respectively). The actual frequency of air masses from each grid square, called the residence time, is normalized by the probability that an air mass originated there by chance alone. For example, as shown in Figure V-9, the probability that air arrived from an area on the Iowa/Illinois border when sulfur concentrations were very high is 4-8 times more likely than chance alone.

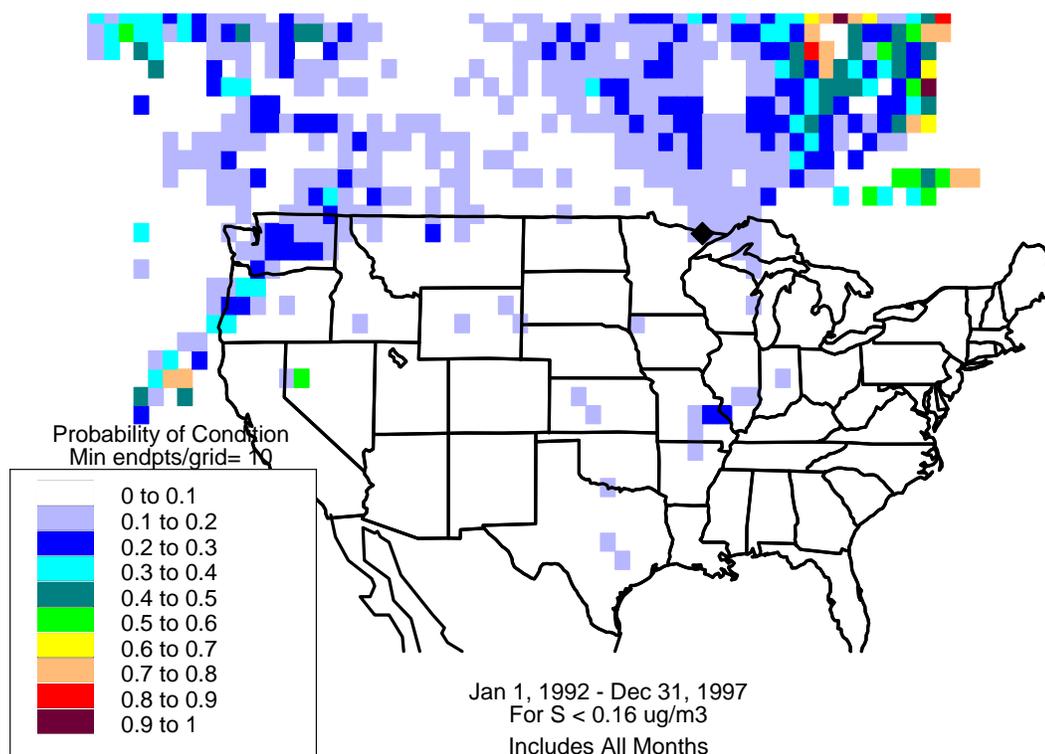


Figure V-6. Conditional Probability, Boundary Waters Canoe Area, Clearest 20%, Sulfur, January 1992 through December 1997. Endpoint heights = 300 – 3000 m, input = atad.

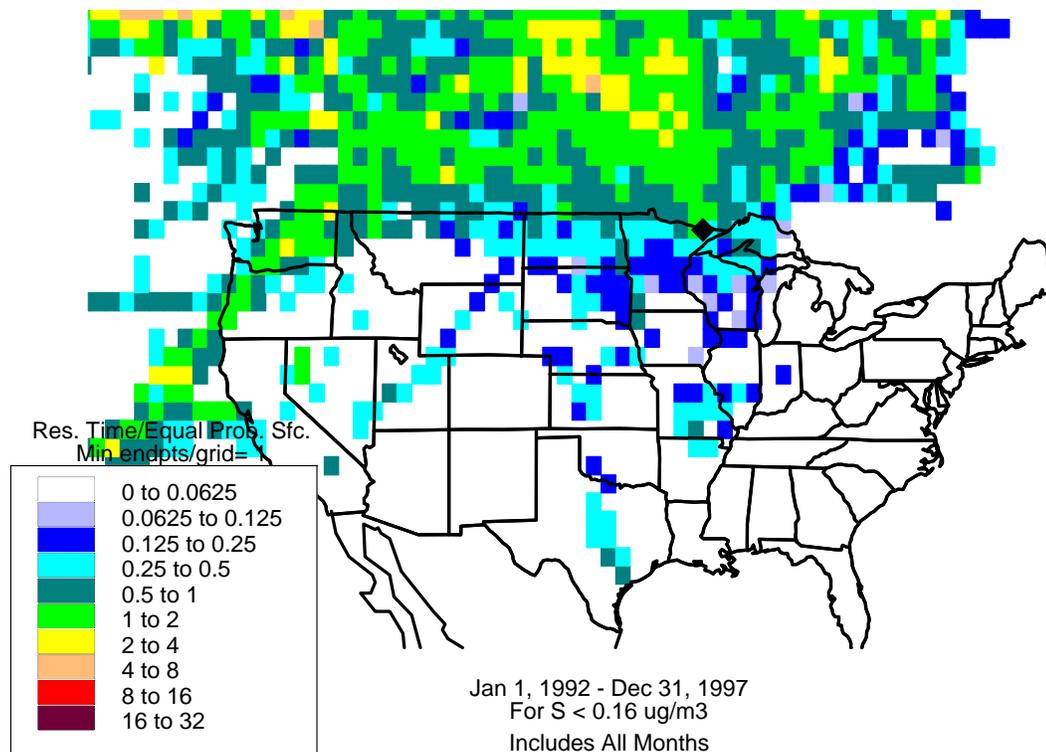


Figure V-7. Source Contribution, Boundary Waters Canoe Area, Clearest 20%, Sulfur, January 1992 through December 1997. Endpoint heights = 300 – 3000 m, input = atad.

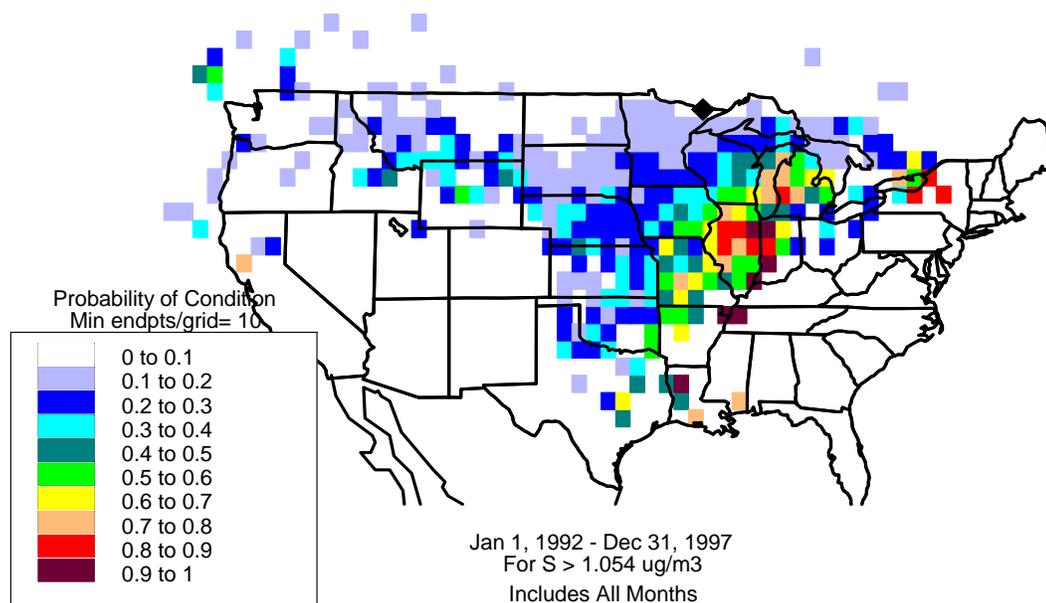


Figure V-8. Conditional Probability, Boundary Waters Canoe Area, Haziest 20%, Sulfur, January 1992 through December 1997. Endpoint heights = 300 – 3000 m, input = atad.

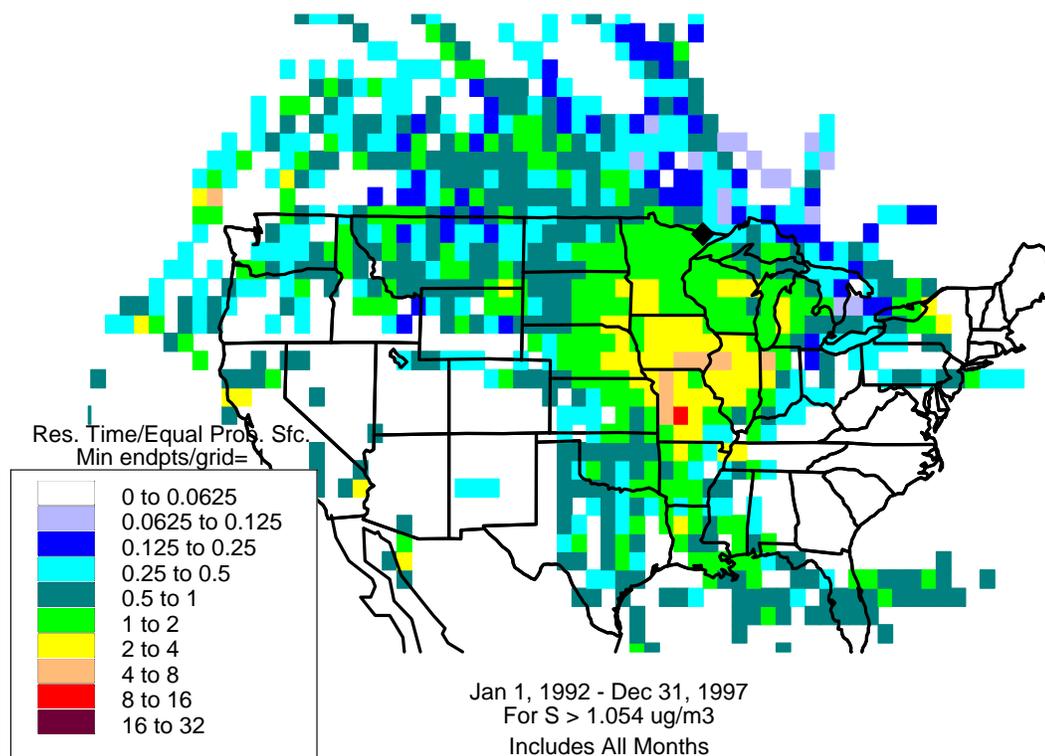


Figure V-9. Source Contribution, Boundary Waters Canoe Area, Haziest 20%, Sulfur, January 1992 through December 1997. Endpoint heights = 300 – 3000 m, input = atad.

g. Forty-Eight-Hour Backward Trajectory Analyses

In the report, *Regional Haze and Visibility in the Upper Midwest* (Midwest RPO(2001)), back trajectories were calculated with HYSPLIT for a 48-hour period and a 200m start height, to assess the meteorological conditions on the 20% worst and 20% best visibility days for Boundary Waters Canoe Area. As seen in Figure V-10, the worst visibility days (red lines) are generally associated with southerly-southwesterly flow, and the best visibility days (blue lines) with northerly flow.

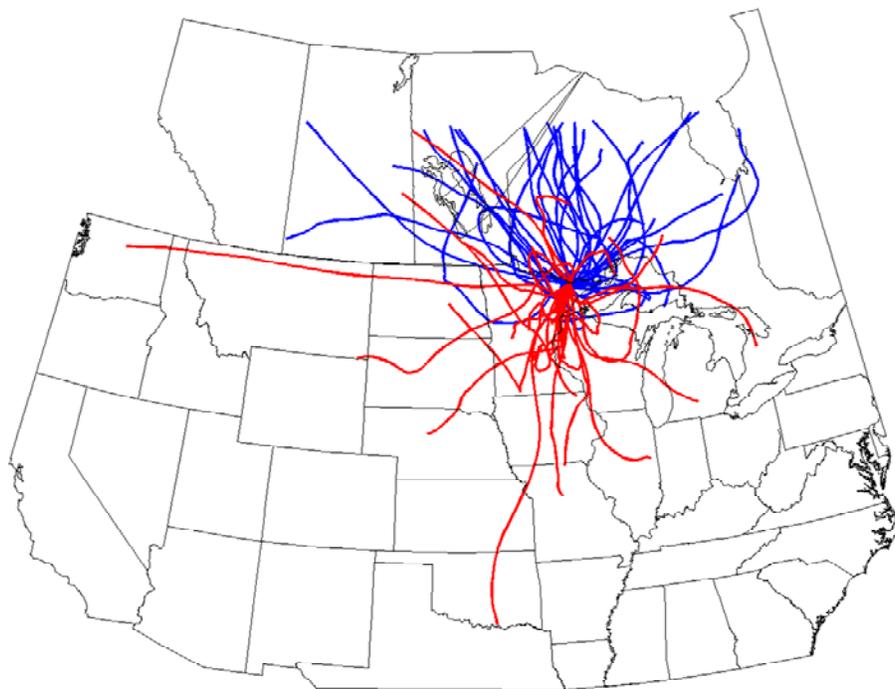


Figure V-10. 48-Hour Back trajectories for 20% worst (red) and 20% best (blue) days in Boundary Waters Canoe Area, 1997–1999. Stat height = 200 m.

h. View Monitoring—Camera Data

An automatic 35mm camera system operated at Voyageurs from September 1986 through June 1994. Color 35mm slide photographs of Martin Island, 4 kilometers to the east, were taken 3 times per day.

View monitoring slides document visual conditions and are an effective tool for interpreting the visual effects of measured optical and aerosol parameters or presenting monitoring program goals, objectives, and results to decision-makers and the public. The Martin Island vista photographs presented in Figure V-11 were chosen to provide a feel for the range of visibility conditions observed during the period of record.

