



Air Quality Related Values (AQRVs) for Great Lakes Network (GLKN) Parks

Effects from Ozone; Visibility Reducing Particles; and Atmospheric Deposition of Acids, Nutrients and Toxics

Natural Resource Report NPS/GLKN/NRR—2016/1167



ON THE COVER

Photograph of air quality related values within various National Park units. Wildflowers, clear views, aquatic species, and lichens may all be threatened by air pollution.

Photographs courtesy of the National Park Service

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Natural Resource Report NPS/GLKN/NRR—2016/1167

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National Park Service
Natural Resource Stewardship and Science
Fort Collins, Colorado

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Summary

This report describes the Air Quality Related Values (AQRVs) of the Great Lakes Network (GLKN). AQRVs are those resources sensitive to air quality and include streams, lakes, soils, vegetation, fish and wildlife, and visibility. The GLKN parks that are included in the NPS Inventory and Monitoring (I&M) Program, and discussed in this report, are Apostle Islands National Lakeshore (APIS), Grand Portage National Monument (GRPO), Indiana Dunes National Lakeshore (INDU), Isle Royal National Park (ISRO), Mississippi National River and Recreation Area (MISS), Pictured Rocks National Lakeshore (PIRO), Saint Croix National Scenic Riverway (SACN), Sleeping Bear Dunes National Lakeshore (SLBE), and Voyageurs National Park (VOYA). Isle Royal NP and VOYA are designated as Class I, giving them a heightened level of protection against harm caused by poor air quality under the Clean Air Act (CAA).

Sullivan et al. (2011a, 2011b) and Kohut (2007a) conducted risk assessments for acidification, eutrophication, and ozone (O_3) for all of the NCCN parks; their results are described in this report. This report also describes air pollutant emissions and air quality, and their effects on AQRVs. The primary pollutants likely to affect AQRVs include nitrogen (N) and sulfur (S) compounds (nitrate [NO_3^-], ammonium [NH_4^+], and sulfate [SO_4^{2-}]); ground-level O_3 ; haze-causing particles; and airborne toxics. Background for this section can be found in “Air Quality Related Values (AQRVs) in National Parks. Effects from Ozone; Visibility Reducing Particles; and Atmospheric Deposition of Acids, Nutrients and Toxics” (Sullivan 2016). Additional material is available on the GLKN website (<http://science.nature.nps.gov/im/units/glkn/>).

Air pollution is an important stressor to natural resources within national park units in the GLKN. Effects have generally been well studied in the Great Lakes region (Charles 1991, Evers et al. 2011a, Greaver et al. 2011, Kohut 2007a, Kohut 2007b). Atmospheric emissions and deposition of S and N vary dramatically across the network region, with relatively low values to the northwest and high values to the southeast.

Based on published research findings and spatial patterns in pollutant load, resource sensitivity, and effects across the Inventory and Monitoring (I&M) parks nationwide, the air pollution effects of greatest concern to GLKN parks appear to include mercury (Hg) methylation and nutrient enrichment of wetlands. Airborne contaminants, including Hg, can accumulate in food webs, reaching toxic levels in top predators. The major source of Hg in the watersheds of this region is atmospheric deposition (Mason and Sullivan 1997, Rolfhus et al. 2003, Wiener et al. 2006), most of which originates from human-caused sources (Lamborg et al. 2002, Lorey and Driscoll 1999, Swain et al. 1992). Within the Great Lakes region, including the northern portions of the GLKN, methylmercury (MeHg) is known as a substantial risk to the health of wildlife. Much of the landscape is conducive to transformation from elemental Hg deposited from the atmosphere to MeHg.

Sulfur and N pollutants can cause acidification of streams, lakes, and soils. Lake acidification is mostly confined to groundwater recharge seepage lakes in the northeastern portion of the network region. Acidification in response to human-caused S and N deposition has not been documented in surface waters in network parks.

Nitrogen pollutants can cause undesirable enrichment of natural ecosystems, leading to changes in plant species diversity and soil nutrient cycling. Wetlands are especially sensitive to N enrichment effects, stimulating the growth of certain plant species, with the subsequent loss of rare or infrequent species. Nitrogen-limited lakes are also vulnerable to excess N enrichment that can cause unwanted increases in productivity and changes in natural plant and phytoplankton species composition.

Ozone pollution can harm human health, reduce plant growth, and cause visible injury to foliage. Ozone is an important stressor to park vegetation in this Network, primarily in the more southerly parks that are in proximity to major nitrogen oxide (NO_x) emissions sources.

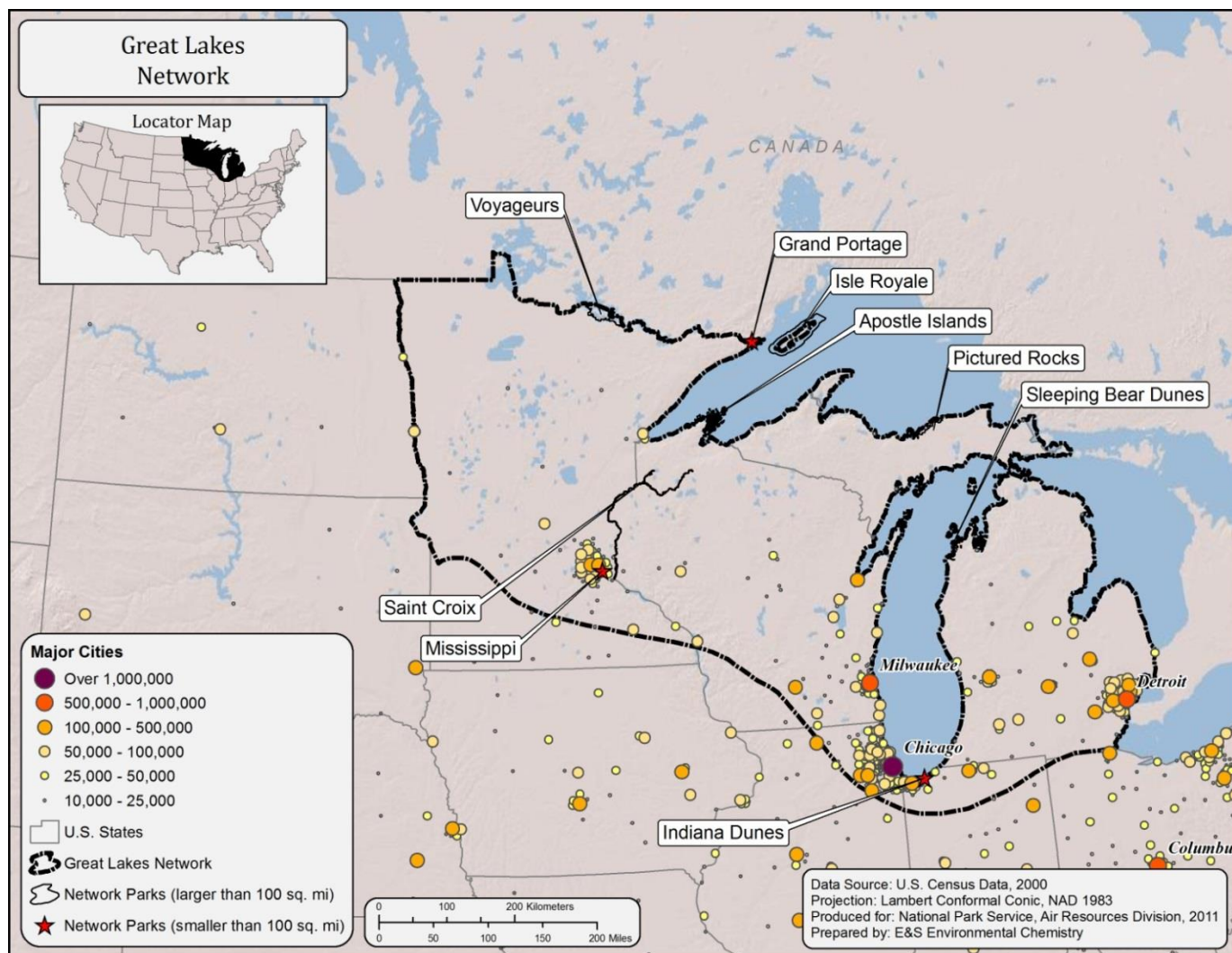
Particulate pollution can cause haze, reducing visibility. Ambient haze, including haze caused by both natural and anthropogenic particles and aerosols, is high on the haziest days in ISRO. Levels of haze are also high at times in other GLKN parks.

Among the parks in the GLKN, INDU appears to be especially sensitive to, and impacted by, air pollution. This park contains a large number of known O₃-sensitive plant species and was rated as being at high risk from O₃ injury to vegetation (along with SLBE). Mercury concentrations in wet deposition in INDU were the third highest among 13 national parks monitored by the National Park Service (NPS; 2010). Tooth, Ryan, and Mukooda Lakes in VOYA have among the highest concentrations of Hg in fish among all studied lakes in Minnesota (Goldstein et al. 2003, Rolfhus et al. 2011).

Background

The Great Lakes Network (GLKN) contains six parks larger than 100 square miles: Apostle Islands National Lakeshore (APIS), Isle Royal National Park (ISRO), Pictured Rocks National Lakeshore (PIRO), Saint Croix National Scenic Riverway (SACN), Sleeping Bear Dunes National Lakeshore (SLBE), and Voyageurs National Park (VOYA). There are also three smaller parks in this network: Grand Portage National Monument (GRPO), Indiana Dunes National Lakeshore (INDU), and Mississippi National River and Recreation Area (MISS). Larger parks generally have more available data with which to evaluate air pollution sensitivities and effects. In addition, the larger parks generally contain more extensive resources in need of protection against the adverse impacts of air pollution.

Map 1 shows the network boundary and the location of each national park, along with human population centers with more than 10,000 people. The largest urban centers in the network region are Chicago, Detroit, Minneapolis/St. Paul, and Milwaukee. Columbus and Indianapolis also have large populations, and lie within a 300-mile radius of the network. Air pollution effects have been well studied in the Great Lakes region, especially mercury (Hg) biomagnification and the acidification of lakes.



Map 1. The GLKN network boundary, locations of the nine network parks, and population centers with more than 10,000 people.

Atmospheric Emissions and Deposition

Sullivan et al. (2011b) identified sulfur dioxide (SO₂) point sources within the GLKN region with emissions higher than 20,000 tons of SO₂ per year. In addition, SO₂ point sources of greater magnitude were found to the southeast, outside of the network boundary. Relatively large nitrogen (N) point sources (greater than 2,500 tons per year) also occur in the GLKN region. Most have been sources of oxidized, rather than reduced, N (Sullivan et al. 2011b). There were also many smaller sources of reduced N near the network, mainly in the southern half of Minnesota. Many of the larger N point sources within the network region are located along the perimeter of the southern section of Lake Michigan.

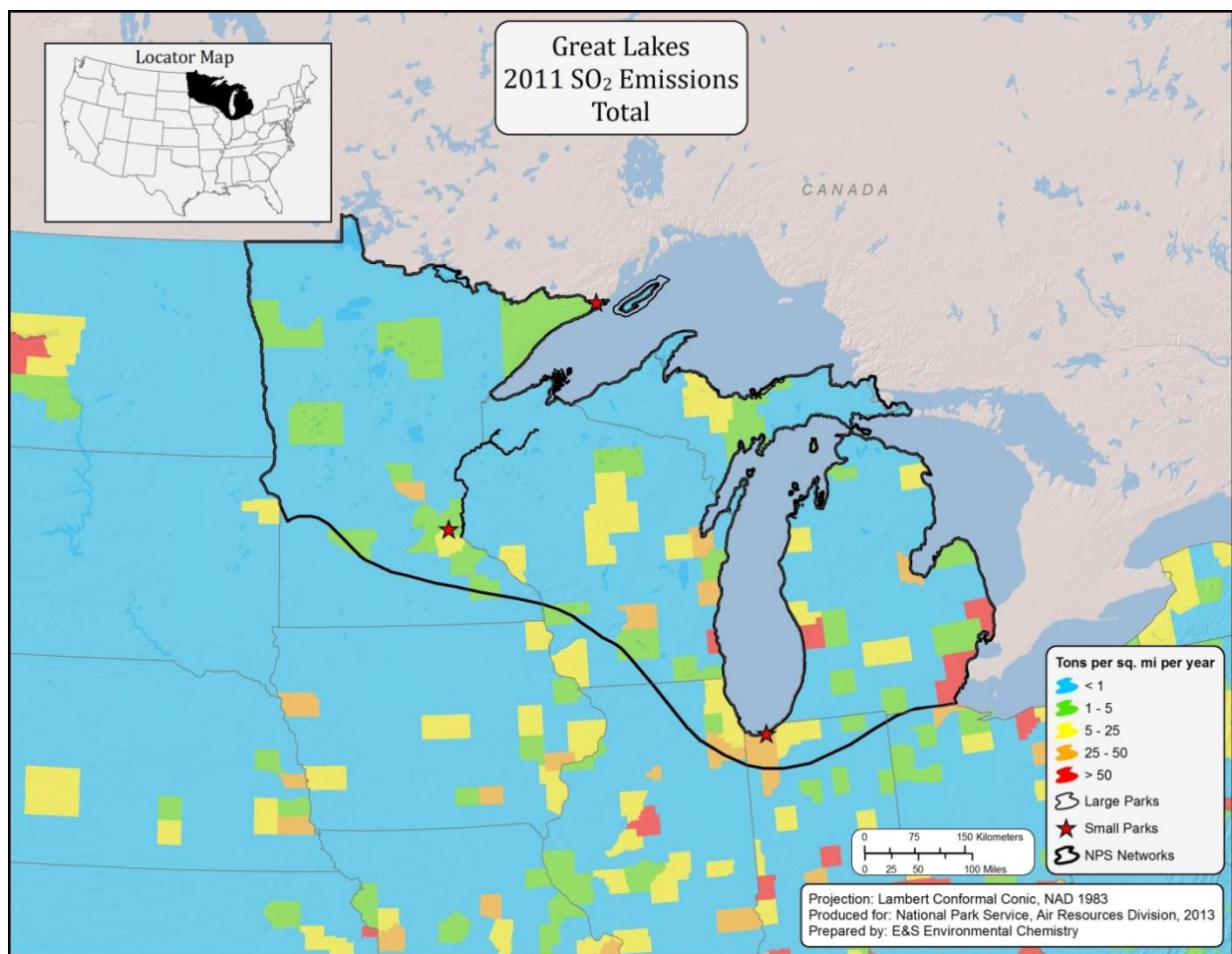
Regional air pollutants reach VOYA and ISRO. Pulp and paper plants in Minnesota and Ontario constitute local sources of oxidized N (NO_x). Power plants, mining, and ore processing are important regional sources of SO₂, particulate matter (PM), and NO_x (Swackhamer and Hornbuckle 2004). ISRO and VOYA are located in the northernmost portion of the network, where emissions and deposition of S and N are generally lowest. Indiana Dunes NL and MISS, are located in the more heavily populated and industrialized portion of the network to the south.

County-level emissions near the GLKN, based on data from the EPA's National Emissions Inventory (NEI) during a recent time period (2011), are depicted in Maps 2 through 4 for SO₂, oxidized N (NO_x), and reduced N (NH₃), respectively. Many counties near GLKN parks had relatively high SO₂ emissions (> 25 tons/mi²/yr; Map 2). Spatial patterns in NO_x emissions were generally similar, with highest values above 50 ton/mi²/yr (Map 3). Emissions of NH₃ near GLKN parks were somewhat lower, with most counties showing emissions levels below 8 tons/mi²/yr (Map 4).

Snowmobile use at VOYA is second only to Yellowstone National Park among national parks (Swackhamer and Hornbuckle 2004). Emissions of N from snowmobiles and boats are potentially important in VOYA, although these impacts are poorly understood.

Estimated total S deposition within the GLKN in 2002 ranged from less than 2 kg S/ha/yr in the northwestern portion of the network region, near the U.S.–Canadian border, to greater than 30 kg S/ha/yr in the south-southeastern portion, near Chicago and Lake Michigan (Sullivan et al. 2011b). In general, the estimated S deposition within the network region ranged from 2 to 15 kg S/ha/yr; higher S deposition occurred to the south and lower S deposition occurred to the north. Total N deposition ranged from 2 to 5 kg N/ha/yr in the north, 15 to 20 kg N/ha/yr near heavily urbanized areas to the south, and up to 20 to 30 kg N/ha/yr at some locations. Throughout much of the network region, total N deposition ranged from 10 to 15 kg N/ha/yr in the south and 5 to 10 kg N/ha/yr in the north (Sullivan et al. 2011b). Wet deposition of Hg is low throughout this network, compared with levels in some other parts of the conterminous United States.

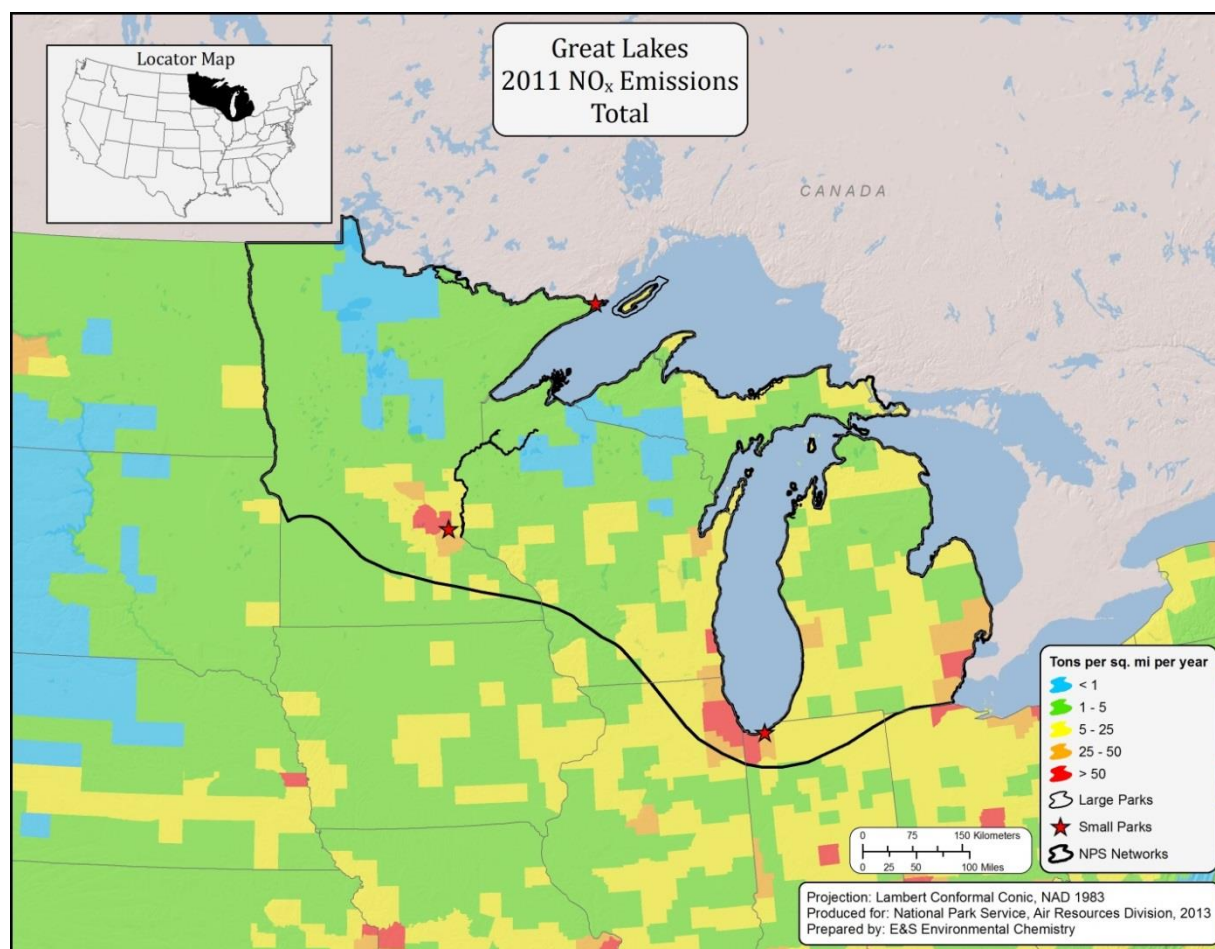
Based on wet deposition at 29 national park locations from 1989 to 2008, nitrate (NO₃⁻) concentration in precipitation declined significantly ($p \leq 0.05$) at only four locations, one of which was INDU where NO₃⁻ declined by 0.49 µeq/L/yr (NPS (2010)). The study also showed that SO₄²⁻ in



Map 2. Total SO₂ emissions, by county, near the GLKN for the year 2011. Data from EPA's National Emissions Inventory.

wet deposition at most parks decreased ($p \leq 0.05$). The largest decrease was at INDU (-1.4 $\mu\text{eq/L/yr}$; NPS 2010). However, in the central United States, from Texas to North Dakota, SO₂ emissions increased during the 1990s, with statistically significant increases in Minnesota (9%) and several other states (Malm et al. 2002). Emissions from these areas may impact sensitive resources in the GLKN.

Recently, Schwede and Lear (2014) documented a hybrid approach developed by the National Atmospheric Deposition Program (NADP) Total Deposition (TDEP) Science Committee for estimating total N and S deposition. This approach combined monitoring and modeling data. Modeling was accomplished using the Community Multiscale Air Quality (CMAQ) model (Byun and Schere 2006). Priority was given to measured data near the locations of the monitors and to modeled data where monitoring data were not available. In addition, CMAQ data were used for N species that are not routinely measured in the monitoring programs: peroxyacetyl nitrate, N₂O₅, NO, NO₂, HONO, and organic NO₃. The total deposition estimates are considered to be dynamic, with updates planned as new information becomes available. TDEP data reported here were developed in late 2013 and are designated version 2013.02.

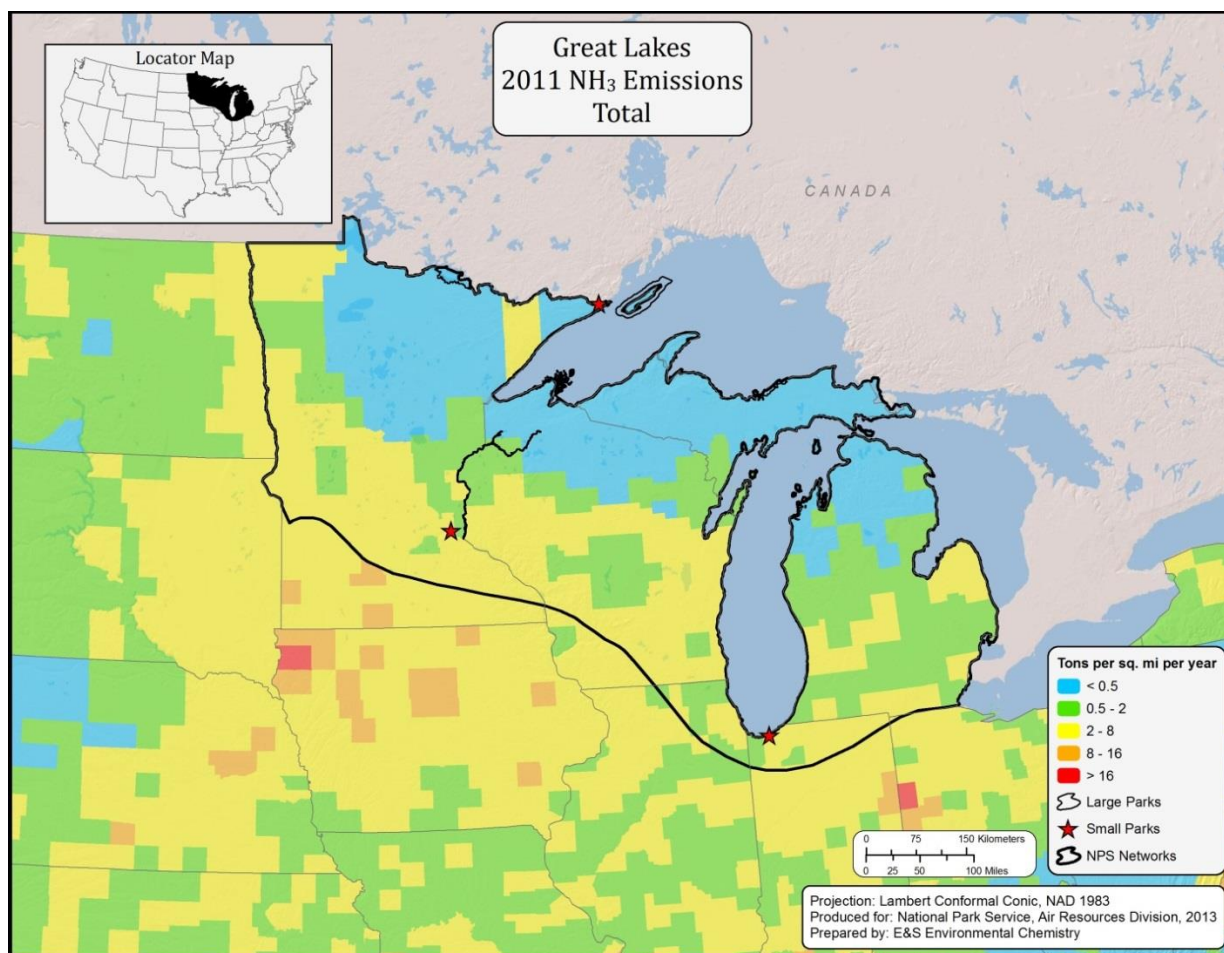


Map 3. Total NO_x emissions, by county, near the GLKN for the year 2011. Data from EPA's National Emissions Inventory.

NO₂, HONO, and organic NO₃. The total deposition estimates are considered to be dynamic, with updates planned as new information becomes available. TDEP data reported here were developed in late 2013 and are designated version 2013.02.

Atmospheric S, and to a lesser extent N, deposition levels have declined at most GLKN parks since 2001, based on TDEP estimates (Table 1). Total S deposition decreased at all parks in GLKN except INDU (increased by 51.7%) and GRPO (increased by 17.1%) over the previous decade. Decreases were as large as 40.6% at SLBI. Estimated total N deposition decreased over that same time period at all network parks except GRPO (increased by 9.8%).

Total S deposition in and around the GLKN for the period 2010-2012 was generally highest (> 5 kg S/ha/yr) to the east and lowest (< 5 kg S/ha/yr) to the west of the network area (Map 5). Oxidized inorganic N deposition for the period 2010-2012 was in the range of 5-10 kg N/ha/yr throughout some of the park lands within the GLKN (Map 6). Most park lands received less than 10 kg N/ha/yr of reduced inorganic N from atmospheric deposition during this same period (Map 7); a few areas received higher amounts. Total N deposition was variable, with generally lowest values to the north (Map 8).



Map 4. Total NH₃ emissions, by county, near the GLKN for the year 2011. Data from EPA's National Emissions Inventory

NO₂, HONO, and organic NO₃. The total deposition estimates are considered to be dynamic, with updates planned as new information becomes available. TDEP data reported here were developed in late 2013 and are designated version 2013.02.

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received higher amounts. Total N deposition was variable, with generally lowest values to the north (Map 8).

Hall et al. (2005) reported total and methylmercury (MeHg) concentrations in precipitation at five sites in the Great Lakes region, including one site at ISRO. Monitoring was conducted from 1997 to 2003. The highest MeHg concentrations were measured during small rain events, suggesting wash-out of MeHg from the atmosphere. This MeHg may have derived from MeHg formed in conjunction with lake-effect clouds and fog, emitted from wetlands around Lake Superior, and/or released into the atmosphere by Lake Superior sediments (Hall et al. 2005).

Risch et al. (2012) reported wet Hg deposition throughout the Great Lakes region during the period 2002-2008, based on data from three Hg and precipitation monitoring networks. Areas in southern Indiana and Illinois, eastern Pennsylvania, and central Michigan had highest estimated wet Hg deposition, ranging from about 10 to 14 $\mu\text{g}/\text{m}^2$. Such high wet deposition levels were caused by high Hg concentration in precipitation ($> 12 \text{ ng}/\text{L}$) and/or high precipitation amount (120-140 cm/yr). There was no trend in deposition over the course of the monitoring period; any small decrease that may have occurred in Hg concentration was apparently offset by increased precipitation (Risch et al. 2012).

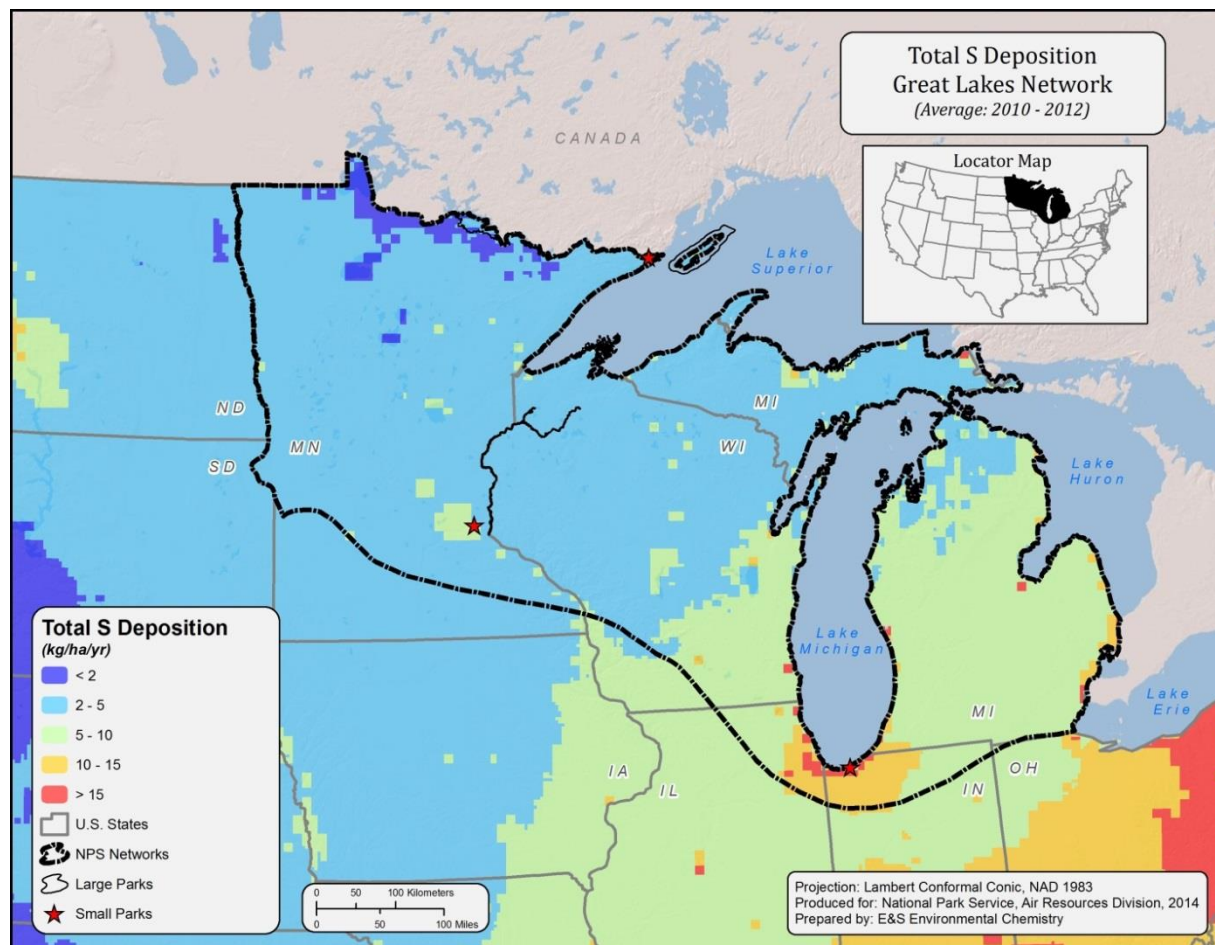
NPS (2010) reported long-term trends in concentrations of Hg in wet deposition between 1996 and 2008, for national parks throughout the United States. Statistically significant ($p \leq 0.05$) decreases in wet Hg deposition were reported for INDU (-0.56 ng/L/yr; 8 years of data) and Allegheny Portage Railroad, in the Eastern Rivers and Mountains Network (-0.17 ng/L/yr; 12 years of data). None of the other parks showed significant trends. NPS (2010) also reported that INDU had the third highest three-year mean annual Hg concentration in wet deposition compared to 13 other parks that had at least two years of valid data during the period 2006-2008.

Table 1. Average changes in S and N deposition between 2001 and 2011 across park grid cells at GLKN parks. Deposition estimates were determined by the Total Deposition Project, TDEP, based on three-year averages centered on 2001 and 2011 for all ~4 km grid cells in each park. The minimum, maximum, and range of 2011 S and N deposition within each park are also shown.