**Voyageurs National Park**  
on a "Good" day

(a)



**Voyageurs National Park**  
on an "Average" day

(b)



**Voyageurs National Park**  
on a "Poor" day

(c)



Figure V-11. Photographs illustrating visibility conditions at Voyageurs National Park. Note: The Voyageurs vista does not provide a suitable target for quantitative analysis. No visual range measurements are provided.

i. Other Studies

In addition to the IMPROVE network, the Great Lakes region has been the focus of many studies that examined visibility, haze, and the sources of pollutants responsible for visibility impairment. Two such studies are *Regional Haze and Visibility in the Upper Midwest* (Midwest Regional Planning Organization (RPO), 2001) and *Voyageurs National Park Visibility Data Summary* (Miller, 1999).

The results from *Regional Haze and Visibility in the Upper Midwest* were compared to data for the nation (Schichtel et al., 2001). A known shortcoming of the Midwest RPO assessment is the absence of sufficient visibility-related measurements in the region. The key findings of the assessment are as follows:

- Visibility impairment exists in two Class I areas in the upper Midwest (Seney National Wildlife Refuge and Isle Royale National Park), in downwind class I areas in the eastern half of the US, and in other areas (e.g. major urban areas). Although current conditions in the upper Midwest Class I areas approach “natural conditions” on the 20% best visibility days, they are significantly worse on the 20% worst visibility days. Fine particles, which play a major role in visibility impairment, also reach unhealthy levels across a large portion of the eastern US.
- Visibility levels and PM<sub>2.5</sub> concentrations vary:
  - Spatially, with better visibility and lower PM<sub>2.5</sub> occurring to the north (near Class I areas in the upper Midwest); and poorer visibility and higher PM<sub>2.5</sub> to the south (near Ohio River Valley);
  - Seasonally, with the worst and best visibility days occurring throughout the year in the Class I areas in the upper Midwest; and the worst visibility days occurring during summer, and best visibility during winter elsewhere in the eastern US;
  - Chemically, with sulfates dominating on the worst visibility days during summer (note, organics are a distant second); and nitrates being important on worst visibility days during winter/fall (note, sulfates are also important and organics are a distant third)

- Worst visibility days are associated with southerly-westerly flow for many sites in the eastern US, and the best visibility days with northerly flow.
- Poor visibility is related to elevated concentrations of the fine particles and (during the summer) ozone.
- Visibility levels deteriorated during the last half-century, but appear to be improving in recent years due to SO<sub>2</sub> emission reductions.

*The Voyageurs National Park Visibility Summary* (Miller, 1999) recaps a study conducted by the NPS and funded by the Boise Cascade Corporation. The purpose of the study was to determine whether emissions from the Boise Cascade pulp mill in International Falls were impacting the park. The study concluded there was insufficient information to determine if emissions from Boise Cascade negatively impacted visibility at Voyageurs during the period monitoring period, 1988 - 1993.

## **B. ATMOSPHERIC CONCENTRATIONS OF NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub>, PM, LEAD**

The NPS is not required to monitor airborne concentrations of criteria pollutants in national parks. However, in a number of NPS areas, a subset of the criteria pollutants and their secondary compounds are monitored.

### **1. Isle Royale National Park**

Because it is so isolated, monitoring air pollutants in Isle Royale is a challenge in any season and near-to-impossible when the park is closed during the winter. A meteorology station was installed on the top of Mount Ojibway, the second highest peak on Isle Royale, to record temperature, relative humidity, and solar radiation. However, the site is only operated when park staff are on the island. Sulfur dioxide was monitored in the park from 1988 to 1991; concentrations were negligible. Ozone has been monitored from May to October, using a continuous monitor from 1987 to 1991, a passive monitor from 1996 to 2002, and a portable monitor from 2002 to 2004

The average seasonal concentrations with the passive monitor ranged from a low of 36 ppb in 2000 to a high of 43 ppb in 1999 and 2002. The estimated 1 hr seasonal maximum ozone concentrations were well below the NAAQS of 120 ppb. (Figure V-12).

When data from the portable ozone monitor are available, they will be directly comparable to the 1 hr and 8 hr NAAQS.

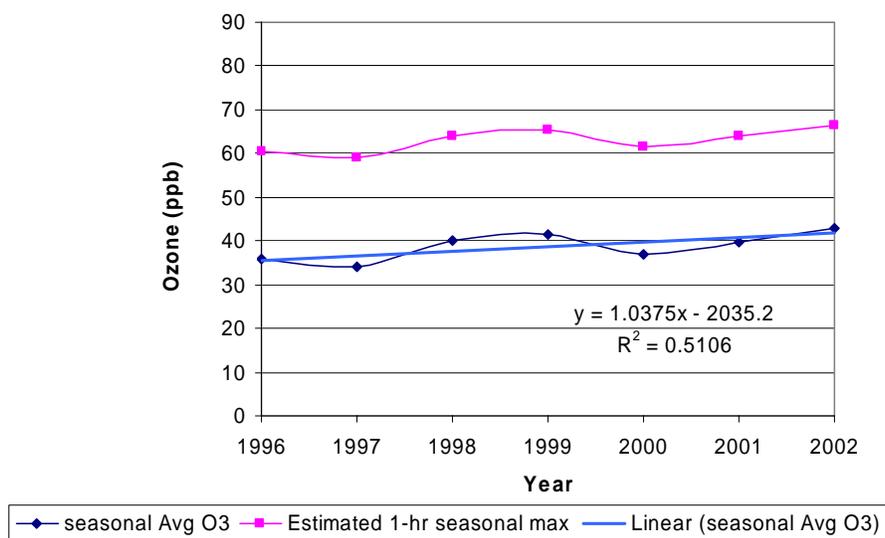


Figure V-12. Seasonal ozone concentrations determined from the passive ozone monitoring program at Isle Royale (pers. comm. J.D. Ray, NPS).

## 2. Voyageurs National Park

Sulfur dioxide was monitored at Black Bay in Voyageurs from 1988 to 1996; concentrations were negligible. Ozone concentrations have been measured at Sullivan Bay since 1986, and were measured at Black Bay from 1987 to 1996. Although ozone concentrations at Voyageurs exhibit very strong diurnal and seasonal variability (Figure V-13), the concentrations are very low, and have not exceeded the NAAQS. The concentrations measured at Voyageurs are consistently in the bottom third of measurements reported at national parks (National Park Service Air Resources Division, 1996, 1997, 1998, 1999, 2000b).

Nevertheless, ozone concentrations are of concern at Voyageurs because data indicate a statistically significant increase in ozone concentrations between 1988 and 1997 (Miller, 2000). The same finding, for the 1990-1999 period, was reported in a NPS memorandum (Joseph, 2001). Recent review of the data indicates ozone is increasing at Voyageurs by ~3.7% per year (personal communication, J.D. Ray, NPS).

### Hourly Ozone Concentrations at Voyageurs National Park

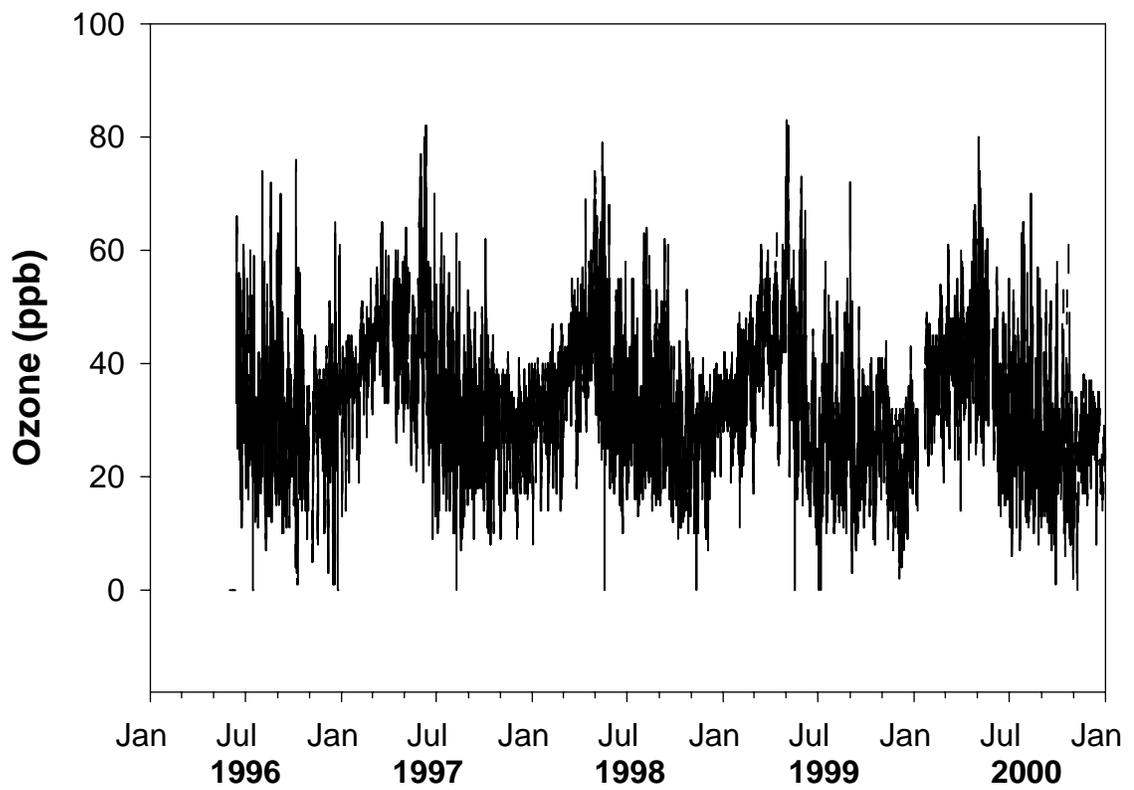


Figure V-13. Hourly ozone concentrations in Voyageurs from 1996 to 2000.

## **C. DEPOSITION OF NITROGEN AND SULFUR COMPOUNDS**

### **1. Wet Deposition**

Deposition of nitrogen and sulfur compounds in the upper Midwest is reported for two pathways: wet deposition and dry deposition. Wet deposition is measured by the National Atmospheric Deposition Program (NADP) by direct collection of precipitation events (snow or rain). NADP sites are located in Voyageurs at Sullivan Bay and in Isle Royale at Wallace Lake. The site at Voyageurs has been active from 1988-1996 and from 2000- present. Wet deposition of SO<sub>4</sub>, chloride, NO<sub>3</sub>, NH<sub>4</sub>, sodium, potassium, calcium, and magnesium is measured as is pH and conductivity. The site at Isle Royale has been in operation since 1985.

Wet nitrogen deposition includes ammonium ion and nitrate. Major anthropogenic sources of nitrogen deposition include combustion sources (vehicle exhaust, power plants) and agriculture (fertilizers). Therefore, regions most heavily impacted by nitrogen deposition include major urban centers and the Midwestern agricultural regions (Figure V-14.)

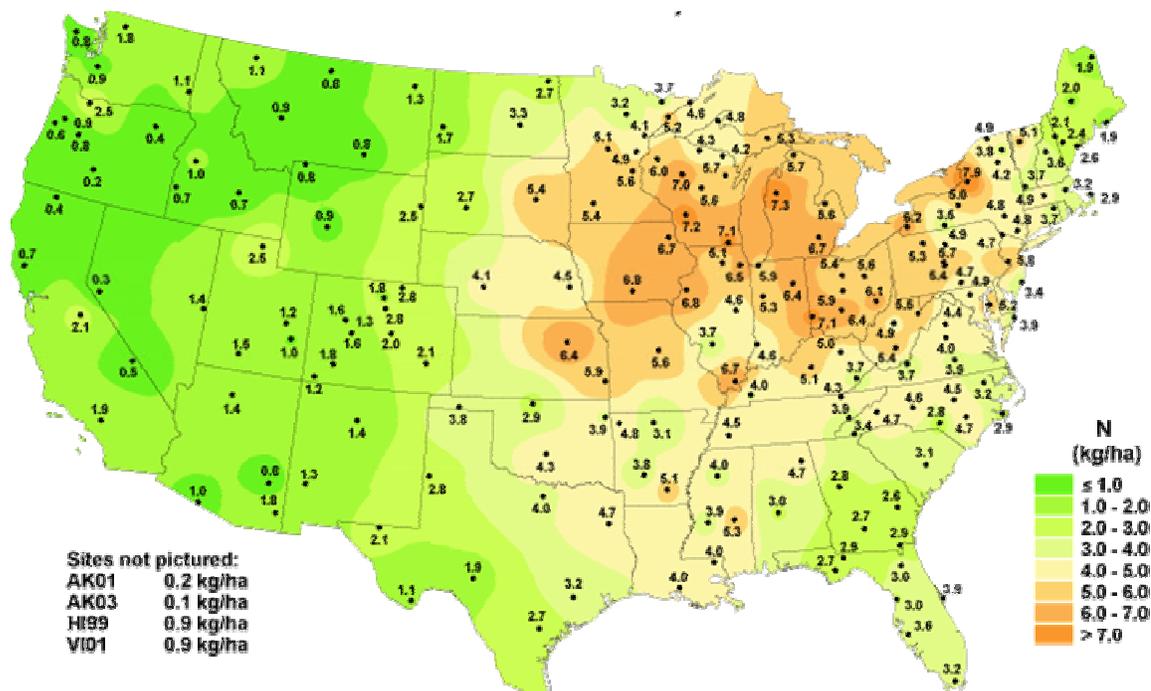


Figure V-14. Inorganic nitrogen wet deposition from nitrate and ammonium, 2001 (<http://nadp.sws.uiuc.edu>).