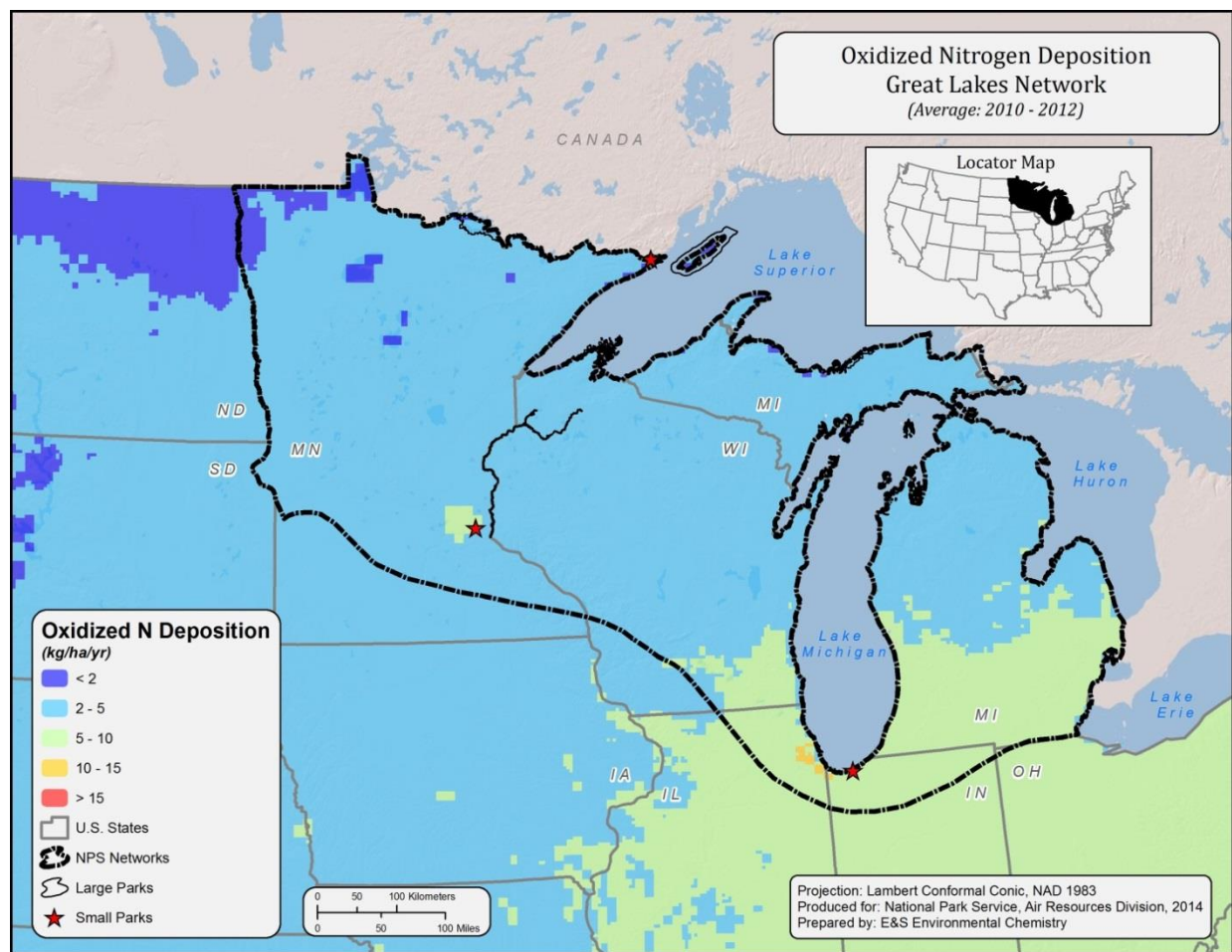
Park Code	Park Name	Parameter	2001 Average (kg/ha/yr)	2011 Average (kg/ha/yr)	Absolute Change (kg/ha/yr)	Percent Change	2011 Minimum (kg/ha/yr)	2011 Maximum (kg/ha/yr)	2011 Range (kg/ha/yr)
APIS	Apostle Islands	Total S	3.69	2.90	-0.79	-21.8%	2.61	4.99	2.38
		Total N	6.19	4.79	-1.41	-22.6%	4.40	6.85	2.45
		Oxidized N	3.27	2.16	-1.11	-33.5%	1.92	3.50	1.58
		Reduced N	2.92	2.62	-0.29	-10.3%	2.45	3.51	1.05
GRPO	Grand Portage	Total S	3.54	4.15	0.61	17.1%	2.93	4.93	2.00
		Total N	5.52	6.06	0.54	9.8%	5.99	6.15	0.16
		Oxidized N	2.81	3.05	0.24	8.6%	3.02	3.09	0.07
		Reduced N	2.71	3.01	0.30	11.0%	2.97	3.06	0.09
INDU	Indiana Dunes	Total S	10.83	16.53	5.70	51.7%	9.79	37.10	27.31
		Total N	12.92	12.30	-0.62	-5.3%	9.05	16.54	7.50
		Oxidized N	8.12	6.33	-1.79	-22.7%	4.30	8.90	4.60
		Reduced N	4.80	5.97	1.17	24.3%	4.70	8.16	3.46
ISRO	Isle Royale	Total S	3.55	3.26	-0.29	-8.4%	2.51	5.17	2.66
		Total N	5.47	4.59	-0.88	-16.2%	3.83	6.07	2.24
		Oxidized N	2.84	2.20	-0.65	-23.1%	1.70	3.26	1.57
		Reduced N	2.62	2.39	-0.23	-8.8%	2.12	2.85	0.73
MISS	Mississippi	Total S	5.91	5.60	-0.31	-2.2%	4.04	9.30	5.26
		Total N	15.84	13.26	-2.58	-15.7%	11.41	15.97	4.56
		Oxidized N	7.15	4.71	-2.44	-33.5%	3.82	6.55	2.73
		Reduced N	8.69	8.56	-0.13	-0.8%	7.04	9.74	2.70

Table 1 (continued). Average changes in S and N deposition between 2001 and 2011 across park grid cells at GLKN parks. Deposition estimates were determined by the Total Deposition Project, TDEP, based on three-year averages centered on 2001 and 2011 for all ~4 km grid cells in each park. The minimum, maximum, and range of 2011 S and N deposition within each park are also shown.

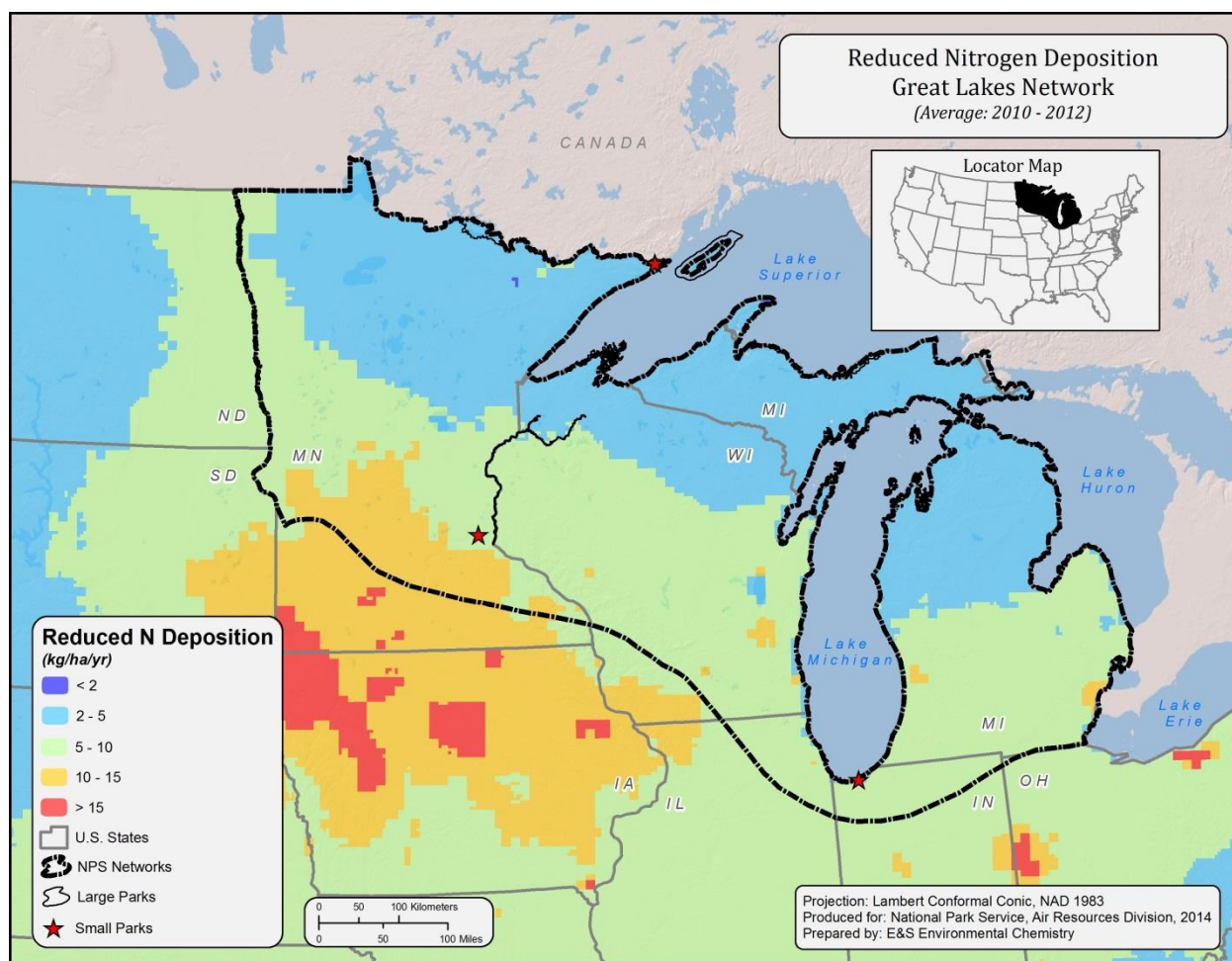
Park Code	Park Name	Parameter	2001 Average (kg/ha/yr)	2011 Average (kg/ha/yr)	Absolute Change (kg/ha/yr)	Percent Change	2011 Minimum (kg/ha/yr)	2011 Maximum (kg/ha/yr)	2011 Range (kg/ha/yr)
PIRO	Pictured Rocks	Total S	5.89	3.97	-1.92	-32.5%	2.99	8.04	5.05
		Total N	8.94	5.41	-3.54	-39.7%	4.36	7.62	3.27
		Oxidized N	5.63	2.66	-2.97	-52.9%	2.00	4.10	2.10
		Reduced N	3.31	2.75	-0.57	-17.3%	2.36	3.56	1.21
SACN	Saint Croix	Total S	5.11	3.43	-1.68	-30.3%	3.06	4.40	1.35
		Total N	11.85	9.73	-2.12	-15.8%	8.17	12.53	4.36
		Oxidized N	5.80	3.64	-2.16	-33.8%	3.15	4.51	1.36
		Reduced N	6.06	6.09	0.04	1.5%	4.40	8.58	4.19
SLBE	Sleeping Bear Dunes	Total S	7.11	4.23	-2.88	-40.6%	3.81	8.61	4.80
		Total N	7.84	6.07	-1.77	-22.7%	5.32	9.30	3.98
		Oxidized N	4.65	3.01	-1.63	-35.3%	2.58	4.97	2.39
		Reduced N	3.20	3.06	-0.13	-4.3%	2.74	4.40	1.67
VOYA	Voyageurs	Total S	2.69	2.63	-0.06	-2.4%	1.41	3.14	1.73
		Total N	5.61	5.05	-0.56	-9.8%	3.67	5.45	1.78
		Oxidized N	3.13	2.32	-0.81	-25.7%	1.61	2.52	0.91
		Reduced N	2.48	2.73	0.25	10.4%	2.05	2.93	0.88



Map 5. Total S deposition for the three-year period centered on 2011 in and around the GLKN. (Source: Schwede and Lear 2014)



Map 6. Total oxidized inorganic N deposition for the three-year period centered on 2011 in and around the GLKN. (Source: Schwede and Lear 2014)

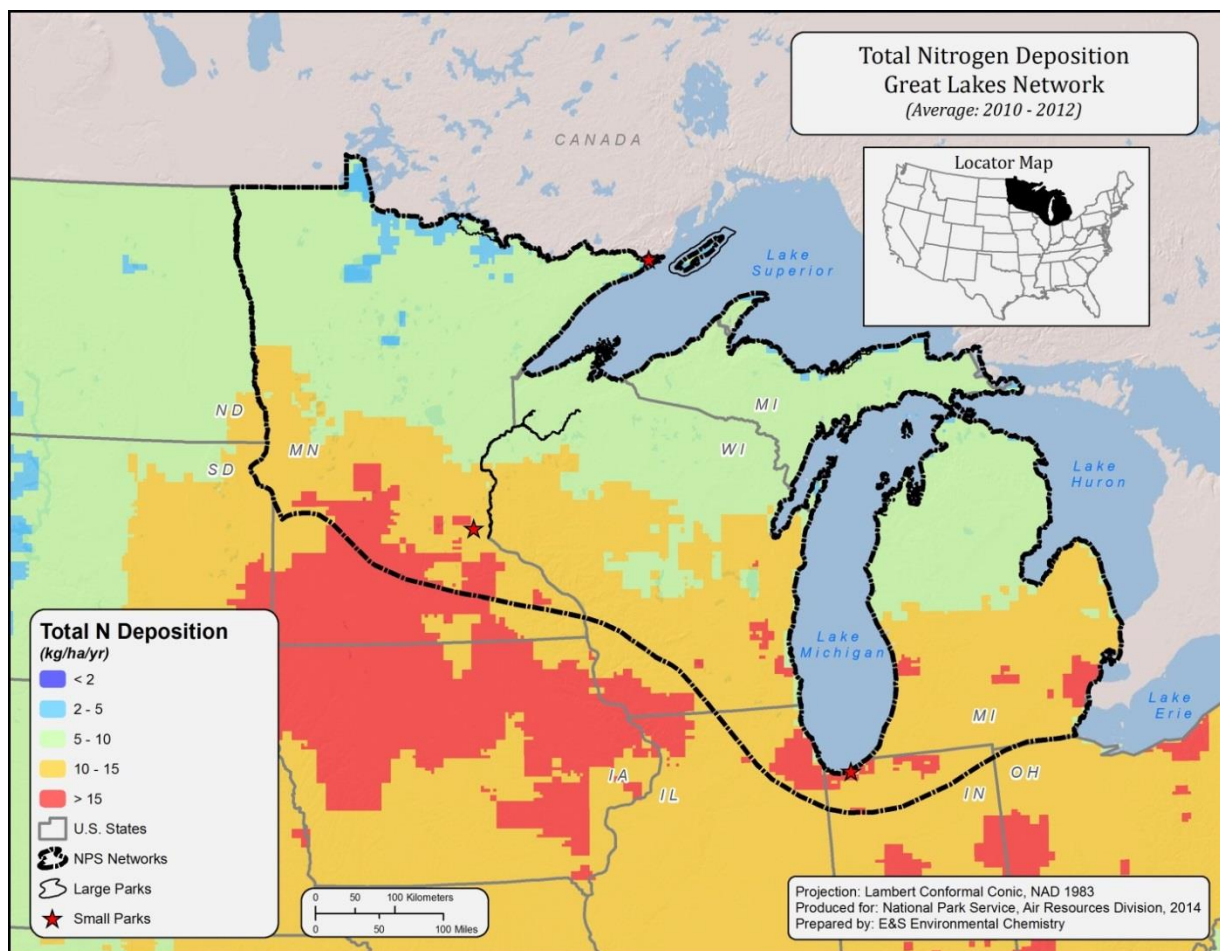


Map 7. Reduced inorganic N deposition for the three-year period centered on 2011 in and around the GLKN. (Source: Schwede and Lear 2014)

Initial scientific focus on Hg contamination in the GLKN region was directed at industrial point sources such as pulp and paper mills and chlor-alkali plants (Turner and Southworth 1999, Wiener et al. 2003, Wiener et al. 2012a). However, point source release of Hg into surface waters decreased substantially in the 1980s, and atmospheric deposition is now the main source of Hg to watersheds in the Great Lakes region. The region contains a number of anthropogenic atmospheric emissions sources that collectively emit more than 50 kg per year of Hg (Wiener et al. 2012a).