Wet sulfur deposition is primarily due to dissolved sulfate. Major anthropogenic sources of sulfate include coal-fired power plants. Therefore the region of the country that experiences the highest sulfur deposition is the eastern Midwestern states of Indiana, Ohio, Pennsylvania and Kentucky, where high sulfur coal is burned and many older power plants still operate which are not regulated by the New Source Review Program of the Clean Air Act (Figure V-15).

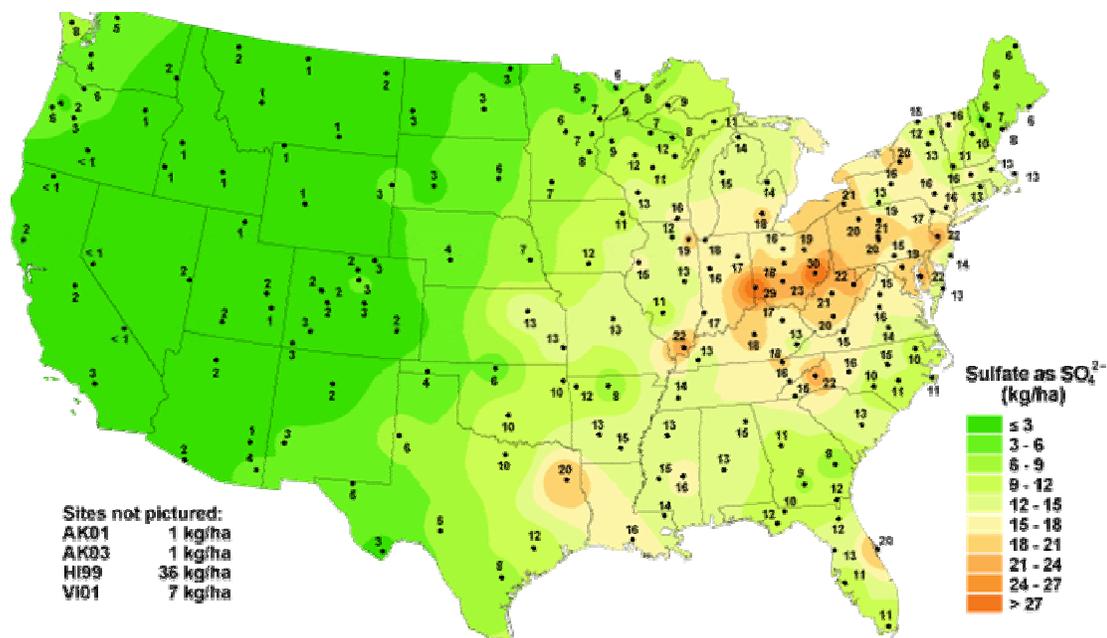


Figure V-15. Sulfate wet deposition, 2001 (<http://nadp.sws.uiuc.edu>).

## 2. Dry Deposition

Dry deposition is determined by the "inferential method", rather than measured directly. This method uses a model to predict deposition of atmospheric constituents measured in the air. The model uses meteorological data and surface characteristics to predict deposition velocities. The US EPA's Clean Air Status and Trends Network (CASTnet) has operated a dry deposition station at Sullivan Bay in Voyageurs on a continuous basis since 1996. CASTnet measures  $\text{NO}_3$ ,  $\text{SO}_4$ ,  $\text{NH}_4$ ,  $\text{SO}_2$ , and nitric acid ( $\text{HNO}_3$ ) in air simultaneous with meteorological data and reports dry deposition values annually. CASTnet does not operate a station at Isle Royale.

## 3. Trends and Impacts of Sulfur and Nitrogen Deposition

Wet and dry deposition of sulfur and nitrogen are major contributors to acid rain and acidification of lakes and wetlands. However, because Voyageurs and Isle Royale are remote parks, they do not experience the high deposition levels of nitrogen and sulfur reported elsewhere in the Midwest (illustrated in the NADP figures above). Deposition of sulfur has decreased since the late 1970s (Kallemeyn et al., 2003) but there has been little change since the mid-1990s (Figures V-16 and V-17).

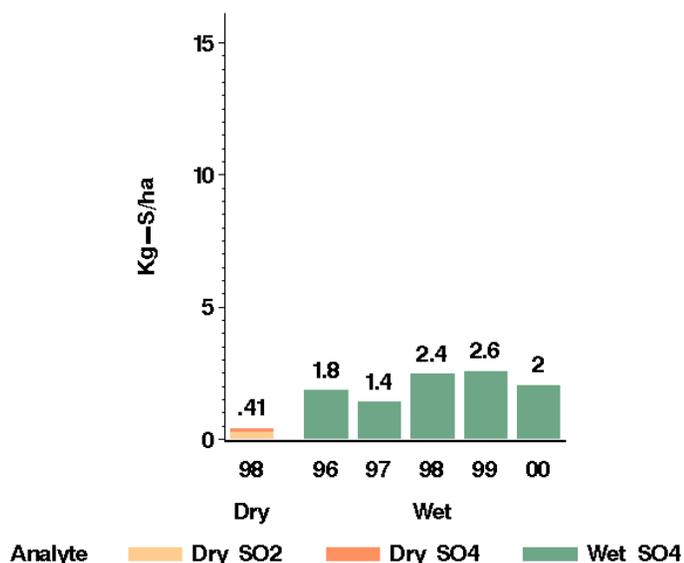


Figure V-16. Wet and Dry Sulfur Deposition at Voyageurs, Sullivan Bay site. Only complete years are shown. Source: CASTnet/NADP-NTN (<http://www.epa.gov/castnet/sites/voy413.html>).

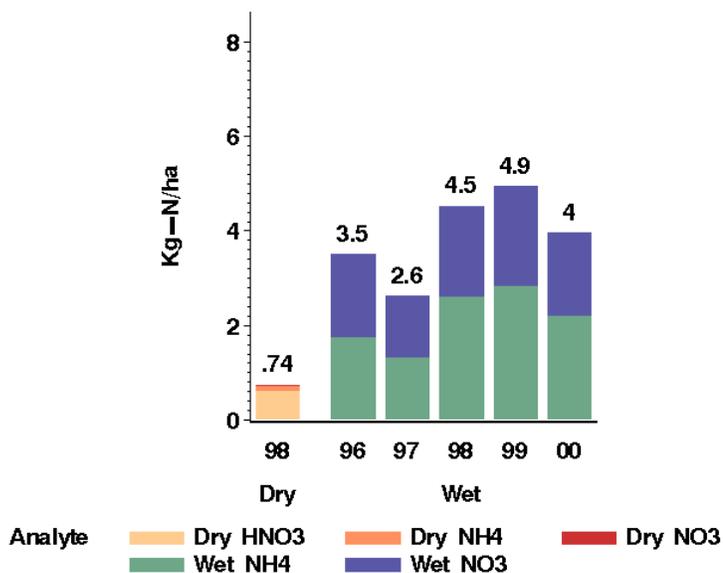


Figure V-17. Wet and Dry Nitrogen Deposition at Voyageurs, Sullivan Bay site. Only complete years are shown. Source: CASTnet/NADP-NTN (<http://www.epa.gov/castnet/sites/voy413.html>).

The impact of acidic sulfur and nitrogen deposition has been an important focus of research in the parks. Prior to the mid-1980s, many regions across the country experienced increasing acidity in rainfall. Current trends in acid deposition in the Midwest, however, indicate improvement. For example, although the pH of precipitation at Isle Royale went from a mean of 6.3 down to a mean of 4.4 for the period of 1979–82 (Stottlemeyer, 1982), and a study from the mid-1980s reported the volume-weighted pH of bulk precipitation to be 4.65 (Stottlemeyer and Hanson, 1989), sulfate deposition has declined since then (Herrmann et al., 2000), and pH levels have increased as a result. The annual 2001 precipitation-weighted mean pH reported by NADP for Isle Royale was 4.92. For Voyageurs, the 2001 precipitation-weighted mean pH was 5.18. (<http://nadp.sws.uiuc.edu/>).

Indirect monitoring of acid deposition has focused on the potential effects on three sensitive resources, including aquatic resources, soils, and plant communities. The effects of acid precipitation in combination with the natural acidity of the predominant peaty soils have also been raised as a concern. Stottlemeyer of the NPS and colleagues have done numerous studies examining the flux and biogeochemical cycling of nitrate, sulfate, ammonium, and other ions in a variety of ecosystems, including Isle Royale (Stottlemeyer and Hanson, 1989; Stottlemeyer et al., 1995; Stottlemeyer et al., 1998; Stottlemeyer and Toczydlowski, 1999b, a). They reported nitrate precipitation flux at Isle Royale was approximately 3 kg/ha-year, and stream water chemistry was not correlated with precipitation chemistry. It appeared little of the stream nitrate came directly from the precipitation or snowmelt. The stream water ion concentrations appeared to reflect trends in soil processes, and thus the researchers concluded that the precipitation was rapidly modified by soil processes. Stottlemeyer and Hanson (1989) found that the sulfate concentration in soils beneath conifers was higher than that beneath aspen-birch stands, and that the sulfate flux was 2–3 times greater. They concluded that boreal forests may be more susceptible to cation leaching than hardwood forests.

Water chemistry studies of the inland lakes have shown that acidification of lake water is not of concern. The basaltic soils of the underlying geology provide sufficient buffering to the inland lake waters, with pH values ranging from 6.77 to 8.25 in a survey

of 22 lakes (Ameel, unpublished data, Center for Water and the Environment, NNR, Duluth, MN).

Mosses (Bryophytes) are highly sensitive to air pollutants and readily take up metals. Their leaves have no cuticle, and their water content reflects their environmental water content. They have a pronounced dependency on the atmosphere to supply their nutrient needs, and thus they can be excellent biomonitors for the deposition and effects of air pollutants. They control nutrient cycling in boreal forests, and at Isle Royale, they are a key ecosystem component because they cover a large surface area compared to vascular plants. At Isle Royale lichens make a significant contribution to the total energy flow, water balance, and nutrient cycling in the ecosystem.

Glime (1986) conducted a series of controlled experiments of acid and lead loadings on mosses. She found that at a pH of 3, there were adverse effects that included increased nutrient leaching and less chlorophyll synthesis. She also examined archived samples from the previous 80 years for a suite of elements, and found elevated sulfur in Isle Royale mosses compared to controls from northern Canada. She concluded that this was a regional effect of sulfate deposition. These experiments suggested that sulfate loads to the park were elevated, but not enough to cause concern.

Lichens have also been widely used as biomonitor species throughout many parts of the world (Rossbach et al., 1999; Falla et al., 2000). They are known to be sensitive to low levels of many atmospheric gaseous pollutants, and are even more sensitive when wet. The extensive presence of lichens on Isle Royale makes them a logical choice for using as a biomonitor. However, the low levels of elements in remote areas like Isle Royale make data interpretation difficult. Extensive sampling over time is required to determine baseline concentrations and detect trends. A major study of elements and metals in lichens was done in 1983–84 (Wetmore, 1985) to establish baseline concentrations of 16 elements in five different lichen species from 10 locations throughout the park. The study was also designed to identify any existing air quality problems. The report documented 482 lichen species identified on Isle Royale and

provided a listing of their sensitivities to SO<sub>2</sub>. Wetmore reported elevated levels of some elements, including sulfur, on ridgetops on the northeastern half of the island.

In a comprehensive study described as a follow-up to the Wetmore report, Bennett (1995) measured 16 elements in two species over a three-year period (1992 to 1994) at 18 locations throughout Isle Royale. He compared his results to those of Wetmore, as well as to reported element concentrations in the earth's crust. He found that nine elements increased over time in both species, including K, B, Cr, Cu, Fe, Ni, S, Al, and P. Lead decreased over the same time period. Geographical analyses of his data revealed that only S increased with elevation in both species. Bennett concluded that abnormal levels of certain toxic elements were present in lichens at Isle Royale, and that their source is atmospheric. He also concluded that some of these elements were approaching concentrations that would be considered deadly to lichens. The data taken in aggregate "may indicate the early stages of pollution entering the area".

#### **D. SENSITIVITY TO ACIDIFICATION AND NUTRIENT DEPOSITION**

Acidification and eutrophication are potential consequences of atmospheric deposition. As discussed above, nitrogen and sulfur deposition is relatively high and precipitation pH is relatively low in the upper Midwest as compared to the much of the U.S. However, there has been a downward trend in sulfur deposition, and upward trend in precipitation pH. This is good news that suggests improved air quality conditions.

Acidification from nitrogen (nitric acid) and sulfur (sulfuric acid) deposition is not a major problem in the upper Midwest although some of the smaller lakes in Voyageurs and Isle Royale are sensitive to acid deposition due to low Acid Neutralizing Capacity (ANC). For example, twelve interior lakes sampled in 1980 and 2000 in Voyageurs show a range of ANC values from approximately 100 to 700  $\mu\text{eq L}^{-1}$ . The most recent evaluation from the Minnesota Pollution Control Agency, as reported by Kallemeyn et al. (2003), indicates that the interior lakes of Voyageurs can be classified as moderately sensitive ( $100 < \text{ANC} < 200 \mu\text{eq L}^{-1}$ ) to non sensitive ( $\text{ANC} > 400 \mu\text{eq L}^{-1}$ ). Similarly, Stottlemeyer et al (1998) reported that surface waters in Isle Royale are not sensitive to the levels of acidic precipitation normal to the area. Because park lakes are only

moderately sensitive, current levels of acid deposition in Voyageurs and Isle Royale are not a concern.