Dry Hg deposition estimates, derived by Zhang et al. (2012) using the CMAQ and Global/Regional Atmospheric Heavy Metals (GRAHM) models, suggested that total annual dry Hg deposition was generally $< 5 \mu\text{g}/\text{m}^2$ to the water surface of the Great Lakes. Estimates were higher, between 5 and $40 \mu\text{g}/\text{m}^2$, to land surfaces. This result was attributed to higher dry deposition velocities to vegetative surfaces as compared with open water.

The Integrated Atmospheric Deposition Network (IADN) has monitored persistent organic pollutants (POPs) in air and precipitation at each of the five Great Lakes since 1990 (Clair et al. 2011).



Map 8. Total N deposition for the three-year period centered on 2011 in and around GLKN. (Source: Schwede and Lear 2014)

Concentrations of many chlorinated POPs have declined over the Great Lakes region in recent decades (Simcik et al. 2000). In particular, decreases have been observed for polychlorinated biphenyls (PCBs) and organochlorinated pesticides (including dieldrin, chlordanes, and endosulfans; Sun et al. 2006, Sun et al. 2007). Monitoring of brominated flame retardants was initiated in recent years and shows some evidence of decline since controls were initiated (Clair et al. 2011, Sun et al. 2007, Venier and Hites 2008). Measurements of polybrominated diphenyl ethers (PBDEs) and various emerging flame retardants in the plasma of nesting bald eagles were reported by Venier et al. (2010).

Acidification

The rankings reported by Sullivan et al. (2011b) in a coarse screening assessment yielded a Network Acidification Risk for the GLKN in the second highest quintile among all 32 NPS I&M networks. The overall level of concern for acidification effects in the GLKN was judged by Sullivan et al. (2011b) to be High.

For the GLKN, Acid Pollutant Exposure rankings were higher in the smaller parks that are located in the more populated and industrialized portions of the network region: INDU was ranked Very High and MISS was ranked High (Sullivan et al. 2011b). The other parks were ranked Moderate or Low for acid Pollutant Exposure (Table 2).

The larger parks varied only slightly in rankings for Ecosystem Sensitivity to acidification. ISRO and SLBE were ranked High, whereas APIS, PIRO, SACN, and VOYA were all ranked Very High for Ecosystem Sensitivity (Table 2). Thus, any effects of acidification on resources within the larger parks that occur in this network appear to be more a function of high resource sensitivity than high ambient air pollution levels. The smaller parks were ranked Moderate or High for Ecosystem Sensitivity. While rankings are an indication of risk, park-specific data, particularly data on ecosystem sensitivity, are needed to fully evaluate risk from acidification.

Table 2. Estimated I&M park rankings¹ according to risk of acidification impacts on sensitive receptors (Source: Sullivan et al. 2011b)

Park Name ²	Park Code	Estimated Acid Pollutant Exposure	Estimated Ecosystem Sensitivity to Acidification
1 -Voyageurs	VOYA	Moderate	Very High
2 -Isle Royale	ISRO	Low	High
3 -Grand Portage	GRPO	Low	High
4 -Pictured Rocks	PIRO	Moderate	Very High
5 -Apostle Islands	APIS	Moderate	Very High
6 -Saint Croix	SACN	Moderate	Very High
7 -Sleeping Bear Dunes	SLBE	Moderate	High
8 -Mississippi NRA	MISS	High	Moderate
9 -Indiana Dunes	INDU	Very High	Moderate

¹ Relative park rankings are designated according to quintile ranking, among all I&M parks, from the lowest quintile (very low risk) to the highest quintile (very high risk).

² Park names are printed in bold italic for parks larger than 100 mi².

Acidification of Terrestrial Ecosystems

Site-specific data are generally not available regarding the sensitivity of terrestrial ecosystems to acidification in the GLKN or the extent to which terrestrial acidification has occurred in the parks in this network. There are no data documenting that terrestrial acidification is an important concern in this network. Nevertheless, sugar maple (*Acer saccharum*) occurs in the GLKN and is known to be sensitive to acidification of base-poor soils. In northern New York, sugar maple is not regenerating on sites that have soil base saturation less than about 12% (Sullivan et al. 2013). It is not known

whether soil acidification has occurred sufficiently within the GLKN to cause damage to this sensitive tree species.

In response to decreased S deposition across the Great Lakes region since the 1980s, there have been large decreases in Michigan in the concentrations of various elements in sugar maple foliage: S (-16%), Ca (-17%), and aluminum (Al; -42%; Figure 1; Talhelm et al. 2011). Thus, the likelihood of acidification effects on sugar maple may be declining in the GLKN in response to decreases over time in S deposition and associated manifestations in tree foliage.

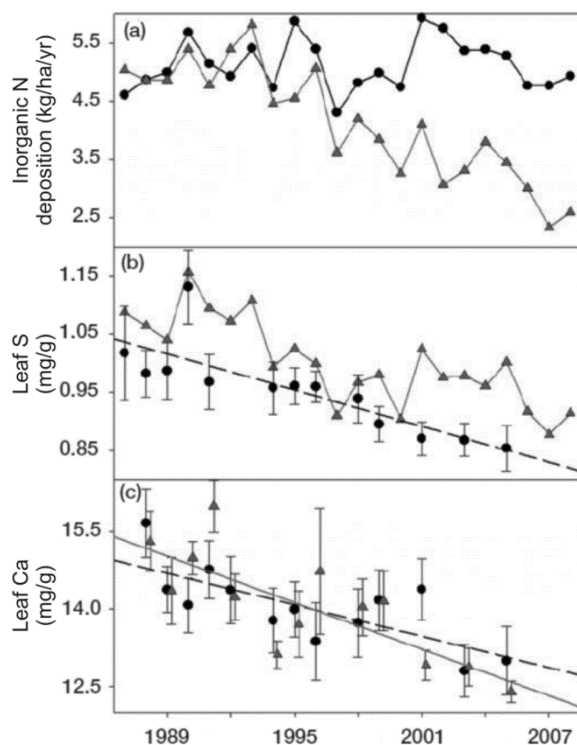


Figure 1. Trends in (a) mean annual acid (triangles) and N (circles) wet deposition averaged from the three atmospheric deposition monitoring sites in the upper Great Lakes region; (b) mean annual SO_4^{2-} wet deposition (triangles) and study-wide mean leaf S concentrations (circles, dashed regression line); and (c) study-wide mean leaf Al concentrations (triangles, solid regression line) and leaf Ca concentrations (circles, dashed regression line). Error bars are ± 1 standard error. (Source: Talhelm et al. 2011)

Bennett and Wetmore (1997) sampled and analyzed over a period of three years the chemical contents of four species of lichen (*Cladina rangiferina*, *Evernia mesomorpha*, *Hypogymnia physodes*, and *Parmelia sulcata*) at 10 sites along a 24-km transect between International Falls, MN and the park boundary of VOYA. There was not a clear pattern of decreasing metal and other element concentrations with increasing distance from S and metal emissions sources in International Falls in any of the lichens studied. However, the researchers concluded that there was sufficient evidence to suggest a high probability of physiological impairment to the lichens collected near VOYA from relatively high atmospheric inputs of S and heavy metals.

Acidification of Aquatic Ecosystems

The Upper Midwest contains numerous lakes created by glaciation. They have been the subject of extensive research on lake acidification (cf., Charles 1991, NAPAP 1991). Acid-sensitive lakes are common within the region, but not specifically within the GLKN parks. The region has little topographic relief. Acid-sensitive surface waters in the GLKN region are mainly groundwater recharge seepage lakes (Eilers et al. 1983). Most drainage lakes and some of the seepage lakes (the flow-through type) in the Upper Midwest receive substantial inflow from groundwater, which is generally high in base cation concentrations from dissolution of carbonate and silicate minerals. Relatively high concentrations of base cations in many of these lakes make them insensitive to acidification from acidic deposition. The seepage lakes that have low base cation concentrations, and that are therefore acid-sensitive, generally receive most of their water input from precipitation directly on the lake surface (Baker et al. 1991). These groundwater recharge seepage lakes can be identified on the basis of having silicon (Si) concentration less than about 1 mg/L (Baker et al. 1991). The acid-sensitivity of streams within the region has not been well studied but is not expected to be especially high.

Current Status

Based on the EPA's Eastern Lakes Survey (ELS), the Great Lakes region had a large population of low acid neutralizing capacity (ANC) lakes, many in the region around PIRO, but relatively few chronically acidic ($\text{ANC} \leq 0$) lakes (Linthurst et al. 1986a, 1986b). Acidic lakes in this region are primarily small, shallow seepage lakes that are hydrologically isolated from the surrounding terrain and that have low concentrations of base cations and Al and moderate SO_4^{2-} concentrations. Organic anions, estimated by both the Oliver et al. (1983) method and the anion deficit method, tended to be less than half the measured SO_4^{2-} concentrations in the acidic lakes (Eilers et al. 1988). Organic anion concentrations were much higher in many of the drainage lakes in the region that are less sensitive to acidification from acidic deposition. These relatively insensitive, high-dissolved organic carbon (DOC) drainage lakes occur mainly in Minnesota in the western portion of the GLKN region.

Groundwater flow-through seepage lakes in the Great Lakes region generally have high pH and ANC, due to groundwater inputs of base cations (e.g., Baker et al. 1991). They are generally not sensitive to acidification. Based on results from the ELS survey, only 6% of these lakes had $\text{ANC} \leq 50 \mu\text{eq/L}$ and none were acidic. Groundwater recharge seepage lakes (identified as those having Si concentration less than 1 mg/L) in the Upper Midwest region of the ELS frequently had low pH and ANC. Five percent were acidic and 9% had $\text{pH} \leq 5.5$. Such lakes tend to be susceptible to acidification from acid deposition.

Lakewater concentrations of inorganic N reported by the ELS were low throughout the Upper Midwest. In addition, snowmelt would not be expected to provide any significant NO_3^- influx to lakes in the Upper Midwest because most snowmelt in this region infiltrates the soil before reaching the drainage lakes, and because snowmelt input of N into seepage lakes would be limited mainly to the snow on the lake surface and immediate near-shore environment.

Aluminum concentrations are far lower in the GLKN region than in lakes of similar pH in the northeastern United States. Base cation production is the dominant ion-enrichment process in most

lakes in the GLKN region. Even in low-ANC groundwater-recharge seepage lakes, base cation production accounts for 72% to 86% of total ANC production (Cook and Jager 1991).

Data from over 12,500 streams and lakes were used by the Critical Loads of Atmospheric Deposition Science Committee (CLAD) of the NADP (<http://nadp.sws.uiuc.edu/committees/clad/>) to develop steady-state critical loads for acidity of surface waters based on multiple approaches for estimating base cation weathering: modified F-factor, regional regression model, and the Model of Acidification of Groundwater in Catchments (MAGIC). Water quality data were obtained from a variety of sources including EPA Long Term Monitoring (LTM) sites, lake surveys, EMAP Assessments, and National Stream Surveys; USGS; NPS Vital Signs program; and USFS air program. The average water quality measurements from the most recent five years of data were used for sites with long-term water monitoring records. The CLAD database included CL estimates for seven sites in VOYA and three of fewer sites in each of ISRO, PIRO, and SLBE. All modeled CL estimates in this network were high (> 311 eq S/ha/yr).

Past Acidification

Space-for-time substitution analysis was used by Sullivan (1990) to infer the general levels of past change in lake water acid-base chemistry in the GLKN region. Such an analysis assumes that study lakes were generally similar in acid-base chemistry prior to the onset of acidic deposition and that the only substantial driver of recent change in acid-base chemistry has been the level of acidic deposition. Across an increasing S depositional gradient from eastern Minnesota eastward to eastern Michigan, ANC expressed as bicarbonate minus hydrogen ion concentration ($\text{HCO}_3^- - \text{H}^+$) decreased and the ratio SO_4^{2-} to the sum of base cation (SBC) concentrations increased in the groundwater recharge seepage lakes. In Michigan and Wisconsin, many groundwater recharge seepage lakes had $\text{SO}_4^{2-} > \text{SBC}$, indicating that the acidity was due to high SO_4^{2-} relative to SBC concentration. There were also many lakes that had high concentrations of DOC, and organic acidity probably accounted for many of these lakes having low ANC. The spatial pattern in the concentration of bicarbonate minus $\text{HCO}_3^- - \text{H}^+$ could not be attributed to DOC, however, which generally showed a decreasing trend with increasing acidic deposition.

The concentration of lakewater ($\text{Ca}^{2+} + \text{Mg}^{2+}$) also decreased with increasing acidic deposition across the Upper Midwest, probably due to hydrologic differences across the region and to lower levels of base cation deposition and greater amounts of precipitation in the eastern portion of the region. Atmospheric deposition is an important source of base cations for groundwater recharge seepage lakes because of minimal groundwater inputs. In the eastern portion of the region, such lakes are more sensitive to pH and ANC depression in response to either elevated SO_4^{2-} or DOC.

Diatom-inferred pH reconstructions were completed for 15 lakes in the Upper Midwest, and summarized by Kingston et al. (1990) and Cook and Jager (1990). Four lakes, all of which had measured $\text{pH} < 5.7$, showed a diatom-inferred pH decline of 0.2 to 0.5 pH units during the preceding 50 to 100 years. Diatom-inferred pH increased in one lake by 0.2 pH units. No change was inferred for the other 10 lakes, including four lakes with $\text{pH} > 6.0$. No major, recent, regional acidification was indicated by the diatom-inferred pH reconstructions. Inferred changes in most lakes were small, and were no greater during the industrial period than during the pre-industrial period (Sullivan 2000).

Although diatom data suggested that some Upper Midwestern lakes may have acidified since pre-industrial times, there is little paleolimnological evidence indicating substantial widespread acidification in this region (Cook et al. 1990, Kingston et al. 1990). The portion of the GLKN region most likely to have experienced acidification from acidic deposition is the Upper Peninsula of Michigan, where acidic seepage lakes are particularly numerous (Baker et al. 1990); acidic deposition is highest for the region, and the $[\text{SO}_4^{2-}]/[\text{SBC}]$ ratio in lakewater is commonly > 1.0 . The only national park in this portion of the GLKN region is PIRO, which was ranked as having Very High sensitivity to acidification. The percentage of acidic lakes in the eastern portion of the Upper Peninsula of Michigan (east of longitude 87°) was estimated to be 18% to 19% in 1984 (Eilers et al. 1988, Schnoor et al. 1986).

Recent Trends

Regional trends analyses for long-term monitoring lakes in the GLKN region during the period 1990 to 2000 suggested that SO_4^{2-} declined in lakewater by $3.63 \mu\text{eq/L/yr}$, whereas lakewater NO_3^- concentrations were relatively constant (Stoddard et al. 2003). The large decrease in SO_4^{2-} concentration in lake water was mainly balanced by a combination of a large decrease in base cation concentrations ($-1.42 \mu\text{eq/L/yr}$) and an increase in ANC ($+1.07 \mu\text{eq/L/yr}$). All of these trends were significant at $p < 0.01$ (Stoddard et al. 2003). In the GLKN region, an estimated 80 of 251 lakes that were acidic in the mid-1980s were no longer acidic in 2000. This change was probably caused by decreased S deposition (Stoddard et al. 2003).

The GLKN continues to monitor the water quality of inland lakes in VOYA, APIS, ISRO, PIRO, INDU, and SLBE. The purpose is to describe the water quality status and to detect trends over time in various limnological parameters (Elias and Damstra 2012).

Effects of Acidification on Aquatic Biota

Studies of the effects of lake acidification on zooplankton have been conducted in and near the GLKN region. Results of such studies are potentially relevant to lakes in GLKN parks, but none of the studies have been specific to any of the parks. Field survey and experimental lake studies, as discussed below, have both indicated that acidification reduces zooplankton species richness. Effects of acidification on community biomass and abundance, however, have not been definitive. Some studies have indicated a lower biomass under low pH conditions, whereas other studies showed no consistent pattern in the biomass-pH relationship.

Reported pH thresholds for altering the zooplankton community have generally ranged from 5 to 6. Holt et al. (2003) reported a threshold for community change at $\text{pH} = 6$ for lakes in southern Ontario, near the GLKN. Locke and Sprules (1994) reported that acidification below $\text{pH} = 5$ in the 1970s reduced the stability of the zooplankton community in Ontario Precambrian Shield lakes. The subset of study lakes that showed pH recovery from acidification 20 years later in 1990 also showed recovery in the stability of the zooplankton community.

Recovery to $\text{pH} 6.1$ in experimentally acidified Lake 223 in the Experimental Lakes Area in Canada (near the GLKN) was studied by Malley and Chang (1995). They reported that the zooplankton community was still in a state of flux. Species diversity that had been reduced during the

acidification phase had partially returned to pre-acidification levels. Rotifers had recovered less than crustaceans.

One decade after cessation of the experimental acidification of Little Rock Lake in Wisconsin, recovery of the zooplankton community was complete (Frost et al. 2006). Recovery did not follow the same trajectory as the initial acidification, however, indicating a substantial hysteresis in zooplankton community recovery. About 40% of the zooplankton species in the lake exhibited a lag of 1 to 6 years to recover to levels noted in the neutral reference basin.

Whole lake experiments and artificial stream channel experiments have shown that acidification can lead to loss of fish species. Work at Little Rock Lake in Wisconsin suggested that rock bass (*Ambloplites rupestris*) suffered recruitment failure at pH 5.6 or below. Artificial channel studies showed poor survival and reproductive success for fathead minnow at pH 5.9 to 6.0.

Nutrient Enrichment

The network rankings developed in a coarse screening assessment by Sullivan et al. (2011a) for nutrient N Pollutant Exposure, Ecosystem Sensitivity to nutrient enrichment, and Park Protection yielded a network Summary Risk ranking for the GLKN that was at the bottom of the highest quintile among networks (Sullivan et al. 2011a). The overall level of concern for nutrient N enrichment effects on I&M parks within this network was judged by Sullivan et al. (2011a) to be High to Very High. However, nutrient N Pollutant Exposure in five of the six larger parks was ranked by Sullivan et al. (2011a) only as Moderate; the sixth large park (ISRO) was ranked Low (Table 3). Nutrient N Pollutant Exposure rankings were higher in the parks that are located in the more populated and industrialized portions of the network (INDU, MISS); both of these parks were ranked Very High. The larger parks showed very diverse rankings for Ecosystem Sensitivity to nutrient enrichment. Saint Croix NSR stretches 250 miles (402 km) from the highly populated southern section to the remote upper sections. It was ranked in the highest quintile for this theme; other large parks were ranked in the middle quintile (SLBE), second lowest quintile (VOYA), or lowest quintile (APIS, ISRO) among parks. The smaller parks also showed considerable variation in the Ecosystem Sensitivity to nutrient enrichment ranking, from the second lowest (GRPO) to the second highest (INDU) quintiles. Although rankings provide an indication of risk, park-specific data, particularly regarding nutrient-enrichment sensitivity, are needed to fully evaluate risk from nutrient N addition.

Table 3. Estimated park rankings¹ according to risk of nutrient enrichment impacts on sensitive receptors (Source: Sullivan et al. 2011a)

Park Name ²	Park Code	Estimated Nutrient N Pollutant Exposure	Estimated Ecosystem Sensitivity to Nutrient Enrichment
1 Indiana Dunes	INDU	Very High	High
2 Mississippi NRA	MISS	Very High	Moderate
3 Saint Croix	SACN	Moderate	Very High
4 Sleeping Bear Dunes	SLBE	Moderate	Moderate
5 Pictured Rocks	PIRO	Moderate	Moderate
6 Apostle Islands	APIS	Moderate	Very Low
7 Voyageurs	VOYA	Moderate	Low
8 Grand Portage	GRPO	Low	Low
9 Isle Royale	ISRO	Low	Very Low

¹ Relative park rankings are designated according to quintile ranking, among all I&M Parks, from the lowest quintile (very low risk) to the highest quintile (very high risk).

² Park names are printed in bold italic for parks larger than 100 mi².

Terrestrial and Transitional Nutrient Enrichment

Terrestrial Ecosystems

Reduced species richness and biodiversity in response to N addition are of concern in the GLKN, in large part because of the potential interactions among diversity and ecosystem processes and functioning. It is more likely that a species-poor plant community may exhibit compromised ecosystem functioning as compared with a species-rich community when exposed to elevated N input.

Reich et al. (2001) investigated the influence of plant species composition and diversity on plant biomass enhancement and carbon (C) acquisition in response to nutrient addition in a grassland in Minnesota. Exposure to added carbon dioxide (CO₂), N, or both, enhanced plant biomass accumulation. The effect was greater in species-rich plant communities, as compared with species-poor communities.

Experimental studies in successional fields in Cedar Creek Natural History Area in Minnesota have shown that N is the major limiting resource in grasslands. Terrestrial plant biomass increases and community composition changes after N addition to grasslands (Tilman 1987, Tilman and Wedin 1991). Increased availability of N to grasses can also affect herbivores that feed on grasses by altering food quality, quantity, and phenology, and also perhaps by changing the relationships between herbivores and their predators (Throop and Lerdau 2004). Nitrogen fertilization at rates of 54 and 170 kg N/ha/yr (as NH₄NO₃) led to a decline in plant species composition in an oak savanna site (Avis et al. 2003). These fertilization levels are much higher than ambient N deposition in the GLKN region. In the control plots, five species collectively accounted for more than 40% of the plant cover versus four plant species in the lower N addition plots. In the higher N addition plots, a single plant species accounted for more than 40% of the plant cover.

Nitrogen additions of 120 kg N /ha/yr in Michigan old fields had a significant positive growth effect on annual dicot biomass but no significant growth effect on annual grass biomass (Huberty et al. 1998). In tallgrass prairie, C₃ grasses (*Elymus virginicus*, *E. canadensis* L.) showed a greater positive growth response to N additions than C₄ grasses (*Andropogon gerardii*, *Schizachyrium scoparium*) and forbs (*Solidago nemoralis*, *S. rigida*; Lane and BassiriRad 2002). Species with smaller initial biomass exhibited the greatest increase in biomass, with a sevenfold to eightfold increase in *S. nemoralis* and *E. canadensis* and only a threefold increase in *S. rigida* (Lane and BassiriRad 2002). In experiments where N fertilization to simulate increased N deposition was applied to common ragweed (*Ambrosia artemisiifolia*), simulated N deposition led to increased vegetative and seed biomass and decreased root:shoot ratios (Throop 2005).

In old agricultural fields in Michigan, increased N deposition changed neither the successional timing nor the gain or loss of species numbers (Huberty et al. 1998). A lack of response in species richness may have been due to mid-growing season fertilization. Huberty et al. (1998) suggested that N additions may change the dominance structure of these successional old-field communities. Other studies in Michigan also indicated that successional grasslands were not N-saturated (Ambus and Robertson 2006) and showed no response to N application of 1 g N/m²/yr, equivalent to about 2.5 times ambient deposition rates. Ambus and Robertson (2006) suggested that the small projected increases in future N deposition in this region would have little effect on these grasslands.

Experimental N addition at > 50 kg N/ha/yr to tallgrass prairie increased productivity and decreased species richness, probably as a consequence of reduced light penetration and increased litter biomass (Baer et al. 2003). Wedin and Tilman (1996) presented results of 12 years of experimental N addition to 162 grassland plots in Minnesota. The N loading dramatically changed plant species composition, decreased species diversity, and increased aboveground productivity in their plots. Species richness declined by more than 50% across the N-deposition gradient, with the greatest losses at levels of N

input of 10 to 50 kg N/ha/yr. This loss of species diversity was accompanied by large changes in plant species composition, with C₄ grasses declining and the weedy Eurasian C₃ grass quackgrass (*Agropyron repens*) becoming dominant at high N addition rates (Wedin and Tilman 1996). The authors concluded that N loading is a major threat to grassland ecosystems and causes loss of diversity, increased abundance of non-native species, and the disruption of ecosystem functioning. A major uncertainty, however, is the rate of N loading at which such changes may be manifested. Total N loading to GLKN ecosystems is lower than the loading rates used in the experimental treatments of Wedin and Tilman (1996) and the other terrestrial effects studies discussed above.

Effects of N fertilization, in turn, can influence faunal populations. For example, fertilization in a Minnesota old-field at relatively low rates (≤ 20 kg N/ha/yr) for 14 years resulted in decreased species diversity of insects in response to decreased diversity of plant food sources. Plant species richness decreased, and quackgrass and Kentucky bluegrass (*Poa pratensis*) became dominant in response to the N addition (Haddad et al. 2000). Changes in the abundance of insect functional groups were also observed. Herbivores (especially the dominant species) increased in numbers; parasitoid insect species decreased. Over the long term, changes in plant species composition would be expected to either increase or decrease insect herbivore activity, depending on whether there is a shift toward or away from herbivore-preferred plant species (Clark 2011, Throop et al. 2004).

In another study, experimental N addition for 12 years to two Minnesota old fields at levels of 10 and 20 kg N/ha/yr decreased the abundance of four grasses by almost 20%, and increase the abundance of invasive Kentucky bluegrass (*Poa pratensis*) and quackgrass (Knops and Reinhart 2000). Losses of grass species and changes in species composition generally increased over time with experimental N addition, especially at lower addition levels (Clark 2011). After 22 years of N addition at a level of 10 kg N/ha/yr, the number of species declined by 17% (Clark and Tilman 2008). Tilman (1993) hypothesized that species loss was caused mainly by increased litter mass, although light limitation from competing plants was also likely important (Hautier et al. 2009).

Much of the work on eutrophication effects of N deposition on grasslands has been conducted in Europe. Nitrophilous plant species have been shown to increase in abundance, and N-sensitive species to decline in European grasslands, over approximately the last half of the 20th century (Bobbink et al. 1998). The clearest evidence that atmospheric N deposition over a large region has actually impacted terrestrial biodiversity was provided by Stevens et al. (2004), who reported results of 68 plot surveys (4 m² quadrants) across a range of atmospheric N deposition from 5 to 35 kg N/ha/yr. Species richness was found to decline as a linear function of N deposition, with a reduction on average of one plant species for every 2.5 kg N/ha/yr of N input.

Forests can also be responsive to nutrient addition. Northern hardwood forests that predominate in the northern portions of Minnesota, Wisconsin, and Michigan are expected to show growth enhancement by some, but not all, tree species in response to N addition. Eastern hardwood forests from Wisconsin to Maine and south to Virginia were shown to have experienced increased growth with increasing N deposition across a depositional gradient from about 3 to 11 kg N/ha/yr (Thomas et al. 2010). Nevertheless, responses were species-specific. Growth increases were most pronounced for red maple (*Acer rubrum*), sugar maple, white ash (*Fraxinus americana*), yellow poplar (*Liriodendron*

tulipifera), black cherry (*Prunus serotina*), balsam fir (*Abies balsamea*), pignut hickory (*Carya glabra*), eastern white pine (*Pinus strobus*), trembling aspen (*Populus tremuloides*), northern red oak (*Quercus rubra*), and scarlet oak (*Quercus coccinea*). Other tree species showed negative response to N addition. Growth decreased to a statistically significant level with increasing deposition for red pine (*Pinus resinosa*), red spruce (*Picea rubens*), and northern white cedar (*Thuja occidentalis*). Mortality increased with increasing deposition for yellow birch (*Betula alleghaniensis*), eastern white pine, basswood (*Tilia*), trembling aspen, bigtooth aspen (*Populus grandidentata*), scarlet oak, chestnut oak (*Quercus prinus*), and northern red oak. At higher rates of N supply on nutrient-poor sites, tree growth might be expected to decline (Pardo et al. 2011b).

Eastern hardwood forests can also respond to increased N deposition with a decrease in herbaceous plant biodiversity (Gilliam et al. 2006). The response of the herbaceous layer of the forest can be pronounced, with initial increases in herbaceous plant cover, followed by decreases in species richness and species evenness, two components of biodiversity. The response time is typically shorter if ambient N deposition is relatively high (Fraterrigo et al. 2009, Gilliam et al. 2006, Gilliam et al. 2011, Royo et al. 2010). Because the plants in the herbaceous layer of eastern hardwood forests tend to have foliage with relatively high nutrient content, herbaceous plants in these forests influence N cycling to a level that is disproportionate to their biomass (Gilliam et al. 2011, Moore et al. 2007, Muller 2003, Welch et al. 2007). Lichens have also been heavily impacted throughout the eastern hardwood forests. High levels of air pollution, including both S and N, has played an important role in causing such impacts (McCune 1988, Wetmore 1988).

Pardo et al. (2011c) compiled data on empirical CL for protecting sensitive resources in Omernik Level I ecoregions across the conterminous United States against nutrient enrichment effects caused by atmospheric N deposition. Available data on empirical CL of nutrient-N suggested that the lower end of the CL range for resource protection was about 3 to 5 kg N/ha/yr at most parks in the GLKN for the protection of mycorrhizal fungi, lichens, and forests (Table 4). Ambient N deposition reported by Pardo et al. (2011c) was higher than the empirical CL at all of the parks in the GLKN that were evaluated by Pardo et al. (2011c). At some parks, empirical CL were also exceeded for protecting herbaceous plants and preventing NO₃⁻ leaching in drainage water. Thus, there appears to be widespread exceedance of these nutrient empirical CL throughout the GLKN parks. This pattern roughly reflects the north-south human population gradient.

A CL exceedance map for VOYA is shown in Map 9. Much of the park is covered by vegetation thought to be sensitive to nutrient-N enrichment. Essentially all of the identified N-sensitive plant community types in this park are in exceedance, based on Pardo et al.'s (2011b) lower limit of the empirical CL of 3 kg N/ha/yr and CAMx model projections of 4-6 kg N/ha/yr of ambient deposition. An analysis of exceedance based on Greaver et al.'s (2011) estimate of peatland CL of 2.7 kg N/ha/yr would yield similar results.

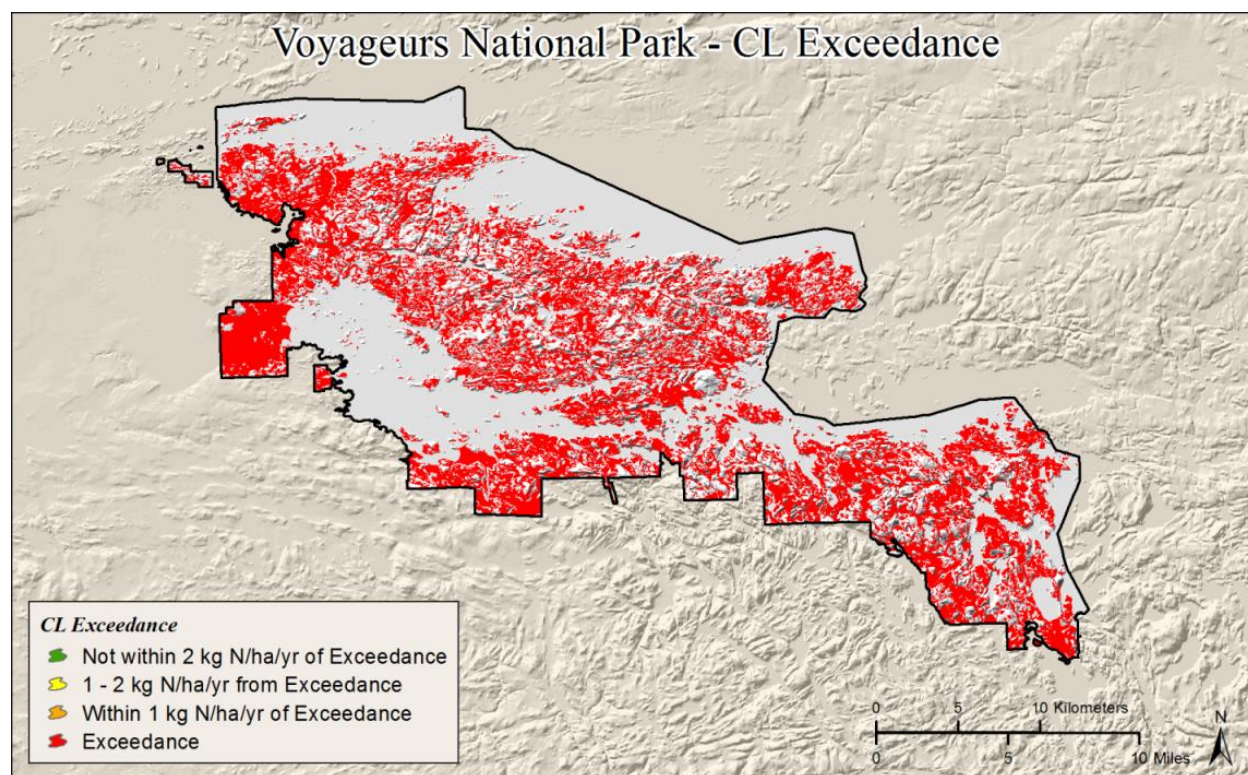
Table 4. Empirical critical loads for nitrogen in the GLKN, by ecoregion and receptor from Pardo et al. (2011c). Ambient N deposition reported by Pardo et al. (2011c) is compared to the lowest critical load for a receptor to identify potential exceedance, indicated by gray cells. A critical load exceedance suggests that the receptor is at increased risk for harmful effects.