Eutrophication of waters in the parks is not a function of nitrogen deposition but rather a function of watershed characteristics and availability of phosphorus in the sediments. For example, Kabetogama Lake in Voyageurs is enriched in nutrients (including phosphorus), chlorophyll-a, and has lower secchi depths than Namakan and Rainy Lakes, both of which are classified as mesoeutrophic lakes. The difference is that Kabetogama Lake receives discharge from the Ash River rather than the Vermilion and Loon Rivers. The Ash River flows over richer geological substrates that supply nutrients (especially phosphorus) for algal growth. The Vermilion and Loon Rivers drain large areas of bedrock and non-calcareous drift (Kallemeyn et al., 2003).

#### **E. OZONE IMPACTS ON VEGETATION**

Plants may be more sensitive than humans to ozone concentrations in air. While humans suffer from acute effects of high ozone concentrations (irritation to lungs and eyes), the effects of ozone on plants are observed from chronic exposures as well as at lower concentrations. For this reason, the US EPA has examined the possibility of secondary ambient air quality standards for ozone that are designed to protect vegetation and other non-human receptors. No secondary standards have yet been established, although the need for such standards has been recognized by some ecologists. In 1996, the US EPA concluded that the current secondary NAAQS for ozone is insufficiently protective of vegetation. Nevertheless, secondary standards for ozone have yet been implemented (Hogsett and Andersen, 1998).

Ozone injury can be induced by a sufficiently high seasonal dose of ozone, high peak concentrations of ozone, or a combination of both. However, ozone uptake and subsequent injury can be influenced by a number of environmental factors, including temperature and soil moisture. In a 1996 workshop, ecologists discussed potential forms for a secondary ozone standard that would reflect doses and concentrations relevant to vegetation (Heck and Cowling, 1997). Participants reached consensus on the SUM06 (the running 90-day maximum sum of the 0800-2000 hourly ozone concentrations of ozone equal to or greater than 0.06 ppm, reported as ppm-hrs) as a

potential form for a secondary ozone standard. Workshop participants also recommended the following ozone thresholds for sensitive vegetation:

	<u>SUM06</u>
Natural Ecosystems	8 - 12 ppm-hr (foliar injury)
Tree Seedlings	10 - 16 ppm-hr (1-2% reduction in growth)
Crops	15 - 20 ppm-hr (10% reduction in 25-35% of crops)

Subsequently, Lefohn et al. (1997) recommended another potential metric for a secondary ozone standard, the W126 (a cumulative index of exposure that uses a sigmoidal weighting function to give added significance to higher concentrations of ozone while retaining and giving less weight to mid and lower concentrations, reported as ppm-hr. The number of hours over 100 ppb (N100) is also considered in assessing the possible impact of the exposure). They recommended the following ozone thresholds:

	<u>W126</u>	<u>N100</u>
Highly Sensitive Species	5.9 ppm-hr	6
Moderately Sensitive Species	23.8 ppm-hr	51
Low Sensitivity	66.6 ppm-hr	135

In 2004, the NPS contracted with an ozone effects expert to assess the risk of ozone-induced foliar injury on sensitive vegetation in a number of NPS units, including Isle Royale and Voyageurs. The risk assessments are based on either monitored (for Voyageurs) or interpolated (for Isle Royale) 1995-1999 average ozone values, the Palmer Z Drought Index, which represents the short-term departure of soil moisture from the average for each month for the site, and park vascular plant lists (R. Kohut, personal communication). Both parks have a number of vascular plant species that are known to be sensitive to ozone.

<b>PARK</b>	<b>STD. SCIENTIFIC NAME</b>	<b>COMMON NAME</b>
Isle Royale	<i>Alnus rugosa</i>	Red alder
Isle Royale	<i>Apocynum androsaemifolium</i>	Spreading dogbane
Isle Royale	<i>Asclepias syriaca</i>	Common milkweed
Isle Royale	<i>Aster macrophyllus</i>	Big-leaf aster
Isle Royale	<i>Clematis virginiana</i>	Virgin's bower
Isle Royale	<i>Fraxinus americana</i>	White ash
Isle Royale	<i>Fraxinus pennsylvanica</i>	Green ash
Isle Royale	<i>Gaylussacia baccata</i>	Black huckleberry
Isle Royale	<i>Parthenocissus quinquefolia</i>	Virginia creeper
Isle Royale	<i>Pinus banksiana</i>	Jack pine
Isle Royale	<i>Populus tremuloides</i>	Quaking aspen
Isle Royale	<i>Prunus serotina</i>	Black cherry
Isle Royale	<i>Prunus virginiana</i>	Choke cherry
Isle Royale	<i>Robinia pseudoacacia</i>	Black locust
Isle Royale	<i>Rubus canadensis</i>	Thornless blackberry
Isle Royale	<i>Rubus parviflorus</i>	Thimbleberry
Isle Royale	<i>Sambucus racemosa</i>	Red elderberry
Isle Royale	<i>Solidago altissima</i>	Goldenrod
Isle Royale	<i>Symphoricarpos albus</i>	Common snowberry
Isle Royale	<i>Vaccinium membranaceum</i>	Huckleberry
Voyageurs	<i>Amelanchier alnifolia</i>	Saskatoon serviceberry
Voyageurs	<i>Apios americana</i>	Groundnut
Voyageurs	<i>Apocynum androsaemifolium</i>	Spreading dogbane
Voyageurs	<i>Apocynum cannabinum</i>	Dogbane, Indian hemp
Voyageurs	<i>Artemisia ludoviciana</i>	Siver wormwood
Voyageurs	<i>Asclepias incarnata</i>	Swamp milkweed
Voyageurs	<i>Asclepias syriaca</i>	Common milkweed
Voyageurs	<i>Clematis virginiana</i>	Virgin's bower
Voyageurs	<i>Corylus americana</i>	American

Voyageurs	Fraxinus pennsylvanica	hazelnut Green ash Black huckleberry
Voyageurs	Gaylussacia baccata Parthenocissus quinquefolia	Virginia creeper Jack pine
Voyageurs	Pinus banksiana	Quaking aspen
Voyageurs	Populus tremuloides	Black cherry
Voyageurs	Prunus serotina	Choke cherry
Voyageurs	Prunus virginiana	Black locust
Voyageurs	Robinia pseudoacacia	Allegheny blackberry Thornless blackberry
Voyageurs	Rubus allegheniensis	Thimbleberry
Voyageurs	Rubus canadensis	Cutleaf
Voyageurs	Rubus parviflorus	coneflower
Voyageurs	Rudbeckia laciniata	American elder
Voyageurs	Sambucus canadensis	Common elderberry
Voyageurs	Symphoricarpos albus	

Ozone air quality data for Isle Royale					
	1995	1996	1997	1998	1999
SUM06 (ppm-hr)	7	4	6	6	9
W126 (ppm-hr)	12.9	11.9	11.7	16.6	18.9
N100 (#)	3	1	3	3	4

Ozone air quality data for Voyageurs					
	1995	1996	1997	1998	1999
SUM06 (ppm-hr)	6	3	8	6	8
W126 (ppm-hr)	9.7	8.7	13.2	12.2	12.3
N100 (#)	0	0	0	0	0

Kohut concluded the low level of ozone exposure at both parks, combined with occasional periods of drought stress, indicates a low risk of foliar ozone injury. Although the ozone exposures during the period 1995-1999 were below those expected to cause

injury to vegetation at either park, it is worth noting that ozone concentrations increased significantly from 1990-1999 (National Park Service, 2002) in the region. If the trend continues, ozone exposures may reach levels sufficient to induce injury. Potential bioindicator species include spreading dogbane, common milkweed, big-leaf aster, white ash, quaking aspen, black cherry, Allegheny blackberry, cut-leaf coneflower, and American elder.

Ozone impacts on vegetation are monitored and reported through the Ozone Biomonitoring Program, sponsored by the United States Department of Agriculture (USDA) and state partners. Review of monitoring results finds no injury to plants in regions near Isle Royale and Voyageurs (Figure V-18)

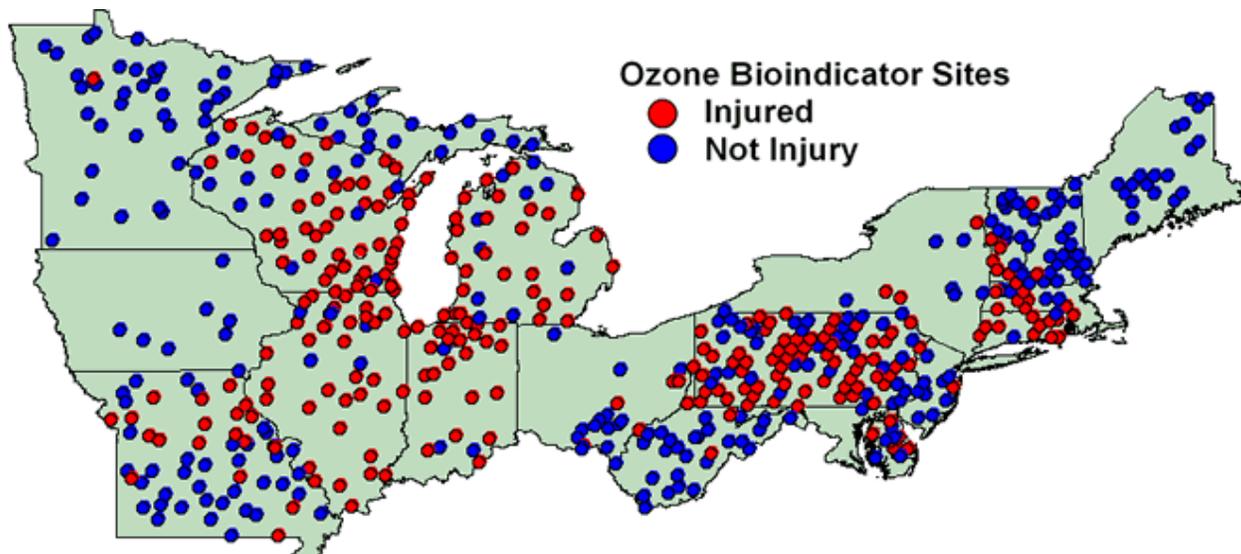


Figure V-18. Visible ozone injury found on bioindicator species using annual data collected from field plots. (Ozone Biomonitoring Program, <http://www.fiaozone.net/maps.html>)

## **F. ATMOSPHERIC CONCENTRATIONS AND DEPOSITION OF PERSISTENT ORGANIC POLLUTANTS (POPS)**

Many of the studies and data discussed below are relevant to the region, and not to one specific park or the other. Thus, this section applies to both Isle Royale and Voyageurs, although many of the studies cited here focused on or near Isle Royale.

Several research studies have focused on the deposition of POPs to Isle Royale. This is because the inland lakes on Isle Royale are subject to atmospheric deposition of POPs following long-range transport, but do not have any other non-atmospheric sources of pollutants or hydrologic exchange with Lake Superior. Thus, these inland lakes are often studied as “reference” sites, or sought after to estimate atmospheric depositional fluxes.

Studies on atmospheric transport and deposition have focused on three basic approaches. One approach is to measure concentrations of POPs in air vapor, particulates, and/or precipitation, and use models to calculate the annual wet and dry deposition and air-water exchange. The second approach is to measure POPs in sediments from the inland lakes. POPs are hydrophobic and readily partition to particles in the water, which eventually accumulate as sediments on the bottom of the lake. If the sediments remain undisturbed over time, vertical cores of these sediments can be sliced and each slice dated and analyzed for POPs, thus providing a timeline of the depositing of POPs. The rate of sediment accumulation is approximately equal to or at least is proportional to the net atmospheric deposition. The third approach is to measure POPs in fish tissue from Isle Royale’s inland lakes. Since fish bioaccumulate POPs, their tissue is easier to measure than either the air or water. The presence of a contaminant accumulated in fish tissue indicates that it was atmospherically deposited, since there are no other known sources of POPs to the lakes. The concentrations in the fish provide information on the potential risks to humans or wildlife from eating the fish. Research studies have included the measurement of POPs in air, precipitation, surface water, sediments, and fish.

## 1. POPs in Fish as Indicators of Air Pollution

The first study to document the presence of POPs on Isle Royale was by Swain (1978), who compared the concentrations of PCBs, DDT, hexachlorobenzene (HCB), alpha-BHC (hexachlorocyclohexane), and dieldrin in lake trout from Siskiwit Lake on Isle Royale to those from lake trout caught in adjacent Lake Superior waters. The concentrations were greater in Siskiwit Lake fish, even after adjusting for differences in lipids. This was the first documentation of the long-range transport of persistent pollutants to Isle Royale and to Lake Superior, and spurred considerable research interest in further understanding the rates of deposition and their impacts.

This approach was taken a step further by Swackhamer and Hites (1988), who examined lake trout from Siskiwit Lake for any and all halogenated compounds to determine which environmental pollutants were subject to long-range transport and subsequent atmospheric deposition. They found PCBs, DDT and metabolites, trans-nonachlor, cis- and trans-chlordane, hexachlorobenzene, octachlorostyrene, pentachloroanisole, decachlorodiphenyl ether, and mirex. In addition, they measured most of these compounds in the water from Siskiwit Lake and reported bioaccumulation factors for these compounds.

The most recent application of this approach was by Kannan et al. (2000), who measured polychlorinated naphthalenes (PCNs) and PCBs in fish from Michigan waters, including lake trout from Siskiwit Lake. PCNs were detected in these fish, indicating an emerging class of toxic compounds subject to long-range transport and deposition.

The EPA National Fish Tissue Study has completed its first of five years of sampling. This study includes fish from 51 lakes in Minnesota, 2 of which are in Voyageurs. Preliminary data show that the highest levels of PCDD/Fs and PCBs in any fish from Minnesota were found in a fish collected in Lac LaCroix in Voyageurs, although this may be due to its age and species. Fish from Lake Namakan, also in Voyageurs, were comparable to those from the rest of the state (McCann, Minnesota Department of Health, personnel communication).