NPS Unit	Ecoregion	N Deposition (kg N/ha/yr)	Critical Load (kg N/ha/yr)				
			Mycorrhizal Fungi	Lichen	Herbaceous Plant	Forest	Nitrate Leaching
Voyageurs NP	Northern Forests	4.7	5 - 7	4 - 6	7 - 21	3 - 26	8
Grand Portage NM	Northern Forests	5.0	5 - 7	4 - 6	7 - 21	3 - 26	8
Isle Royale NP	Northern Forests	5.0	5 - 7	4 - 6	7 - 21	3 - 26	8
Apostle Islands NL	Northern Forests	6.7	5 - 7	4 - 6	7 - 21	3 - 26	8
Pictured Rocks NL	Northern Forests	8.9	5 - 7	4 - 6	7 - 21	3 - 26	8
Sleeping Bear Dunes NL	Eastern Temperate Forests	9.3	5 - 12	4 - 8	17.5	3 - 8	8
Saint Croix NSR	Eastern Temperate Forests	14.2	5 - 12	4 - 8	17.5	3 - 8	8
Saint Croix NSR	Great Plains	14.2	12	NA	5 - 25	NA	10 - 25
Saint Croix NSR	Northern Forests	14.2	5 - 7	4 - 6	7 - 21	3 - 26	8
Indiana Dunes NL	Eastern Temperate Forests	15.9	5 - 12	4 - 8	17.5	3 - 8	8
Mississippi NRA	Eastern Temperate Forests	18.0	5 - 12	4 - 8	17.5	3 - 8	8
Mississippi NRA	Great Plains	18.0	12	NA	5 - 25	NA	10 - 25

Ellis et al. (2013) estimated the CL for nutrient-N deposition to protect the most sensitive ecosystem receptors in 45 national parks. The lowest terrestrial CL of N is generally estimated for protection of lichens (Geiser et al. 2010). Changes to lichen communities may signal the beginning of other changes to the ecosystem that might affect structure and function (Pardo et al. 2011a). Ellis et al. (2013) estimated the N CL for ISRO and VOYA in the range of 3-8 kg N/ha/yr for protection of forests.

Common vegetation types within VOYA that are considered potentially sensitive to nutrient-N enrichment effects attributed to atmospheric N deposition include forests, wetlands, and mycorrhizal fungi (Pardo et al. 2011b). Based on the analysis of Thomas et al. (2010), the CLs for protecting forest ecosystems in VOYA were assumed to be as low as 3 kg N/ha/yr for protecting forest trees, 7 kg N/ha/yr for protecting cover of herbaceous plant species (Hurd et al. 1998), and 5 kg N/ha/yr for

protecting ectomycorrhizal community structure (Lilleskov et al. 2008). The forest types that are thought to be sensitive to nutrient-N enrichment in this network, based on the work of Thomas et al. (2010) occur at scattered locations throughout much of VOYA (Sullivan and McDonnell 2014).



Map 9. Locations of vegetation types in Voyageurs National Park that exhibit CL exceedance due to nutrient-N enrichment. The area of sensitive vegetation is labeled red if total N deposition in year 2008 is in exceedance of the lower limit of the critical load (CL; 3 kg N/ha/yr) estimated by Pardo et al. (2011b) for the sensitive vegetation types found in the park. The remaining areas of sensitive vegetation are classified according to the extent to which total N deposition is below the CL. Areas showing the background color do not contain vegetation types identified by Pardo et al. (2011b) as being highly sensitive to nutrient-N enrichment. (Source: Sullivan and McDonnell 2013).

Transitional Ecosystems

Wetlands are common throughout the GLKN region. They contribute to high production of organic matter which is reflected in high DOC concentrations in many lakes. Wetlands considered sensitive to N deposition typically contain plants species that have evolved under N- limited conditions. It is believed that the balance of competition among plant species in some sensitive wetland ecosystems can be altered by N addition, with resulting displacement of some species by others that can utilize the excess N more efficiently (U.S. EPA, 1993). This effect has been well documented in heathlands in The Netherlands, where common heather (*Calluna vulgaris*) has been replaced by grass species (Heil and Bruggink 1987, Tomassen et al. 2003). It is important to note, however, that N deposition in The Netherlands has been much higher (about 20 to 60 kg N/ha/yr) than levels commonly encountered in wetland areas in the GLKN (usually, but not always, less than 10 to 15 kg N/ha/yr).

There is a great deal of diversity in terms of types of wetlands. Ombotrophic bogs are typically acidic and are dominated by mosses. They are especially common in northern boreal forested regions and develop where precipitation is higher than evapotranspiration water loss in areas that exhibit an impediment to downward drainage in the soil (Mitsch and Gosselink 2000). Freshwater marshes develop where water inputs in groundwater plus surface water inflow approximate precipitation input (Koerselman 1989). Vegetation is primarily tall graminoid plants. Freshwater swamps have hydrological conditions that are generally similar to marshes, but vegetation is forested (Greaver et al. 2011).

The response of freshwater wetlands to N addition varies with hydrological conditions. Wetlands, such as bogs, that receive much of their water input directly from precipitation are most sensitive to the effects of N input (Morris 1991). At one end of the N deposition responsiveness threshold are the ombotrophic bogs. Most of their nutrient supply comes from precipitation and as a consequence plants are adapted to low inputs of N and other nutrients (Bridgham et al. 1995, Shaver and Melillo 1984). Atmospheric N deposition generally has greater impact on the bog systems as compared with other kinds of wetlands.

Peat-forming bog ecosystems are among the most sensitive transitional ecosystems to the effects of N deposition. In the conterminous United States, peat-forming bogs are most common in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (U.S. EPA, 1993). Bogs can host several federally listed rare and endangered plant species. These include multiple species of quillworts (*Isoetes* spp.), sphagnum mosses (*Sphagnum* spp.), and the green pitcher plant (*Sarracenia oreophila*; Greaver et al. 2011).

Nutrient concentrations in wetland waters associated with the Laurentian Great Lakes suggest that algal productivity in coastal Great Lakes wetlands is N-limited. Historically, freshwater ecosystems, including the open-waters of the Great Lakes themselves, have been considered P-limited (Hutchinson 1971, Rose and Axler 1998). However, Hill et al. (2006) found that more coastal wetlands were N- than P-limited at each of the five Laurentian Great Lakes, and Morrice et al. (2004) measured a low ratio of N to P in Lake Superior coastal wetlands, also suggesting N-limitation. These results are consistent with the apparent general N-limitation of North American marsh lands (Bedford et al. 1999), and may be due to differences in nutrient cycling in wetlands as compared to open-water ecosystems (Morrice et al. 2004). Wetlands sediments tend to be O₂-poor and organic carbon oxidation by primary producers in anoxic environments can be limited by the availability of NO₃⁻ for use as an electron acceptor (Sundareshwar et al. 2003).

Nutrient loading to coastal wetlands is a concern throughout the lower Great Lakes (Lakes Erie and Ontario, and the southern part of Lake Michigan), which would include INDU, and in some localized areas of the upper lakes (Hill et al. 2006). Both agricultural and atmospheric sources of nutrients contribute to this stress. Atmospheric N deposition has been shown to increase from Lake Superior (north) to Lake Ontario (south), with N deposition in the upper lakes classified by the NADP as “moderately high”, as compared to “very high” in the lower lakes (Hill et al. 2006, NADP 2004). Agricultural inputs of nutrients to wetlands also follow this north-south trend, with the highest chemical loading to Lake Erie and the lowest to Lake Superior (Hill et al. 2006).

Hill et al. (2006) showed that total N dissolved in surface waters of Great Lakes wetlands is directly correlated with atmospheric N deposition and the degree of nearby agricultural activity. Consistent with this, they also found lower N concentrations in wetland sediments in upper lakes (Lakes Superior and Huron) as compared with lower lakes. This can result in greater increases in eutrophication, turbidity, sedimentation, and algal blooms in watersheds associated with the lower lakes.

One of the adverse impacts of eutrophication on estuarine, coastal, and Great Lakes ecosystems is a decrease in the extent of submerged aquatic vegetation. Investigators in some parks are delineating the extent of submerged aquatic vegetation in coastal and Great Lakes waters to provide data needed for more effective resource management. USGS and NOAA have partnered with NPS to map submerged resources in nine coastal and Great Lakes parks (Cross and Curdts 2011).

Increased N availability in nutrient-poor wetland environments may lead to a decrease in plant species diversity and increased risk of extinction for some of the more sensitive and rare species (Moore et al. 1989). Peatlands and bogs are among the most vulnerable transitional ecosystems to adverse nutrient-enrichment effects of N deposition (Krupa 2003). The sensitivity of peatland *Sphagnum* species to elevated atmospheric N deposition is well documented in Europe (Berendse et al. 2001, Tomassen et al. 2004). *Sphagnum squarrosum* and *S. fallax* have been observed to be negatively affected by experimentally elevated atmospheric N and S inputs in Europe (Kooijman and Bakker 1994). Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson 1994).

In other studies, wetland species such as *Calluna vulgaris* can successfully compete with grasses even at relatively high rates of N deposition, as long as the vegetative canopies are closed (Aerts et al. 1990). However, N deposition causes nutrient imbalances, including increase in the shoot-to-root ratio, and therefore increases in the sensitivity of shrubs to drought stress, frost stress, and attack by insect pests (Heil and Diemont 1983). These can result in gaps in the canopy of the shrub layer, which can then be readily invaded by grasses that are more efficient in using the additional N and therefore gain a competitive advantage (Krupa 2003).

The extent to which wetlands in the GLKN have been affected by nutrient enrichment from N deposition is not clear. Wetlands are widely distributed, including within parks that receive moderate levels of N deposition. The moderate levels of N deposition commonly found in areas that contain appreciable areas of wetland may or may not be sufficiently high to cause shifts in wetland plant species. If such effects do occur, they are most likely in wetlands such as bogs and poor fens that normally receive most of their nutrients from atmospheric inputs. Such ecosystems in the GLKN tend to occur in areas that receive much lower levels of N deposition than do the affected wetlands in Europe. It is not clear to what extent such effects occur under ambient N deposition levels. The risk of species composition change is important, in part because wetland ecosystems often contain relatively large numbers of rare plant species.

Greaver et al. (2011) estimated that the CL of atmospheric N deposition to protect peatlands from increased productivity was in the range of 2.7 to 13 kg N/ha/yr. This estimate was based on

consideration of the results of the studies of Aldous et al. (2002), Moore et al. (2004), Rochefort et al. (1990), and Vitt et al. (2003).

Aquatic Nutrient Enrichment

Some studies on nutrient limitation have been conducted on the Great Lakes. Baron et al. (2011) estimated that 37% of 8,755 lakes in this region represented in the ELS were likely N-limited, based on having dissolved inorganic N (DIN):total P (TP) ratio less than 4. It is generally believed that the Laurentian Great Lakes are P-limited (Downing and McCauley 1992, Rose and Axler 1998, Schelske 1991). Water quality in the open waters of these lakes has been improving in recent years in response to controls on point sources of P (Nicholls et al. 2001). Work by Levine et al. (1997), however, suggested a more complicated pattern of response to nutrient addition for Lake Champlain. They added nutrients to *in situ* enclosures and measured indicators of P status, including alkaline phosphatase activity and orthophosphate turnover time. Although P appeared to be the principal limiting nutrient during summer, N addition also resulted in algal growth stimulation. Phosphorus (P) sufficiency appeared to be as common as P deficiency. During spring, phytoplankton growth was not limited by P, N, or silica (Si), but perhaps by light or temperature (Levine et al. 1997).

In Lake Erie, N input was found to be limiting to phytoplankton on a seasonal basis (Moon and Carrick 2007, North et al. 2007). Lake NO_3^- concentrations in Lake Superior increased over the 20th century, causing strong P-limitation (Finlay et al. 2007, Sterner et al. 2007).

Silica depletion due to nutrient enrichment has been reported for the Great Lakes (Conley et al. 1993). Increased growth of silicate-utilizing diatoms as a result of NO_3^- - and phosphate (PO_4^-)-induced eutrophication, and subsequent removal of fixed biogenic Si via sedimentation, has the potential to change the ratios of nutrient elements Si, N, and P. In turn, such changes might cause shifts from diatoms to non-siliceous phytoplankton (Ittekkot 2003).

A diatom biomonitoring program is conducted by the GGLN as a complement to water quality monitoring efforts. In 2011 and 2012, it included monitoring of 21 lakes, lagoons, and flowages in APIS, INDU, SACN, MISS, and ISRO (Edlund et al. 2013). Recent data collected in this monitoring effort suggest that many GGLN lakes are undergoing biological change. Continued monitoring will be needed to determine the cause(s) and effects.

Recent changes in water chemistry in the Great Lakes could also result from the 1989 and 1991 introduction of two exotic dreissenid mussel species, whose filtration capacity can drastically deplete phytoplankton nutrient levels and lake production (Mills et al. 1993). Mills et al. (2006) found declines in open-water P concentrations from 1995 to 2005 in Lake Ontario that are thought to be detrimental to healthy levels of ecosystem productivity. This result is consistent with observed increases in water transparency (Barbiero et al. 2006) and declining phytoplankton biomass (Munawar et al. 2006) in the lake. Specifically, diatom abundances in Lake Ontario have decreased since the invasion of dreissenid mussels, leading to a corresponding increase in Si concentrations in lake water in response to reduced Si uptake by diatoms (Millard et al. 2003).

Dove (2009) found that the proportion of total filtered P has been increasing since 1992, particularly in nearshore waters where mussels are most abundant. Excretion by invasive mussels may also explain the elevated proportion of soluble reactive P (SRP), a measure of biologically available P, observed in nearshore waters as compared with low SRP levels in open waters (Dove 2009). Thus, the increasing incidence of nuisance algal blooms along Lake Ontario's shore may be, at least in part, a result of mussel activity rather than further nutrient addition (Dove 2009).

Nitrate appears to be accumulating in Lake Ontario (Dove 2009) and in Lake Superior (Finlay et al. 2007). This is mostly likely due to nitrification of N derived from external sources such as agriculture, human waste, and atmospheric deposition (Bennett 1986, Finlay et al. 2007). As a result, N:P ratios in these lakes are relatively high; this relative N abundance and P depletion may help protect lake waters against cyanobacteria blooms, which tend to dominate at low N:P (Dove 2009, Smith 1983).

The EPA Great Lakes National Program has set trophic state goals for each of the Laurentian Great Lakes. Most recent data show that the upper lakes (Lakes Superior, Huron, and Michigan) are currently meeting their oligotrophy goals. Surface water quality in these lakes is considered "excellent", and water quality in Lakes Huron and Michigan shows improvement since monitoring began in the 1980s (EPA; <http://www.epa.gov/glindicators/water/trophicb.html>). Lake Ontario is also currently meeting its trophic state goal of oligomesotrophy. However, Lake Erie shows signs of concern. Historically, it was the first lake to show evidence of nuisance algal blooms and O₂-depletion problems associated with eutrophication. Lake Erie is also most affected by proximate agriculture and urban areas. Surface waters in Lake Erie's eastern, central, and western basins are currently meeting their EPA trophic state goals of oligotrophy, oligomesotrophy, and mesotrophy, respectively. However, the central basin has experienced elevated P concentrations since the 1990s and shows a corresponding summer O₂-depletion in its deeper waters, jeopardizing the health of fish and other aquatic biota (EPA; <http://www.epa.gov/glindicators/water/trophicb.html>).

Ozone Injury to Vegetation

The O₃-sensitive plant species that are known or thought to occur within the GLKN parks are listed in Table 5. Those considered to be bioindicators, because they exhibit distinctive symptoms when injured by O₃ (e.g., dark stipple), are designated in the table by an asterisk. Each park within the network supports a number of O₃ sensitive and bioindicator plant species.