## 2. Concentrations in Air and Precipitation

Strachan (1985) measured POPs in precipitation collected near Isle Royale in Lake Superior in 1983. Triplicate samples of approximately 22 L collected over 6 weeks in the summer were measured for PCBs, alpha-BHC, lindane, endrin, dieldrin, heptachlor epoxides, methoxychlor, DDT, and HCB. Chlordanes, toxaphene, and mirex were also targeted but were not detected. Concentrations were used to calculate volume-weighted annual fluxes due to wet deposition. One can assume that estimates of precipitation to Lake Superior will be similar to what is deposited on Isle Royale.

Eisenreich and colleagues have made numerous measurements of PCBs in air and precipitation over Lake Superior, and used them to estimate deposition rates (Capel and Eisenreich, 1985; Eisenreich, 1987a; Eisenreich, 1987b; Eisenreich et al., 1992). His research, along with measurements being made by Environment Canada, prompted a series of workshops sponsored by the International Joint Commission, where all data were pooled and first-order estimates made of atmospheric deposition to each of the Great Lakes. The ultimate goal of these workshops was to determine how much of each POP came from atmospheric sources, and how much came from non-atmospheric sources. These workshops were published as two reports (Strachan and Eisenreich, 1988; Eisenreich and Strachan, 1992), and one of their conclusions relevant to Isle Royale was that greater than 90% of the POPs found in Lake Superior were from atmospheric deposition following long-range transport. Given the proximity of Voyageurs to Lake Superior, these estimates of deposition would apply to Voyageurs as well.

Another technique developed to monitor atmospheric concentrations of POPs is to measure concentrations in tree bark. The advantages of this technique are that it is easier and less expensive to sample, can cover wide geographic areas, and provides excellent data for relative comparisons (Meredith and Hites, 1987). A study of concentrations of PCBs in tree bark throughout the US included data from Isle Royale, and found that while PCBs were in low concentrations, they were measurable and verified the long-range transport of POPs (Hermanson and Hites, 1990).

Given the assumption that more than 90% of POPs in Lake Superior are from the atmosphere, and since Isle Royale sits within Lake Superior, it is reasonable to

extrapolate estimates of atmospheric deposition made for Lake Superior to the park. Hornbuckle et al. (1994) collected air and water samples on Lake Superior and air from the Integrated Atmospheric Deposition Network (IADN) site on the Keweenaw Peninsula, MI. They found that atmospheric deposition of PCBs was highly seasonal, with the greatest deposition occurring in the summer, when air concentrations were highest. Hoff et al. (1996) summarized the air monitoring data from the Atmospheric Environment Service of Environment Canada, and calculated atmospheric deposition to the Great Lakes for a range of POPs.

Around the Great Lakes, air monitoring is conducted jointly by the US EPA and Environment Canada via IADN. Two of the master sites that have been monitored since 1990 are on Lake Superior: at the Brule River mouth, WI, and at Eagle Harbor, MI. While the site at Brule River can be influenced by local air pollution from Duluth (Buehler et al., 2001) the Eagle Harbor site receives atmospheric deposition that is likely comparable to that of Isle Royale. The monitoring has been conducted for over a decade, offering sufficient data to determine time trends and environmental half-lives (Hillery et al., 1998; Cortes and Hites, 2000). The most current data are summarized in Table V-3.

The half-lives are of the same order of magnitude in vapor and in rain and similar for different compounds, and range from 2-14 years. This indicates that the concentrations in air and rain have generally been declining over the last few decades, and should continue to decline. The concentrations and fluxes from the IADN site are considered background levels for North America, and are a result of the long-term reservoir of POPs in the global atmosphere.

Table V-3. Estimates of half-lives and atmospheric depositional fluxes from air measurements for POPs in the Lake Superior airshed. A non-significant decline over time is indicated by “ns.”

Contaminant	Half-life, years in atmospheric vapor phase (Cortes and Hites, 2000)	Half-life, years in precipitation (Simcik et al., 2000)	Wet and Dry Depositional Flux pg/cm <sup>2</sup> -year (Cortes et al., 1998)
PCBs	ns	ns	202
DDT	4.1	1.7	106 (sum all compounds)
DDE	3.9	ns	
DDD	2.7 <sup>a</sup>	2.7	
α-HCH	3.0	2.0	99 (sum α + γ)
γ-HCH	4.4	3.1	
HCB	14	3.1	
α-Chlordane	ns	ns	
γ-Chlordane	6.9	1.9	
Trans-nonachlor	ns	3.0	
dieldrin	3.7	6.2	
toxaphene	-	-	22.9 <sup>c</sup>
PAHs	3-8 <sup>b</sup>	ns	
phenanthrene	-	-	426

<sup>a</sup> (Cortes et al., 1998)

<sup>b</sup> (Cortes and Hites, 2000)

<sup>c</sup> estimate from Swackhamer et al. (1999)

While PCBs and other organochlorine compounds have shown first-order (exponential) loss in the atmosphere, in water, and fish of the Great Lakes, the concentrations measured in air and precipitation at Eagle Harbor from 1990-1997 did not show such declines (Hillery et al., 1997; Hillery et al., 1998; Simcik et al., 1998; Simcik et al., 2000). This may be due to the high variability in air concentrations, infrequent sampling, and the dynamic exchange between air water. These factors make changes difficult to detect (Simcik et al., 2000). The most recent analyses are detecting statistically significant decreases in concentrations of POPs at Eagle Harbor, with the exception of trans-nonachlor and alpha-chlordane (Cortes and Hites, 2000).

Whether the same can be said for Isle Royale is not known, and would depend on the concentrations of POPs in water of the inland lakes.

Few studies of atmospheric deposition have included snow or snowmelt due to the difficulties involved in sample collection, and in the large volumes of snow needed. However, a recent study of concentrations of PCBs and PAHs in snow and snowmelt from the upper Midwest has shown that dry deposition is a negligible contribution to snowfall (Franz and Eisenreich, 2000). Winter loadings of PAHs and PCBs are approximately 20–30% of total precipitation loadings, and are representative of cold, remote conditions. Concentrations of PCBs in snow from Isle Royale from 1975 to 1985 declined from 230 ng/L (Swain, 1978) to 17 ng/L (Swackhamer et al., 1988). In their report, Franz and Eisenreich found concentrations of 1.3–2.3 ng/L in snow from remote locations in Minnesota and Michigan collected in 1991-92.

Toxaphene has contaminated the Great Lakes and the inland lakes in Isle Royale (Swackhamer et al., 1998). The main depositional process is air-water exchange (Hoff et al., 1993). Lake Superior is saturated, and is currently degassing (Jantunen et al., 1998; Swackhamer et al., 1999; James et al., 2001). This means that Lake Superior is actually a net source of toxaphene to the atmosphere rather than a sink, as is the case for all the other POPs. Because the concentrations of toxaphene in the waters of Isle Royale's inland lakes have not been measured, the net exchange of toxaphene in the inland lakes cannot be estimated.

The samples collected as part of IADN can also be used to evaluate the presence and concentrations of newer pollutants of emerging concern. For example, Strandberg et al. (2001) examined the 1997–99 samples for polybrominated diphenyl ethers (PBDE), and found atmospheric concentrations of about 5 pg/m<sup>3</sup>. These concentrations were similar to other organochlorine compounds such as DDT or PCB congeners. PBDEs are used as fire retardants in many products and materials, and are increasing exponentially in the environment (Betts, 2002). PBDEs have also been found in freshwater mussels collected from 10 inland lakes in Isle Royale (Chernyk et al., 2002). Concentrations of congener #47, the most abundant congener, were on the order of approximately 0.1 ng/g wet weight. While the toxicological significance of these concentrations is unknown, this study demonstrates that emerging contaminants of

concern that are persistent and bioaccumulative are effectively transferred from the atmosphere to the aquatic foodweb.

Chlorothalonil and Dachthal have also been reported in measurable concentrations in air and precipitation samples collected from IADN (James and Hites, 1999). Chlorothalonil is a fungicide for peanuts and potatoes, and Dachthal is a pre-emergence herbicide used widely on onions and broccoli.

Triazine pesticides were studied on Isle Royale from 1992 to 1994 (Thurman and Cromwell, 2000). Atrazine, its two degradation products, deethylatrazine and deisopropylatrazine, plus cyanazine were detected in Isle Royale rainfall from mid-May to early July at concentrations of  $<0.005$ – $1.8$   $\mu\text{g/L}$ . Concentrations were highest in the spring, and decreased by several orders of magnitude by summer. These concentrations are similar to, and in some cases greater than, concentrations found in precipitation throughout the upper Midwestern United States (Majewski and Capel, 1995; Goolsby et al., 1997). Atrazine is used extensively on corn and sorghum production, and more than 75% of its use is in the states of Illinois, Nebraska, Indiana, Iowa, Kansas, and Ohio (Majewski and Capel, 1995). There is a strong geographic relationship between application rates and concentration in precipitation (Majewski and Capel, 1995). Low levels of pesticides were found in all the lakes sampled. The study showed that atrazine is degraded more readily in soil environments and shallow lakes, and more slowly in deeper lakes, with residence times of up to 10 years.

### **3. Using Sediments to Estimate Atmospheric Deposition**

Sediments have been used by many researchers to estimate current loadings of particulate-associated pollutants to aquatic systems, as well as to estimate historical loadings. Undisturbed sediments will contain an archive of the loading of pollutants to the lake, and this history can be determined from dated cores. In the absence of point sources, runoff, or other significant non-atmospheric inputs, the sediments can be used to estimate the atmospheric inputs of hydrophobic compounds (Swackhamer and Armstrong, 1986). Regardless of whether they entered the water body by wet or dry deposition or gaseous sorption, hydrophobic contaminants will sorb to the particulate matter in the water column and ultimately end up in the sediments.

One of the first applications of this technique was by Gschwend and Hites (Gschwend and Hites, 1981), who compared PAH atmospheric fluxes measured in remote sediments to those in the Boston area. The remote site they chose was Siskiwit Lake on Isle Royale, and they reported fluxes of approximately  $1 \text{ ng/cm}^2\text{-year}$  for individual PAH compounds, which they attributed to the background atmospheric contamination of combustion products. The sediments indicated that this anthropogenic signal appeared about 100 years earlier.

Another class of combustion products of great interest are the PCDD/Fs. Early research by Czuczwa and Hites (Czuczwa et al., 1984; Czuczwa and Hites, 1984; Czuczwa et al., 1985; Czuczwa and Hites, 1986b; Czuczwa and Hites, 1986a) established the presence of PCDD/Fs in sediments from Siskiwit Lake, and attributed them to atmospheric deposition following long-range transport. Atmospheric sources included the combustion of chemical and municipal waste, particularly that containing chloro-aromatic compounds. A study of PCDD/F deposition to the Great Lakes (Pearson et al., 1997, 1998) found that deposition to Lake Superior was similar to that reported for Siskiwit Lake. This points out the utility of using flux estimates for Lake Superior for estimating fluxes to Isle Royale.

A follow-up study was conducted on cores obtained from Siskiwit Lake in 1998 (Baker and Hites, 2000). The history of PCDD/F fluxes were determined in Siskiwit Lake, and compared to the soil flux measured at Ryan Island. Their results showed that the atmospheric deposition of PCDD/Fs increased dramatically from 1930 to the mid-1970s, and then began to decline. The deposition rate peaked at  $9.5 \text{ pg/cm}^2\text{-year}$ , and has declined approximately 50% since then. A representative core showing the accumulation over time for PCDD/Fs in Siskiwit Lake is shown in Figure V-19.

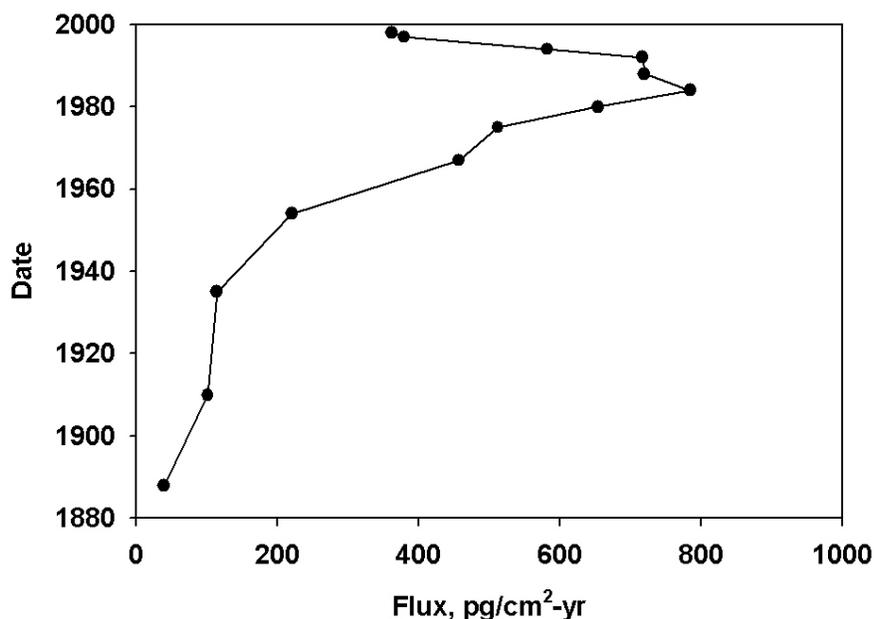


Figure V-19. Total PCDD/F flux to the sediments as a function of time in a sediment core from Siskiwit Lake. Data from (Baker and Hites, 2000).

An extensive study of PAH and PCB deposition and cycling in Siskiwit was done in the mid-1980s by Hites and colleagues. This study used measurements of air, water, and sediments from over a two-year period to determine the air-water exchange of PAHs (McVeety and Hites, 1988) and PCBs (Swackhamer et al., 1988), and to construct a mass balance of these pollutants for Siskiwit Lake. Siskiwit Lake was again chosen to represent a remote system that received pollutants only from the atmosphere.

#### 4. Uptake by Plants

Plants take up gas and particulate phase organic compounds by direct deposition, uptake through the leaf stomata, and absorption into the cuticle (Barber et al., 2002). The large surface area available and the waxy nature of the cuticle give plants a high potential for accumulation of organic pollutants. Accumulation of organic contaminants does not appear to harm plants in any way, but the phenomena is useful in evaluating the mechanisms for transfer to terrestrial wildlife and regional exposure to the compounds. Deposition of PCBs, PAHs and chlorinated pesticides to *Sphagnum* moss in northern Minnesota have been used to describe the history of atmospheric

deposition to terrestrial surfaces (Rapaport and Eisenreich, 1988), similar to the use of sediments described above. McLachlan et al. showed that spring leaf-out may result in a measurable decline in atmospheric concentrations of POPs due to rapid uptake by new foliage (McLachlan and Horstmann, 1998). Plants, however, are unlikely to be permanent sinks for POPs – some fraction of the sorbed pollutants is re-released as the climate warms. Hornbuckle et al. (1996) reported a diurnal cycle of POPs gas-phase concentrations in northern Minnesota that suggests a strong relationship of plant uptake and release of POPs with local climate. This relationship with climate prevents the use of plants as direct biomonitors of POPs pollution. High concentrations of POPs in plants can be due to the proximity of sources but could also be due to low local or regional temperatures or leaf age (Ockenden et al., 1998).

## **5. Other Studies**

A recent study of contaminants in bald eagle nestlings (*Haliaeetus leucocephalus*) in the upper Great Lakes area included 13 samples from Voyageurs that were collected in 1999 (Rowe, 2001). Concentrations of PCBs and p,p-DDE ranged from 2-22 and 2-21 µg/kg, respectively, in plasma, which is typical for the upper Great Lakes region.

Voyageurs is the area chosen for a study underway by Dr. Matt Simcik of the University of Minnesota-Twin Cities to evaluate the atmospheric flux of perfluorooctane sulfonate (PFOS). This toxin is a by-product in the manufacture of Scotchguard (3M Company), and a component of many other manufactured goods such as fire-fighting foams. Water, air, and fish samples from two of the inland lakes in Voyageurs have been collected. Although final data are still forthcoming, PFOS was found in all samples.

## **G. CONCENTRATIONS AND DEPOSITION OF MERCURY**

Mercury deposition is a concern in the upper Midwestern US (Nater and Grigal, 1992; Engstrom and Swain, 1997); however, it is of particular concern in both Voyageurs and Isle Royale, since these are water-based parks where fishing is a dominant activity. From the discussion of the mercury cycle in Section III.A.6, it is clear that the biggest concern is not the concentrations in the air, but the concentrations of

MMHg in fish—and the resulting human and wildlife exposures from consuming these contaminated fish. Because no one fully understands details of the factors that control the bioaccumulation of MMHg in fish, a variety of research activities are underway in both parks. However, both parks may be more susceptible to the effects of mercury deposition given that wetlands have been shown to increase the rate at which mercury is transformed to MMHg.

Measurements of mercury (total and MMHg) in the vapor and particulate phases in air, and in wet deposition, have been made at several locations in the western Lake Superior airshed, including Isle Royale, by Dr. Jerry Keeler, who directs the University of Michigan Air Quality Laboratory (UMAQL). These concentrations and estimates of deposition are also reasonable first approximations for deposition occurring at Voyageurs.

Weekly air and precipitation samples were collected at Eagle Harbor, MI (collocated with IADN site) in 1995-96. Vapor phase concentrations of total Hg were generally between 1-2 ng/m<sup>3</sup>. Particulate Hg concentrations varied considerably, ranging from 2-80 pg/m<sup>3</sup>. Summer concentrations were generally 8-10 pg/m<sup>3</sup>, and winter concentrations were generally about half that, with a few large spikes in the spring. Precipitation concentrations varied from 5-80 ng/L, with most concentrations <30 ng/L. These correspond to wet deposition rates of 0.01–0.4 µg/m<sup>2</sup>, with a clear seasonal pattern. Deposition was lowest in winter, increased in spring, and peaked in July-August in both 1995 and 1996.

In 1997 UMAQL expanded the study to include additional sites, and to include measurements of indirect as well as direct sources of Hg to better understand the cycling and deposition of Hg to the system. The indirect measures included fog water deposition, snowmelt runoff, forest throughfall, and litterfall. Results of the monitoring were not available at the time of this report.

The precipitation data are comparable to the Mercury Deposition Network (MDN) data of the National Atmospheric Deposition Program. The site most representative of Voyageurs and Isle Royale is MDN site MN18, at Fernberg, Minnesota, within the Superior National Forest. Data on mercury wet deposition and concentrations in precipitation are available for 1995 to 2002. Mean volume-weighted concentrations of

mercury in precipitation were 9 ng/L at this site during 1995-1996, and ranged from 1-104 ng/L. The mean concentration of mercury in precipitation from 1996-2002 was 13 ng/L, with a range of 0.1 – 104 ng/L (discounting one outlier measurement of 397 ng/L). However, the vast majority of measurements were < 30 ng/L. The mean weekly deposition rate was 163 ng/m<sup>2</sup>.

## 1. Isle Royale

The major receptor of concern for mercury contamination is fish, and consumers of fish, due to the bioaccumulation of methylmercury in foodwebs. Several studies at Isle Royale have focused on determining the levels of Hg in fish. In addition, there has been an intensive, multidisciplinary research effort at Isle Royale to determine what factors might explain the concentrations of Hg observed in fish from the park.

The Michigan Department of Natural Resources (MDNR) analyzes lake trout from Lake Superior waters in the park for a wide range of contaminants, including mercury. In addition, they collect lake trout from Siskiwit Lake. These data are used to help establish fish consumption advisories for the state. While mercury concentrations in Lake Superior lake trout are below the level that would trigger fish consumption advisories, the concentrations of mercury in lake trout from Siskiwit Lake routinely exceed this level (500 ng/g wet weight), both currently and historically (Kelly et al., 1975; MIDNR, 1997; Kallemeyn, 2000).

Kallemeyn of the USGS conducted an extensive study of the fish community structure of Isle Royale, including 32 inland lakes from Isle Royale (Kallemeyn, 2000). He compared his data to a similarly rigorous study conducted in 1929 (Koeltz, 1929) in order to assess the long term changes in fish community structure in the park. In addition, Kallemeyn reported mercury concentrations in fishes from the current study. The concentrations of mercury in fish fillets varied by species and by lake, and ranged from 30–1720 ng/g wet weight. Concentrations in top predators such as lake trout (*Salvelinus namaycush*), walleye (*Sander vitreus*), and northern pike (*Esox lucius*) were similar and greater than those in white sucker (*Catostomus commersoni*) or whitefish (*Coregonus clupeaformis*), which are benthivores. Perch concentrations were generally intermediate, reflecting their omnivore diet. However, there were also significant

differences among lakes for a given species. Figure V-20 shows the mean mercury concentrations for northern pike fillets, adjusted to standard fish lengths of 550 and 610 mm (legal size), for 25 inland lakes. Five of the lakes had mean Hg concentrations in 610 mm pike that exceed the 0.5 ppm (500 ng/g) Michigan fish consumption guideline, and included Angleworm, Eva, Sargent, Shesheeb, and Wagejo lakes. The concentrations correlated weakly to the pH of the lake ( $r^2 = 0.18$ ;  $p = 0.035$ ). The lakes with highest mercury concentrations all lie on a 4.8 km long north-to-south transect from Eva Lake to Angleworm Lake. While others have suggested that the mineral content of the Keeweenawan basalt may have higher mercury content and thus serve as a natural source (Kelly et al., 1975), a recent study by Cannon and Woodruff (2000) concluded that the native copper deposits and historic mining activities did not appear to be contributing mercury to the soils or lakes on Isle Royale. They concluded that the higher mercury levels in some soils on the island were due to atmospheric deposition followed by redistribution processes.

The concentrations in northern pike from Isle Royale lakes were similar to those reported for Michigan lakes (Grieb et al., 1990), and slightly below those reported for Minnesota lakes (Sorensen et al., 1990).

Walleye concentrations from lakes Whittelsey and Chickenbone could be compared to those reported in 1975 by Kelly et al. (1975). Mean concentrations declined from 420 ng/g in 1929 and 475 ng/g in 1975 to approximately 205 ng/g in the mid-1990s.

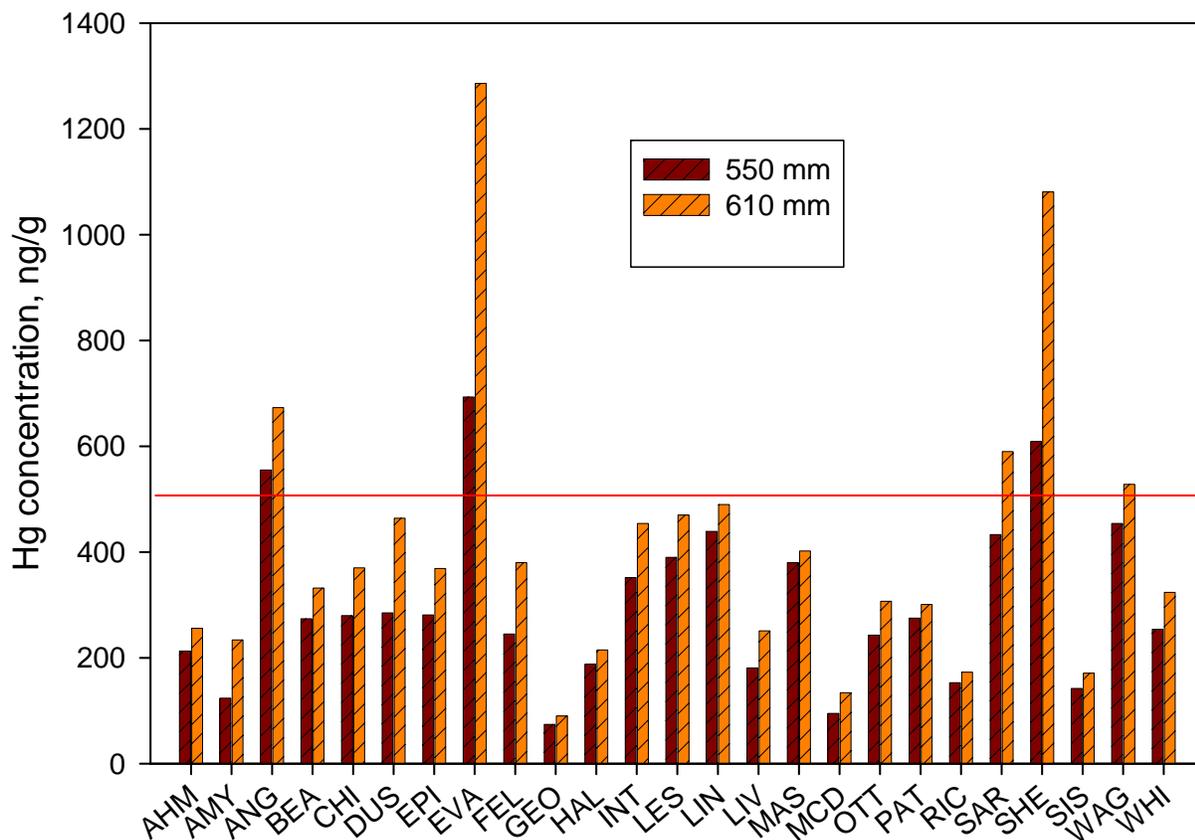


Figure V-20. Mean mercury concentrations in northern pike from 25 inland lakes at Isle Royale adjusted to the standard length of 550 mm, and to the legal take length of 610 mm (Kallemeyn, 2000). The Michigan fish advisory is 500 ng/g, and is indicated by the horizontal red line.

One surprising finding of the Kallemeyn study was the unusually high concentrations of mercury found in yellow perch (*Perca flavescens*) from Harvey Lake. Five perch ranging in size from 269 – 335 mm in length had concentrations of 649-1720 ng/g Hg, all above the 500 ng/g Michigan fish consumption advisory limit. Stomach content analyses revealed that several of these perch were piscivorous. This finding was the impetus of a multidisciplinary study of the effect of foodweb dynamics on mercury accumulation.

The Mercury Foodweb Study involved several subprojects, including one on the aquatic foodweb (Gorski et al., 2002) and several on the terrestrial foodweb. The main objective of the aquatic study was to measure mercury (total and MMHg) in the foodweb of a lake with elevated mercury in northern pike (Sargent Lake) and compare it to a similar lake with low levels of mercury in northern pike (Richie Lake). The factors affecting the differences in bioaccumulation between the lakes were identified and evaluated.

Based on reconstructed histories of mercury accumulation in lake sediments, the researchers concluded that the source of mercury to Isle Royale is atmospheric, and that there was no increase in mercury to the inland lakes as a result of local mining activities in the 1870-80s (Gorski et al., 2002). The researchers found little difference in the water concentrations of Hg or MMHg, which were similar to other small remote lakes. The concentrations of mercury in zooplankton, adult perch, and northern pike from Sargent Lake were greater than those from Richie, and these differences were attributed to a number of possible factors, including (1) differences in dissolved organic carbon (DOC), suspended particulate matter, chlorophyll a, and pigment signatures, which may result in greater bioavailability of MMHg to zooplankton in Sargent Lake; (2) differences in the foodweb structure. Sargent's foodweb is more pelagic-based, while Richie has a greater benthic component. Pelagic foodwebs usually lead to greater biomagnification of contaminants in top predators (Campbell et al., 2000); and (3) differences in fish concentrations could be a result of differences in growth rates, diet, and age/length population structure.