The W126 and SUM06 exposure indices calculated by NPS staff are given in Table 6, along with Kohut's (2007a) O₃ risk ranking. The NPS and Kohut ranking systems differ. The NPS ranking system (NPS 2010) is a quick assessment of O₃ condition that ranks O₃ exposure levels according to injury thresholds from the literature (Heck and Cowling 1997), using a 5-year average of either the W126 or SUM06 index. The former is a measure of cumulative O₃ exposure that preferentially weights higher concentrations; the latter is a measure of cumulative O₃ exposure that includes only hourly concentrations over 60 ppb. Both metrics are calculated over a 3-month period. The W126 was classified as Moderate exposure at values between 7 and 13 ppm-hr, as defined by NPS (2010). Values higher than 13 ppm-hr were classified as High exposure, and values lower than 7 ppm-hr were classified as Low exposure. The SUM06 was classified as Moderate at values between 8 and 15 ppm-hr. Higher and lower values were classified as High and Low, respectively, as defined by NPS (2010).

Kohut's approach constitutes a rigorous assessment of potential risk to plants. It considers both O₃ exposure and environmental conditions (soil moisture). Kohut also used injury thresholds from the literature, but evaluated a different O₃ metric (after Lefohn et al. 1997), the W126 over a 5-month period in conjunction with the N100 (number of hours over 100 ppb O₃). The rationale for the N100 statistic is that higher O₃ concentrations are most likely to cause plant injury. Kohut examined five individual years of O₃ exposure and soil moisture data and considered the effects of low soil moisture on O₃ uptake each year when assigning risk. Soil moisture is important because dry conditions induce stomatal closure in plants, which has the effect of limiting O₃ uptake and injury. In areas where low soil moisture levels correspond with high O₃ exposure, uptake and injury are limited by stomatal closure even when exposures are relatively high. Ozone condition, as rated by NPS, ranged from Low to Moderate in the GLKN parks. Kohut's evaluation of risk to plants ranged from Low to High, with highest risk in INDU and SLBE.

The results of both ranking systems should be considered when evaluating the potential for O₃ injury to park vegetation. The Kohut approach considered environmental conditions that significantly affect plant response to O₃, but exposures have likely changed since the time of the assessment (1995-1999). The NPS approach considers more recent O₃ conditions (2005-2009), but not environmental conditions.

Kohut (2007b) assessed O₃ exposure to plants in the nine parks within the GLKN, based on O₃ monitoring in two parks (INDU and VOYA) and values from surrounding monitoring stations for the other seven parks. Most of the parks supported numerous plant species that are sensitive to foliar injury from O₃ exposure. None of the parks showed a clear association between O₃ exposure and soil

moisture conditions. Soil moisture varies throughout the growing season, and locally from one area to another within a park. During periods of water stress, the likelihood of injury may be reduced.

Under mild water stress, however, the soil moisture level may not be low enough as to significantly constrain the uptake of O₃ into foliage and consequent injury to vegetation (Kohut 2007b). In seven of the parks, the criteria for injury under the SUM06 and W126 indices were generally not satisfied. Similarly, Swackhamer and Hornbuckle (2004) reported that there was no evidence of plant damage from O₃ exposure in ISRO or VOYA. However, Davis (2007) reported O₃ injury on spreading dogbane (*Apocynum androsaemifolium*), common milkweed (*Asclepias syriaca*), and black cherry (*Prunus serotina*) at Seney National Wildlife Refuge in the Upper Peninsula of Michigan during annual surveys conducted between 1999 and 2004. In two parks (INDU and SLBE), both indices exceeded the O₃ levels considered necessary for foliar injury. These levels of O₃ exposure can potentially injure vegetation in these two parks. The overall risk of foliar O₃ injury in the parks in this network is highly variable, and was judged by Kohut (2007a) to be Low in six parks, Moderate in PIRO, and High in INDU and SLBE.

Percy et al. (2007) developed dose-response regression relationships to predict growth decreases in trembling aspen in the Great Lakes region based on measured O₃, expressed as the fourth-highest daily maximum 8-hour average O₃ concentration, growing degree days, and wind speed. The models had high statistical significance. They estimated appreciable (> 25%) growth reductions in aspen trees throughout substantial portions of the Great Lakes region due to relatively high ambient O₃ exposure.

Table 5. Ozone sensitive and bioindicator plant species known or thought to occur in the I&M parks of the GLKN. (Data Source: E. Porter, National Park Service, pers. comm., August 30, 2012); lists are periodically updated at <https://irma.nps.gov/NPSpecies/Report>).

Species	Common Name	Park ¹												
		APIS	GRP	O	INDU	ISRO	MISS	PIRO	SAC	N	SLB	E	VOY	A
<i>Ageratina altissima</i> *	White snakeroot							X				X		
<i>Ailanthus altissima</i> * (non-native)	Tree-of-heaven				X							X		
<i>Alnus incana</i> spp. <i>rugosa</i> *	Speckled alder					X		X	X	X				
<i>Amelanchier alnifolia</i>	Saskatoon serviceberry													X
<i>Apios americana</i> *	Groundnut				X		X			X	X			
<i>Apocynum androsaemifolium</i> *	Spreading dogbane	X	X	X	X	X	X	X	X	X	X	X	X	
<i>Apocynum cannabinum</i>	Dogbane, Indian hemp	X	X	X			X			X	X	X		X
<i>Artemisia ludoviciana</i> *	Silver wormwood						X			X	X	X		X
<i>Asclepias exaltata</i> *	Tall milkweed				X		X			X	X			
<i>Asclepias incarnata</i>	Swamp milkweed	X			X	X	X	X	X	X	X	X	X	
<i>Asclepias syriaca</i> *	Common milkweed	X			X	X	X	X	X	X	X	X		X
<i>Cercis canadensis</i> *	Redbud				X									
<i>Clematis virginiana</i>	Virgin's bower	X	X	X	X	X	X	X	X	X	X			
<i>Corylus americana</i> *	American hazelnut	X			X		X			X				X
<i>Eurybia macrophylla</i> *	Big-leaf aster	X	X			X		X	X	X	X	X		X
<i>Fraxinus americana</i> *	White ash				X		X	X	X	X	X			
<i>Fraxinus pennsylvanica</i>	Green ash	X			X	X	X	X	X	X	X	X		X
<i>Gaylussacia baccata</i> *	Black huckleberry	X			X		X	X	X	X	X			
<i>Liriodendron tulipifera</i> *	Yellow-poplar				X									
<i>Parthenocissus quinquefolia</i>	Virginia creeper	X			X		X	X	X	X	X	X		X
<i>Philadelphus coronarius</i>	Sweet mock orange				X					X				
<i>Pinus banksiana</i>	Jack pine	X	X	X	X	X	X	X	X	X	X	X		X
<i>Platanus occidentalis</i> *	American sycamore				X									
<i>Populus tremuloides</i> *	Trembling aspen	X	X	X	X	X	X	X	X	X	X	X		X
<i>Prunus serotina</i> *	Black cherry				X		X	X	X	X	X	X		X
<i>Prunus virginiana</i>	Chokecherry	X	X	X	X	X	X	X	X	X	X	X		X
<i>Robinia pseudoacacia</i> (non-native)	Black locust	X			X		X			X	X			
<i>Rubus allegheniensis</i> *	Allegheny blackberry	X			X	X	X	X	X	X	X	X		X
<i>Rubus canadensis</i> *	Thornless blackberry	X				X		X	X	X	X	X		X
<i>Rubus parviflorus</i>	Thimbleberry	X	X			X		X	X	X	X	X		X
<i>Rudbeckia laciniata</i> *	Cutleaf coneflower	X			X		X	X	X	X	X	X		X
<i>Sambucus nigra</i> spp. <i>canadensis</i> *	Black elderberry											X		
<i>Sambucus racemosa</i> var. <i>racemosa</i> *	Red elderberry					X	X					X		
<i>Sassafras albidum</i>	Sassafras				X							X		
<i>Solidago altissima</i>	Goldenrod									X				
<i>Solidago canadensis</i>	Goldenrod					X								
<i>Solidago gigantea</i>	Goldenrod							X				X		
<i>Symphoricarpos albus</i> *	Common snowberry			X		X	X			X	X	X		X
<i>Vaccinium membranaceum</i> *	Huckleberry							X						
<i>Vitis labrusca</i> *	Northern fox grape				X									

¹ Park acronyms are printed in bold italic for parks larger than 100 mi².

* Bioindicator species

Table 6. Ozone assessment results for I&M parks in the GLKN based on estimated average 3-month W126 and SUM06 ozone exposure indices for the period 2005-2009 and Kohut's (2007a) ozone risk ranking for the period 1995-1999¹.

Park Name ¹	Park Code	W126		SUM06		Kohut O ₃ Risk Ranking
		Value (ppm-hr)	Ranking	Value (ppm-hr)	Ranking	
<i>Apostle Islands</i>	APIS	4.01	Low	3.61	Low	Low
Grand Portage	GRPO	4.51	Low	4.22	Low	Low
Indiana Dunes	INDU	9.01	Moderate	11.31	Moderate	High
<i>Isle Royale</i>	ISRO	4.95	Low	4.97	Low	Low
Mississippi NRA	MISS	6.33	Low	6.99	Low	Low
<i>Pictured Rocks</i>	PIRO	6.61	Low	7.82	Low	Moderate
<i>Saint Croix</i>	SACN	5.23	Low	5.54	Low	Low
<i>Sleeping Bear Dunes</i>	SLBE	8.47	Moderate	10.60	Moderate	High
<i>Voyageurs</i>	VOYA	4.38	Low	3.78	Low	Low

¹ Parks are classified into one of three ranks (Low, Moderate, High), based on comparison with other I&M parks.

² Park names are printed in bold italic for parks larger than 100 mi².

Visibility Degradation

Natural Background and Ambient Visibility Conditions

The Clean Air Act (CAA) set a specific goal for visibility protection in Class I areas: “the prevention of any future, and the remedying of any existing, impairment of visibility¹ in mandatory Class I federal areas which impairment results from manmade air pollution” (42 U.S.C. 7491). In 1999, EPA passed the Regional Haze Rule (RHR), which requires each state to develop a plan to improve visibility in Class I areas, with the goal of returning visibility to natural conditions in 2064. Natural background visibility, the goal of the Clean Air Act, assumes no human-caused pollution, but varies with natural processes such as windblown dust, fire, volcanic activity and biogenic emissions.

Visibility is monitored by the Interagency Monitoring of Protected Visual Environments (IMPROVE) Network and is typically reported using the haze index deciview² (dv).

Current visibility estimates reflect current pollution levels and were used to rank conditions at parks in order to provide park managers with information on spatial differences in visibility and air pollution. Rankings range from very low haze (very good visibility) to very high haze (very poor visibility). Only parks with on-site or representative data from IMPROVE monitors were used in generating the baseline visibility ranking. Table 7 gives the relative park haze rankings on the 20% clearest, 20% haziest, and average days.

Natural background and ambient visibility conditions have been estimated by IMPROVE for the 20% clearest visibility days, the 20% haziest visibility days, and the average days at two I&M park within the GLKN: ISRO and VOYA. Data are also available that are considered to be representative of visibility conditions in one Class II area (PIRO), based on measured values taken from a representative IMPROVE site (SENE1). A monitor is considered representative by EPA if it is located within 60 mi (100 km) and 425 ft (130 m) elevation of a park.

Natural background visibility, the goal of the CAA and RHR, assumes no human-caused pollution. At all three of the assessed parks, natural haze is relatively high in comparison with other I&M parks for the 20% clearest natural haze conditions and for the average of all natural haze conditions (Table 7). Natural haze levels are particularly high at these parks on the 20% haziest days. This may be partly due to the influence of fire. The measured haze for the period 2004 through 2008 was considerably higher than the estimated natural condition largely due to organic mass. Current haze in ISRO was classified as Moderate for the 20% clearest and average days and High for the 20% haziest days. Current haze in VOYA was ranked as Moderate for all groups. PIRO was ranked Moderate for the 20% clearest days and High for the 20% haziest and average days.

¹ Visibility impairment means any humanly perceptible change in visibility (light extinction, visual range, contrast, coloration) from that which would have existed under natural conditions.

² The *deciview* visibility metric expresses uniform changes in haziness in terms of common increments across the entire range of visibility conditions, from pristine to extremely hazy conditions. Because each unit change in deciview represents a common change in perception, the deciview scale is like the decibel scale for sound. A one deciview change in haziness is a small but noticeable change in haziness under most circumstances when viewing scenes in Class I areas.

IMPROVE data allow estimation of visual range (VR). Data indicate that air pollution at ISRO has reduced average VR from 110 miles to 60 miles (177 to 97 km). On the haziest days, VR has been reduced from 65 to 30 miles (105 to 48 km). Severe haze episodes occasionally reduce visibility to 7 miles (11 km). At VOYA, pollution has reduced average VR from 110 miles to 60 miles (177 to 97 km). On the haziest days, VR has been reduced from 70 to 35 miles (113 to 56 km). Severe haze episodes occasionally reduce visibility to 11 miles (18 km). At the Seney National Wildlife Refuge, MI, IMPROVE site (SENE1), representative of PIRO, pollution has reduced average VR from 110 to 45 miles (177 to 72 km). On the haziest days, VR has been reduced from 65 to 20 miles (105 to 32 km). Severe haze episodes occasionally reduce visibility to 8 miles (13 km).

Table 7. Estimated natural haze and measured ambient haze in I&M parks averaged over the period 2004 through 2008¹.

			Estimated Natural Haze					
Park Name ²	Park Code	Site ID	20% Clearest Days		20% Haziest Days		Average Days	
			dv		dv		dv	
<i>Apostle Islands</i>	APIS	No Site						
Grand Portage	GRPO	No Site						
Indiana Dunes	INDU	No Site						
<i>Isle Royale</i>	ISRO	ISLE1	3.72		12.37		7.33	
Mississippi NRA	MISS	No Site						
<i>Pictured Rocks</i> ³	PIRO	SENE1	3.74		12.65		7.38	
<i>Saint Croix</i>	SACN	No Site						
<i>Sleeping Bear Dunes</i>	SLBE	No Site						
<i>Voyageurs</i>	VOYA	VOYA2	4.26		12.06		7.58	
			Measured Ambient Haze (For Years 2004 through 2008)					
Park Name	Park Code	Site ID	20% Clearest Days		20% Haziest Days		Average Days	
			dv	Ranking	dv	Ranking	dv	Ranking
<i>Apostle Islands</i>	APIS	No Site						
Grand Portage	GRPO	No Site						
Indiana Dunes	INDU	No Site						
<i>Isle Royale</i>	ISRO	ISLE1	6.31	Moderate	21.55	High	12.54	Moderate
Mississippi NRA	MISS	No Site						
<i>Pictured Rocks</i>	PIRO	SENE1	6.71	Moderate	24.58	High	14.11	High
<i>Saint Croix</i>	SACN	No Site						
<i>Sleeping Bear Dunes</i>	SLBE	No Site						
<i>Voyageurs</i>	VOYA	VOYA2	6.54	Moderate	19.43	Moderate	11.96	Moderate

¹ Parks are classified into one of five ranks (Very Low, Low, Moderate, High, Very High).

² Park names are printed in bold italic for parks larger than 100 mi².

³ Data are borrowed from a representative site for PIRO at Seney National Wildlife Refuge (SENE1).. A monitoring site is considered by IMPROVE to be representative of an area if it is within 60 mi (100 km) and 425 ft (130 m) in elevation of that area.

Composition of Haze

Various pollutants make up the haze that causes visibility degradation. IMPROVE measures these pollutants and reports them as ammonium sulfate, ammonium nitrate, elemental carbon, coarse mass, organic mass, sea salt, and soil. Sulfates form in the atmosphere from SO_2 emissions from coal-burning power plants, smelters, and other industrial facilities. Nitrates form in the atmosphere from NO_x emissions from combustion sources including vehicles, power plants, industry, and fires. Organic compounds are emitted from a variety of both natural (biogenic) and anthropogenic sources, including agriculture, industry, and fires. Soil can enter the atmosphere through both natural processes and human disturbance.

The majority of the total particulate light extinction (b_{ext}) in all three of the parks monitored in the GLKN is attributable to SO_4^{2-} (Figure 2a-c). On average, about half of particulate b_{ext} was attributable to SO_4^{2-} , and NO_3^- contributed about 20%. On the 20% clearest visibility days, SO_4^{2-} accounted for more than 50% of extinction, followed by organics, coarse mass, and NO_3^- . On the 20% haziest days, SO_4^{2-} again was the dominant source of b_{ext} in all three parks, followed by NO_3^- and organics (Figure 2-c). The largest difference between clear days and hazy days in all parks is that coarse mass contributes more extinction on clear days, and NO_3^- contributes more on hazy days.

Trends in Visibility

There are no clear trends across the full period of available monitoring data in the haze measurements in any of the monitored parks in the GLKN. However, measurements since about 2005 do suggest more recent improvement (Figure 3), especially in ISRO and PIRO.