Concerns about impacts on fish-eating birds and wildlife from mercury exposure through the aquatic foodweb (Wiener and Krabbenhoft, 1999) led to a study of mercury exposure to the common loon within Isle Royale (Kaplan and Tischler, 2000). Blood and feathers from loons were collected from populations from several inland lakes, including Sargent Lake on Isle Royale, and Lake Superior. While there were no differences in mercury concentrations in adult loons, there were significantly greater concentrations in both blood and feathers of juvenile loons from Sargent Lake compared to Lake Superior. The adult loons from the inland lakes forage in Lake Superior, while the diet of the juveniles is derived entirely from the inland lake where they reside. Overall,

concentrations were comparable to other North American sites (see discussion for both parks, below). The mean concentration of Hg in blood was 1.06 µg/mL, and this compares well to a mean value of 1.11 µg/mL reported by Evers et al. (1998). There was evidence for a relationship of decreasing productivity (fledgling rate and hatching success) with increasing mercury exposure, but the small sample size precluded firm statistical confirmation. Studies on loon toxicity associated with mercury exposure from eating contaminated fish suggest that reproductive effects, such as reduced egg laying and decreased use of breeding territory, may begin to occur when prey concentrations are in the range of 0.3 – 0.4 µg/g wet weight (Barr, 1996; Wolfe et al., 1998). The Hg concentrations in pike from Sargent Lake are in this range, suggesting that the loons may be at risk but effects would be subtle and difficult to document statistically. Ten percent of the adult loons sampled at Isle Royale had feather concentrations greater than 20 µg/g, a benchmark for risk of toxic effects (Scheuhammer and Bond, 1991).

A related study evaluated the concentrations of mercury in deer mice collected from within and outside of the watershed of Sargent Lake (Vucetich et al., 2001). They found that the concentrations in deer mice livers were greater outside the watershed, and that the concentrations in kidneys were not significantly different by location. This supports the conclusion that the differences in fish Hg concentrations in the inland lakes are a result of in-lake processes and not related strongly to the watershed. The authors caution that the concentrations of mercury in deer mice may be of concern due to their role in the terrestrial foodweb on Isle Royale.

Deciduous teeth from moose have been used as bioindicators of mercury exposure and to examine time trends of contamination (Eide et al., 1997). Metals are incorporated into the dentine at the time of tooth formation. Studies of mercury in moose teeth from Isle Royale have demonstrated that concentrations increased on the island from 1945-1980, and have declined since then (Peterson et al., 2002). These results are consistent with other reports of declining atmospheric concentrations (Engstrom and Swain, 1997; Pirrone et al., 1998).

## 2. Voyageurs

A study of Hg deposition and the history of accumulation in lake sediments throughout Minnesota was done by Swain and Engstrom (Engstrom et al., 1999). They determined the history of mercury deposition in 50 lakes distributed throughout the state, and included 5 lakes from Voyageurs in their study. The reconstructed histories of accumulation were used to determine 1) the impacts of local sources compared to those resulting from long-range transport from regional and global sources of mercury; and 2) to assess anthropogenic influences on the rate at which inorganic mercury is converted to MMHg. They found that the median accumulation rate prior to European settlement was  $9 \mu\text{g}/\text{m}^2/\text{year}$ , and that accumulation rates rose steadily following settlement. The median accumulation rate in 20 northeastern lakes (including 5 from Voyageurs) at present is  $36 \mu\text{g}/\text{m}^2/\text{year}$ . The sediment concentration and accumulation rate of mercury in the 5 Voyageurs lakes increased by more than a factor of 2. Curiously, they report that the accumulation rates have declined in lakes in the vicinity of Voyageurs and Grand Rapids, but not in other rural or remote regions in the state. They attribute this to the declining use of mercuric fungicides by the Boise Cascade pulp mill at International Falls and the Blandin pulp mill at Grand Rapids. The use of these fungicides in pulping operations began in the 1940s and was nearly eliminated by 1980 (Engstrom and Swain, 1997). However, MMHg concentrations and accumulations did not decline over the same timeframe. This is because the rate of methylation also increased by factors of 2–3 in these northeastern lakes between 1940 and 1970. Thus, the increased mercury deposition rates, combined with the increase in methylation, indicate that the exposure to MMHg increased by factors of approximately 6 since pre-industrial times.

Glass and Sorenson (Glass and Sorensen, 1999) measured total mercury in precipitation from 1990-1995 twice weekly at six sites in North Dakota, Minnesota, and Michigan. The northeastern Minnesota sites included Ely, International Falls, Marcel, and Duluth. The mean annual wet deposition was  $7.4 \mu\text{g}/\text{m}^2\text{-yr}$ , and varied considerably among sites and with season. MMHg accounted for 1.5% of total mercury concentrations, on average.

Recent studies have evaluated contaminant trends in bald eagle nestlings and found that the mercury concentrations in feathers declined from 20 µg/g in 1985-1989 (Bowerman et al., 1994) to 8.8 µg/g in 1999-2000 (Rowe, 2001). The decline is thought to be due to the stabilization of water levels in large lakes in the park as a result of water management practices by the International Joint Commission (Rowe, 2001). Fluctuations of water levels may lead to a greater rate of methylation in the watershed by enhancing the activity of sulfate-reducing bacteria through changes in redox condition.

An important study was done in the early 1980s by Glass of the US EPA Mid-continent Ecology Division of the National Health and Ecological Effects Research Laboratory in Duluth, Minnesota (unpublished; data submitted to MPCA). Glass looked at mercury levels in fish from about 10 lakes, including lakes in the park. The highest concentrations of mercury in the study were found in fish from Voyageurs. Northern pike from Ryan and Tooth Lakes were found to have elevated concentrations compared to fish from the rest of the state, a finding confirmed by analyses of samples collected in 2000-2002 by J.G. Wiener, M.B. Sandheinrich (both at University of Wisconsin-La Crosse), B.C. Knights (U.S. Geological Survey), and J. Jeremiason (MPCA).

The Minnesota Fish Contaminant Monitoring Program has sampled fish for mercury since 1970 to assess concentrations, spatial patterns, and time trends. They sampled fish throughout the state in 1998 and 1999 to assess current concentrations and spatial trends. These data indicated that fish in the northeastern part of the state had the highest concentrations, including those from lakes in Voyageurs.

These results were the impetus for a study by the MPCA that began in 2000 and is currently underway. This collaborative study includes researchers from the MPCA, the MDNR, the University of Wisconsin-LaCrosse, Gustavus Adolphus College, the NPS, the USGS, and the St. Croix Watershed Research Station of the Science Museum of Minnesota. The focus of the study is to evaluate the ecosystem characteristics that influence MMHg accumulation in fish. Initially, 1-year-old yellow perch were collected from 15 lakes in the park. These one-year old fish feed primarily on zooplankton and small benthic invertebrates, and thus differences in MMHg should reflect differences in ecosystem production of MMHg rather than foodweb differences. While concentrations

in fish tissue from Tooth Lake were typical for the state (approx. 100 ng/g wet weight), the concentrations in Ryan Lake were about twice that value. Concentrations correlated positively with DOC, an indicator for wetland influence. The researchers have tentatively concluded that extent of connected wetlands will strongly influence MMHg production and bioaccumulation in fish (Wiener et al., 2002).

Northern pike were also sampled from 11 lakes in the park. Concentrations of MMHg from Ryan and Tooth lakes were found to be about 5 times greater than for the rest of the state. The researchers speculated that northern pike in these two lakes may occupy higher trophic levels than in other lakes. A secondary objective of this study is to determine the trophic positions of perch and pike in 11 lakes using stable isotopes of nitrogen (Wiener et al., 2002).

While the likely explanation for the variation in MMHg concentrations in fish is due to differences in methylation efficiencies related to watershed characteristics (Post et al., 1996), other possible explanations have been explored. To rule out differences in atmospheric deposition, air samples were taken near one of the Voyageurs lakes. Concentrations were not elevated over typical atmospheric background levels. To assess whether natural geological contributions are a source of mercury to these lakes, researchers from the USGS analyzed soil layers and bedrock for mercury (Woodruff et al., 2002). They concluded that the elevated MMHg in fish was not a result of increased mercury loading to the lakes from geological sources (L. Woodruff, personal communication).

During 2001 and 2002 the sampling of both 1-year-old perch and northern pike was repeated. One of the objectives of this sampling was to assess the relationship between MMHg concentrations in fish and biomarkers for reproductive success. Previously conducted laboratory studies with fathead minnows showed that exposures to environmentally relevant MMHg concentrations correlated to a repression of reproductive success, decreased levels of reproductive hormones, delayed spawning, and decreased egg production (Hammerschmidt et al., 2002). The data from the wild fish are still being evaluated at this time (M. Sandheinrich, personal communication).

Krabbenhoft (USGS, Madison, WI) and Jeremiason (Gustavus Adolphus College, St. Peter, MN) recently evaluated a set of sediment cores from 5 Voyageurs lakes

differing in their watershed areas and wetland types. Three replicate cores were injected with mercury and the rate of methylation was followed for a 24 hour period. Preliminary data do not indicate any differences in methylation rate over this time frame (J. Jeremiason, personal communication).

A comparative study of mercury exposure to the common loon was conducted in the early-mid 1990s (Evers et al., 1998). The study compared loon body burdens across North America, including those from Alaska, the Pacific Northwest, the upper Great Lakes, New England, and the Canadian Maritimes. The sites from the upper Great Lakes included loons from both Voyageurs and Isle Royale. Blood and feathers were analyzed in adult females and males and in juveniles. The study reported that males had significantly greater concentrations of mercury in both feathers and blood than did females. This likely reflects the fact that males are larger, and are thought to eat different species of fish than females. Adults had significantly greater concentrations than juveniles. Both of these observations are supported by other studies (Scheuhammer et al., 1998; Kaplan and Tischler, 2000). Feather concentrations were greater than and weakly correlated to blood concentrations.

The concentrations reported by Evers et al. (1998) revealed an increasing gradient of Hg body burdens in loons from west to east across North America, with the Great Lakes sites lying in the middle of the concentration range. Adult female loons from Isle Royale and Voyageurs had mean blood concentrations of  $0.78 \pm 0.21$  (standard deviation) and  $1.06 \pm 0.42$   $\mu\text{g/mL}$ , respectively. Male loon blood concentrations from Isle Royale and Voyageurs were  $1.43 \pm 0.38$  and  $1.7 \pm 0.61$ , respectively. These values were intermediate within the range observed for the other 7 upper Great Lakes sites.

The risk of reproductive effects to loons from mercury exposure has been estimated from prey concentrations (Barr, 1986), feathers (Scheuhammer and Bond, 1991) and egg concentrations (Heinz, 1979). Direct toxicity to adults or juveniles may have lower risk. A study by Kenow et al. (2003) showed no effects to juveniles hatched from eggs dosed with environmentally representative concentrations of mercury, suggesting that the juveniles may be protected by the high excretion rates of MMHg from their feathers. Concentrations of Hg in prey fish from some lakes from both parks

are above the benchmark for risk to loons for adverse reproductive effects, and loon feather concentrations indicate that a small proportion of adults are above the threshold for potential effects. A study by Meyer et al. (1998) on loons from Wisconsin lakes showed a trend of decreasing productivity and reproductive success with increased exposure concentrations in loon blood, but the relationships were confounded by the correlation between mercury exposure concentrations and lake pH value. The higher pH values in the lakes at both parks may help mitigate some of the risk (Scheuhammer and Blancher, 1994). However, the occurrence of such impacts should be watched for carefully. A study of mercury concentrations in loons from 33 lakes from 1992 – 2000 revealed a 4.2% decline in body burdens (Fevold et al., 2003), and trend analyses should be done in both parks to see if a similar trend is observed.

## **H. INVENTORY OF KNOWN VULNERABILITIES**

The common attributes that make these parks sensitive to threats from atmospheric pollutants include their location in the upper Midwest, their water-dominated geography, and their Laurentian geological underpinnings. Despite their distance from most point sources, the movement of continental air masses over North America is such that their location makes them vulnerable to long-range transport of persistent atmospheric pollutants. Once these air masses deliver pollutants by long-range transport, they are subject to removal by vapor absorption, and wet and dry deposition. As discussed previously, the fact that such a large percentage of their surface areas is covered by water makes both parks particularly vulnerable to these depositional processes.

Voyageurs is situated very close to a major point source of virtually all the pollutants considered: CO, PM, NO<sub>x</sub>, SO<sub>2</sub>, mercury, PAH, dioxins. The Boise Cascade plant, located in International Falls, reports emissions of NO<sub>x</sub>, PM<sub>10</sub>, and SO<sub>2</sub> that are two orders of magnitude greater than estimated emissions from activities within the park. Emissions of mercury and dioxin from this plant are probably the single most important point source of these compounds to the park environment.

Voyageurs has the added impacts of human use during the winter months, and much of this activity includes snowmobile use. The assessment of the impacts of

snowmobile use presented here demonstrates that this intense use in a small geographic area has the potential to cause elevated CO and VOC concentrations in the park. Although emissions of other pollutants from snowmobiles in Voyageurs are significant, they are much smaller than those released from the paper mills in International Falls and (likely) Fort Frances, Ontario.

Mercury, dioxins, and other persistent organic pollutants are atmospheric pollutants of most concern to both parks. The category of POPs is a broad one, and while concentrations of the now-banned organochlorine compounds, such as PCBs and DDT, are declining, they can still cause chronic effects at very low exposures. More importantly, there are “new” POPs that are now being documented in the environment that are increasing in concentration. These include polybrominated diphenyl ethers (PBDEs) and perfluorooctane sulfonate (PFOS), both of which have been detected in remote environments including in Lake Superior lake trout (Swackhamer, unpublished data).

While some lakes in both parks are vulnerable to acid deposition, current levels of deposition are not a threat. Moreover, emission reductions associated with air quality regulations appear to be decreasing loadings of excess hydrogen ion in the region. Sulfur dioxide emissions are still of concern; however, given their significant contribution to visibility impairment in the region. States will likely need to focus on SO<sub>2</sub> sources to meet their Regional Haze visibility goals. Ozone levels are currently low at both parks, although increasing concentrations at Voyageurs suggest ozone could become a problem in the upper Midwest in the future. Neither Voyageurs or Isle Royale are vulnerable to threats that other regions of the country might face, such as eutrophication or plant damage from SO<sub>2</sub>.

The specific vulnerabilities of the parks as a result of these threats include the following:

- **Impacts on fish-eating birds and wildlife.** Trace levels of mercury and POPs bioaccumulate in aquatic foodwebs, and consumption of fish by either wildlife such as mustelids or fish-eating birds such as loons may have an impact on reproduction and productivity.
- **Impacts on anglers.** Both parks are highly valued for recreational boating and canoeing, and for fishing. Fish from several of the lakes from both parks have

levels of mercury that exceed the health guidelines. The states of Minnesota and Michigan have issued fish consumption advisories for lakes within Voyageurs and Isle Royale.

- **Impacts on terrestrial foodwebs.** The terrestrial foodweb, especially in Isle Royale, is a narrow one with limited species. Top predators are subjected to elevated exposures of POPs and mercury due to biomagnification within the foodweb. Previous sections of the report document the presence of measurable levels of mercury in deer mice and moose at Isle Royale. It is not unreasonable to assume that concentrations in wildlife at Voyageurs are similar, since both parks receive approximately the same atmospheric loadings of contaminants. Impacts on animals at the top of the terrestrial foodweb are not known.

## I. RESEARCH AND MONITORING NEEDS

The Organic Act of 1916 mandates that the NPS must manage these precious natural resources in such a way that they remain as unimpaired as possible. However, one of the most striking observations from this report is that there is no organized structure or plan at either Isle Royale or Voyageurs for routine monitoring of POPs or Hg, identified as the most important threats above, or for research to fill data gaps and lack of understanding of processes. The efforts that have been summarized here are generally piecemeal, and not integrated into a larger vision for assessing and maintaining the natural resources. A complete inventory of all the species of plants and animals at either park is not available. This is not a condemnation of the park resource managers in any way, as it is clear that they share this frustration, as well as frustration at the lack of financial resources to do more. However, a strategic vision of natural resource management is needed, and we recommend that an ecosystem-based approach be emphasized. To assess the threats to the parks, one must consider the entire ecosystem and the ecological services and functions within it. Ad hoc studies that are not woven into an integrated understanding of the system are not helpful to meeting the NPS's mandate.

### 1. Monitoring

As described in prior sections of this report, air quality and air pollution effects-related monitoring activities are ongoing in both Isle Royale and Voyageurs. Ambient air quality monitoring at Isle Royale includes seasonal NADP wet deposition, seasonal

hourly ozone, and year-round IMPROVE aerosol sampling. Air quality monitoring at Voyageurs includes year-round NADP wet deposition, CASTNet dry deposition, hourly ozone and IMPROVE aerosol sampling. Surface water chemistry and fish tissue mercury concentrations have been monitored in both parks, but not on a routine or systematic basis.

Under the NPS Inventory and Monitoring (I&M) Program, the Great Lakes Vital Signs Network, which includes Isle Royale NP, Voyageurs NP, and seven other NPS units, was established in 2002. The two components of the I&M program include completion of select baseline inventories and initiation of long-term ecosystem monitoring. The goals of the inventory effort are to document occurrence of  $\geq 90\%$  of vertebrate and vascular plant species estimated to occur within each park and to describe the distribution and relative abundance of species of special concern. The Network is in the process of developing the long-term monitoring plan for Network parks. As part of this process, the Network is identifying park-specific natural resource-related monitoring needs, distinguishing needs that are relevant to all or most Network parks, and prioritizing crosscutting issues.

Estimates of the impact of air pollution in Voyageurs could be greatly improved with a program for recording human activities within the park. Current efforts to more precisely estimate visitors to Voyageurs are ongoing (Davenport et al., 2003; Flitsch et al., 2004) but without a permitting system or controlled entry, estimates will always have significant uncertainty. Snowmobile activity, in particular, should be better monitored. Snowmobile use at Voyageurs is second only to Yellowstone in annual visits to a national park. However, the trends and patterns of snowmobile use at Voyageurs are poorly understood, largely because there is no permitting system or uniform entry system for snowmobile access to Voyageurs. In addition to a system for recording daily use of snowmobiles, information regarding the type of snowmobile and average length of visit should be collected. It is not advised, however, that snowmobiles be funneled through a single entry as the high concentrations of pollutants at Yellowstone are a result of focusing snowmobiles at a few entrances.

A trend monitoring program for contaminants of concern in fish is needed. Concentrations of many air pollutants are not well estimated for either park due to lack

of data for the region. In particular, concentrations of persistent, bioaccumulating organic compounds such as PCBs and MMHg are of concern. These compounds are accumulated in fish at levels that pose risk to humans and animals in the parks. Therefore, regular monitoring of mercury and a select set of organic contaminants in fish is recommended for lakes that have already been identified as having elevated concentrations in fish. Organic contaminants of concern include PCBs, PCDD/PCDF, PBDEs, PFOS, and chlorinated pesticides. Such a program will only be successful if there are standardized procedures established for the collection, compositing, and analyses of fish samples. In order to link the mercury concentrations in fish to atmospheric deposition processes, monitoring of wet deposition of Hg is also recommended. It is important to remember that even if the air concentrations of pollutants decline due to regulatory actions, fish concentrations may continue to be elevated for decades afterwards. Loons are also excellent bioindicators (Scheuhammer et al., 1998; Evers et al., 2003), and a regular monitoring program of Hg in adult blood and/or chick feathers and blood coupled to measures of productivity is recommended. The details of such a monitoring program (when, where, how often, using what methods, etc.) should be done with expert consultation both inside and external to the NPS, and with as much partnering with other agencies as possible. For instance, current fish collections by the states might be enhanced to meet a schedule designed by the NPS for certain designated lakes in the parks. Much could be learned by coordinating with existing monitoring programs, such as the US EPA Great Lakes Fish Monitoring Program.

## **2. Research**

Research needs for improved estimates of the impacts and risk associated with air pollutants in Isle Royale and Voyageurs include studies of emissions of organic contaminants from snowmobiles (Voyageurs only), long-range transport of air pollutants to the park, and the processes contributing to the bioaccumulation of contaminants in fish and fish-eating animals.

Emissions of organic contaminants from snowmobiles and marine engines are poorly known. For snowmobiles, research is needed to determine the emissions of

PAHs and VOCs. For marine engines, research is needed to determine the relative contributions of all air pollutants to air and directly to water.

Long-range transport of mercury, persistent organic pollutants, and criteria pollutants clearly impacts the parks. However, it appears no studies have been undertaken to compare the impact of local sources to more distant sources and their relative importance to air quality in the parks. Since both Voyageurs and Isle Royale are remote parks with few local sources, it is likely that long-range transport is affecting air quality in the parks (although the impact of sources in Thunder Bay, Ontario on Isle Royale is frequently raised as an unresolved issue). Therefore a modeling research study is recommended, with focus on ozone precursors, mercury, polycyclic aromatic hydrocarbons (PAHs) and current use pesticides. These pollutants have adequate emission inventories available to allow a successful modeling outcome. Such a study would be focused specifically on the parks and be done in greater detail than the regional efforts by NOAA. In addition, a model could be used to determine if increasing ozone trends in Voyageurs are due to large sources of NO<sub>x</sub> in nearby International Falls and Fort Frances. PAHs and current use pesticides (including Atrazine) could be successfully modeled as their sources are reasonably well understood and documented. PAHs are released from all internal combustion engines, including snowmobiles, outboard motors, and vehicles. A model comparing in-park sources to long-range sources would provide interesting and valuable information. Although PCBs may be accumulating in fish at unacceptable levels, it is difficult to estimate emissions of this banned compound. Efforts could also be undertaken to model new POPs such as PBDEs to place the NPS ahead of the curve on this issue. A current study on PBDE accumulation in Siskiwit Lake sediments on Isle Royale by researchers at the University of Illinois at Chicago could help elucidate the historical deposition of these compounds, but also is an example of the piecemeal nature of some of the research. This study needs to be put into a larger context to better understand fate and transport.

Research is also needed to identify the risks associated with accumulated toxics in fish and fish-eating animals. Concentrations of mercury and POPs in fish are known for some lakes and some species, but the potential effects of these contaminants should be assessed. Research on birds of prey should continue and expansion of

these studies to mammals should be considered. Research on the mechanisms and endpoints of endocrine disruption in fish and wildlife need considerable study, with a focus on reproduction, growth, and development.

In particular, there is a need to better understand the processes of mercury cycling and bioaccumulation. It is strongly recommended that the NPS encourage research regarding the relationships and linkages between atmospheric deposition, watershed characteristics and processes, methylation and de-methylation, and transfer up the foodweb. The composition and structure of the foodweb and their impacts on foodweb accumulation need further study. Isle Royale and Voyageurs are both ideally suited for research studies on these topics, as they have a variety of lakes with different characteristics that can be studied. The excellent work being conducted on mercury, particularly at Voyageurs by James Wiener and colleagues, would provide even more value information if it were part of a coordinated strategy of the NPS. Such a strategy should acknowledge and build on the large scale projects recently completed (e.g. the Everglades) or currently underway (e.g. METALLICUS) on mercury processes in the environment.

Lastly, research is also needed to map the pathway between atmospheric sources and ecosystem impacts of many other pollutants. For example, it is not clear if accumulated PAHs, particulate matter, and hydrocarbons in snowpack are efficiently transferred to the lakes after snowmelt. In Voyageurs, this is an important question, due to the heavy use of snowmobiles and outboard marine engines.

## VI. APPENDICES

### A. LIGHT EXTINCTION COEFFICIENT

Aerosol data are used to calculate the atmospheric light extinction coefficient from experimentally determined extinction efficiencies of important aerosol species. The equation used by the IMPROVE Program to estimate reconstructed particle light extinction in  $\text{Mm}^{-1}$  is:

$$b_{\text{ext}} = b_{\text{ray}} + 3f(\text{RH})[\text{sulfates}] + 3f(\text{RH})[\text{nitrates}] + (4)[\text{organics}] + (1)[\text{soil}] + (0.6) [\text{coarse mass}] + (10)[\text{light absorbing carbon}]$$

where [ ] indicate mass concentration of the individual species. Some sulfates and nitrates are hygroscopic, so their scattering properties must be adjusted for the effects of relative humidity ( $f(\text{RH})$ ).

### Visual Range

Visual Range (VR) can be expressed in terms of the light extinction coefficient as:

$$\text{VR} = 3912 / (b_{\text{ext}} + b_{\text{ray}})$$

where  $b_{\text{ext}}$  is the extinction coefficient expressed in  $\text{Mm}^{-1}$ ;  $b_{\text{ray}}$  is the site specific Rayleigh values (elevation dependent) and 3912 is the constant derived from assuming 2% contrast detection threshold. The theoretical maximum VR is 391 km. Note that  $b_{\text{ext}}$  and VR are inversely related: for example, as the air becomes cleaner,  $b_{\text{ext}}$  values decrease and VR values increase. A related metric is the Standard Visual Range (SVR). This metric is indexed to Rayleigh conditions at 1800 meters elevation rather than actual Rayleigh conditions at a specific location, (i.e., set to  $10 \text{ Mm}^{-1}$ ).

### Haziness

Haziness as expressed in deciview is defined as:

$$\text{Haziness (dv)} = 10 \ln(b_{\text{ext}} / 10 \text{ Mm}^{-1})$$

where  $b_{ext}$  is the extinction coefficient expressed in  $Mm^{-1}$ . A one dv change is approximately a 10% change in  $b_{ext}$ , which is a small but perceptible scenic change under many circumstances. The deciview scale is near zero (0) for a pristine atmosphere and increases as visibility is degraded.

**B. SNOWMOBILE EMISSIONS ESTIMATES.**

Report	units	Type of snowmobile	HC	CO	NO <sub>x</sub>	PM	HC	CO	NO <sub>x</sub>	PM
			Reported Values				g/visit <sup>b</sup>	g/visit <sup>b</sup>	g/visit <sup>b</sup>	g/visit <sup>b</sup>
Wright and White (SAE), 1998	g/kW-hr	Ski-Doo 503cc	141.1	582.5	0.98		11796	48697	81.93	
	g/kW-hr	Arctic Cat 440 cc	168.7	506.2	0.55		14103	42318	45.98	
Bishop, 1999 <sup>a</sup>	g/kg	Variety	662	460			21057	14632		
Bishop, 2001 <sup>a</sup>	g/kg	liquid cooled snowmobiles	484	356			15395	11324		
	g/kg	fan cooled snowmobiles	456	411			14504	13073		
NPS Feb 2000 document	g/hp-hr	average	141	386	0.54	1.83	9024	24704	34.56	117.1

<sup>a</sup> Calculated from 0.08 toluene/HC ratio, Bishop, 2001

<sup>b</sup> Conversion Factors and assumptions used Table above.

1 hp = 0.746 kW  
 2.84 kg/gal  
 6.26 lbs per gallon

4 hours/ visit 11.2 gallons /visit 16 hp 20.9 KW
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