Development of State Implementation Plans

According to the RHR, states and tribes must establish and meet reasonable progress goals for each federal Class I area to improve visibility on the 20% haziest days and to prevent visibility degradation on the 20% clearest days. The national goal is to return visibility in Class I areas to natural background levels in 2064. States must evaluate progress by 2018 (and every 10 years thereafter) based on a baseline period of 2000 to 2004 (Air Resource Specialists 2007). The measurements made during the most recent years of monitoring at each park suggest progress towards compliance with the RHR (Figure 4). Visibility improvement in the GLKN may be on track to attain natural visibility conditions (~ 12 dv) by 2064. This will require a reduction of approximately 50% in haze on the 20% haziest days (Figure 4).

Toxic Airborne Contaminants

In large part because of the common occurrence of wetlands, Hg methylation and bioaccumulation are important concerns for parks in the GLKN. Estimates of Hg methylation potential generated by USGS (Last modified February 20, 2015) for watershed boundaries (based on eight-digit hydrologic unit codes [HUCs]) containing national park lands in the GLKN suggested high methylation potential at most parks considered in this analysis (Map 10). This result is likely driven mainly by relatively high concentrations of total organic carbon in surface waters.

ISRO

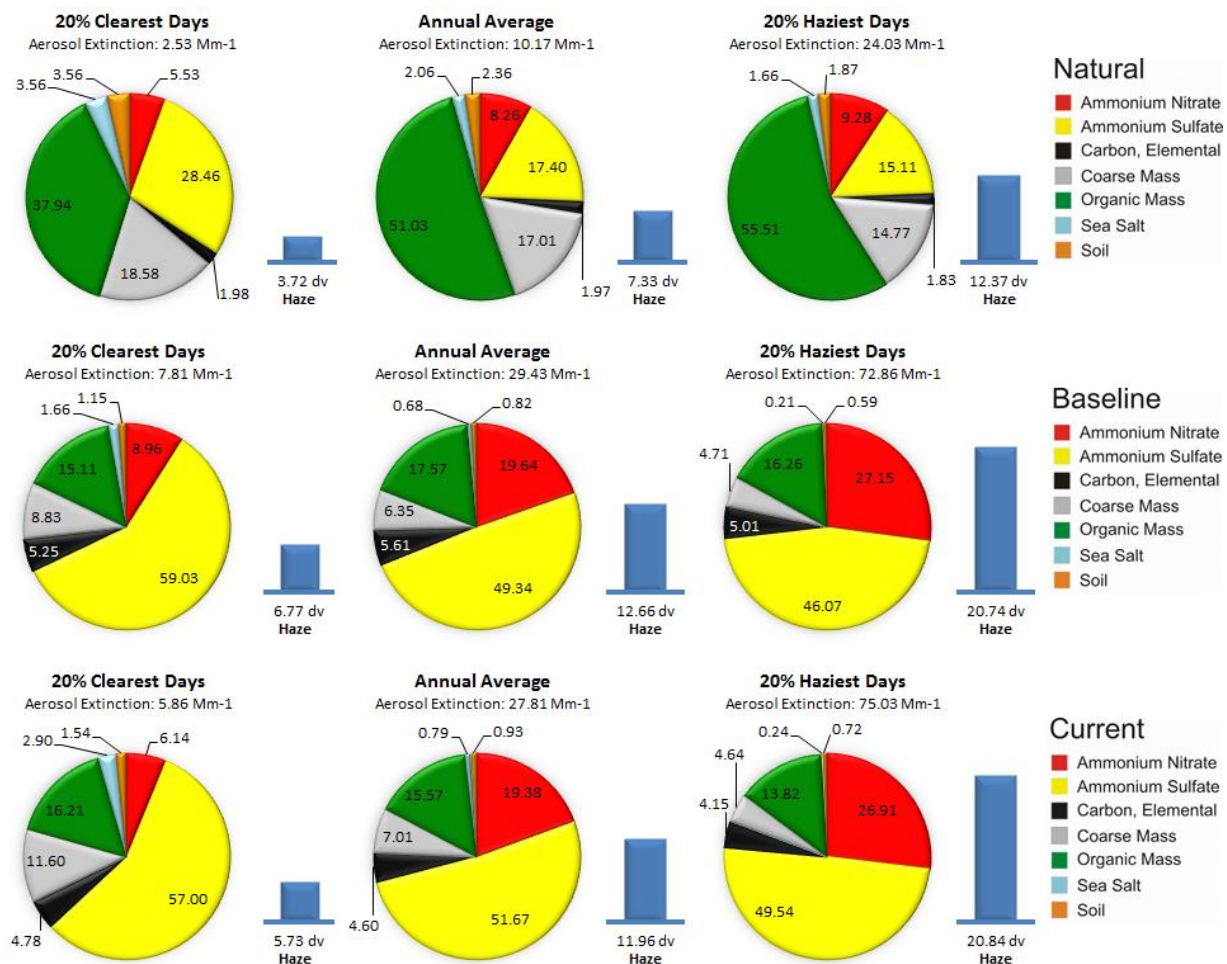


Figure 2a. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for ISRO. Data Source: NPS-ARD

Seney National Wildlife Refuge (for PIRO)

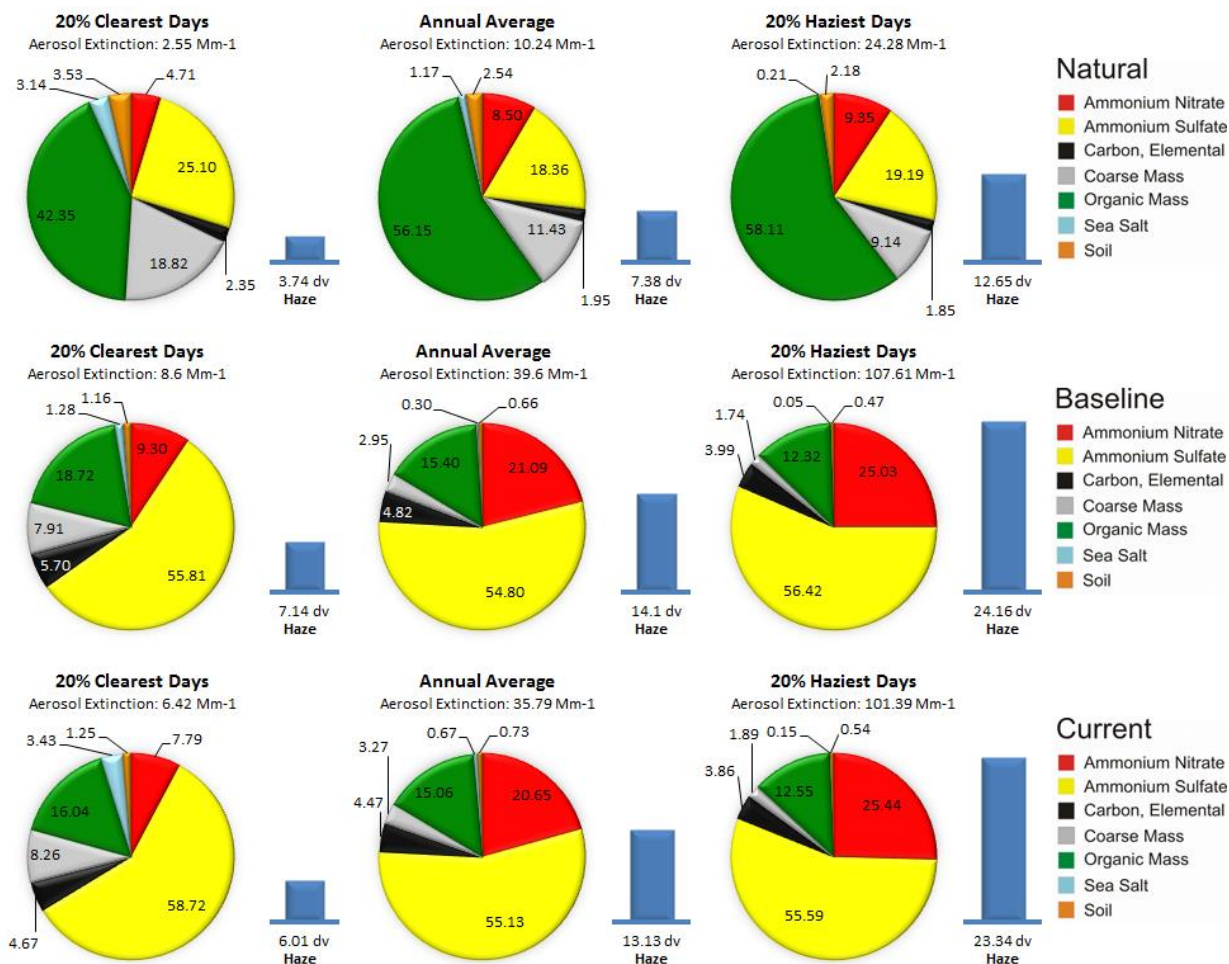


Figure 2b. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for PIRO. Data for PIRO were taken from a representative site at Seney National Wildlife Refuge (SENE1). Data Source: NPS-ARD

VOYA

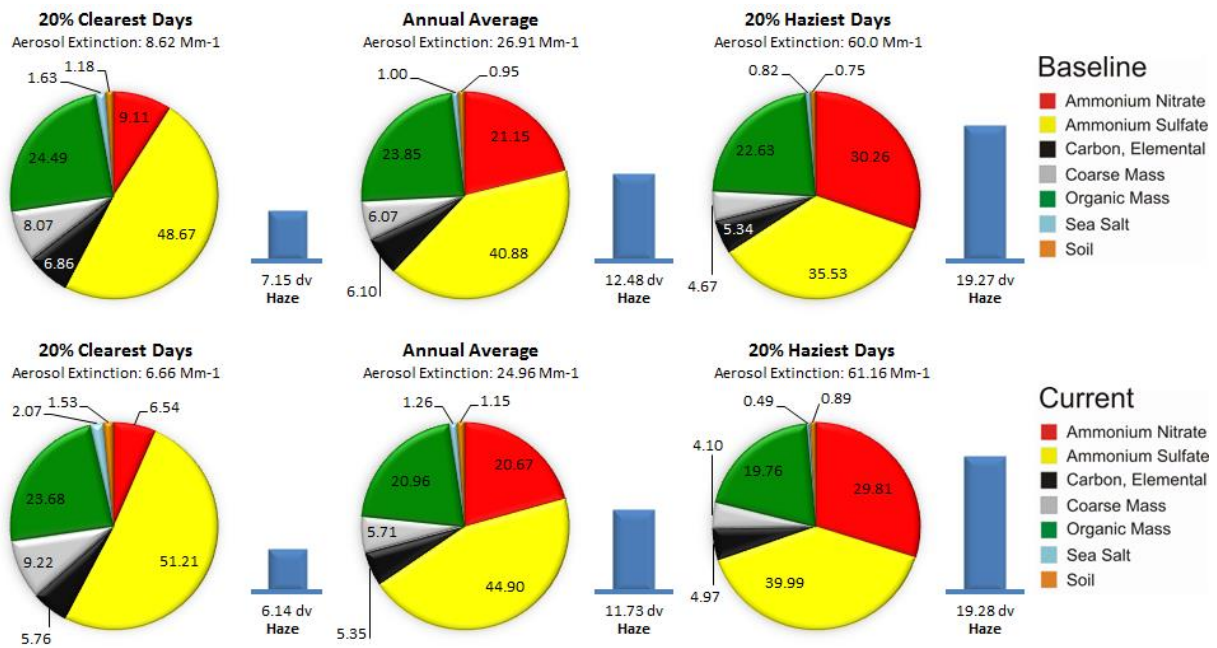


Figure 2c. Estimated natural (pre-industrial), baseline (2000-2004), and current (2006-2010) levels of haze (blue columns) and its composition (pie charts) on the 20% clearest, annual average, and 20% haziest visibility days for VOYA. Note that there were no data available for natural conditions at VOYA. Data Source: NPS-ARD

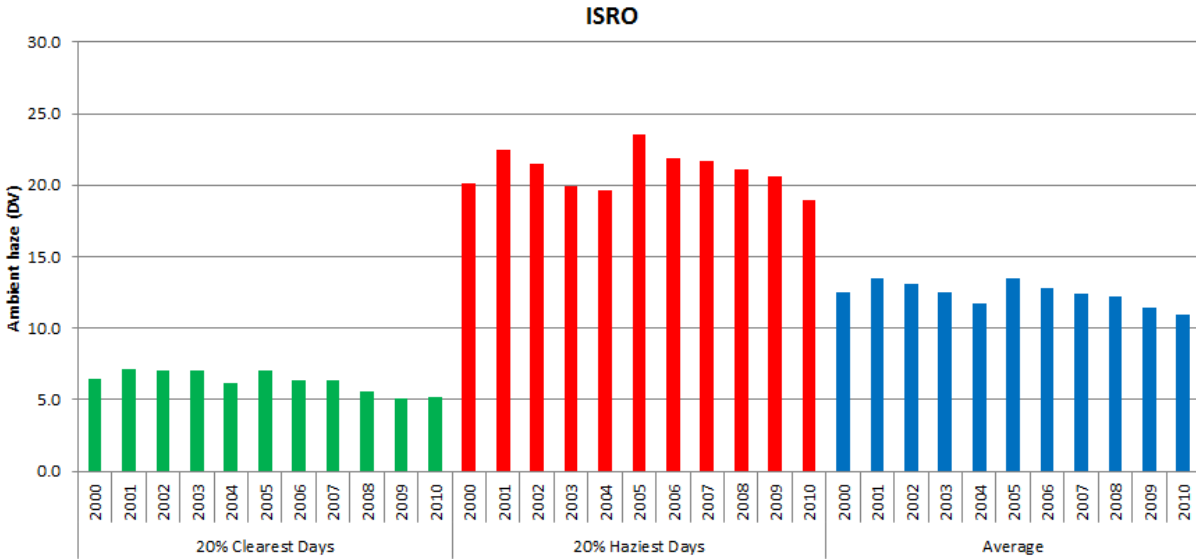


Figure 3a. Trends in ambient haze levels at ISRO based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

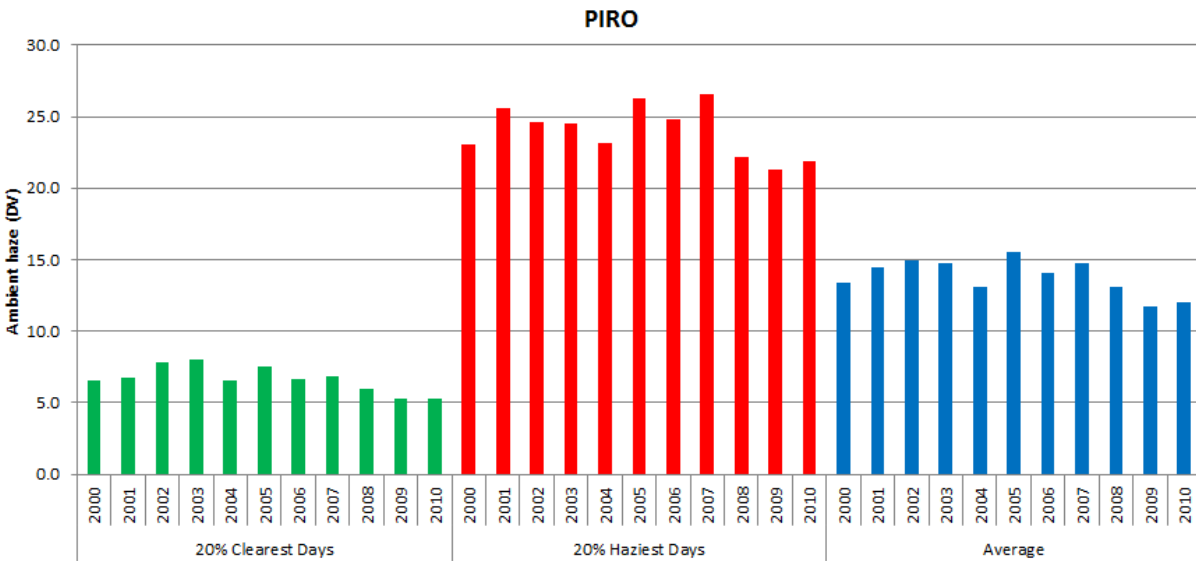


Figure 3b. Trends in ambient haze levels at PIRO based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Data for PIRO were taken from a nearby site (SENE1) Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

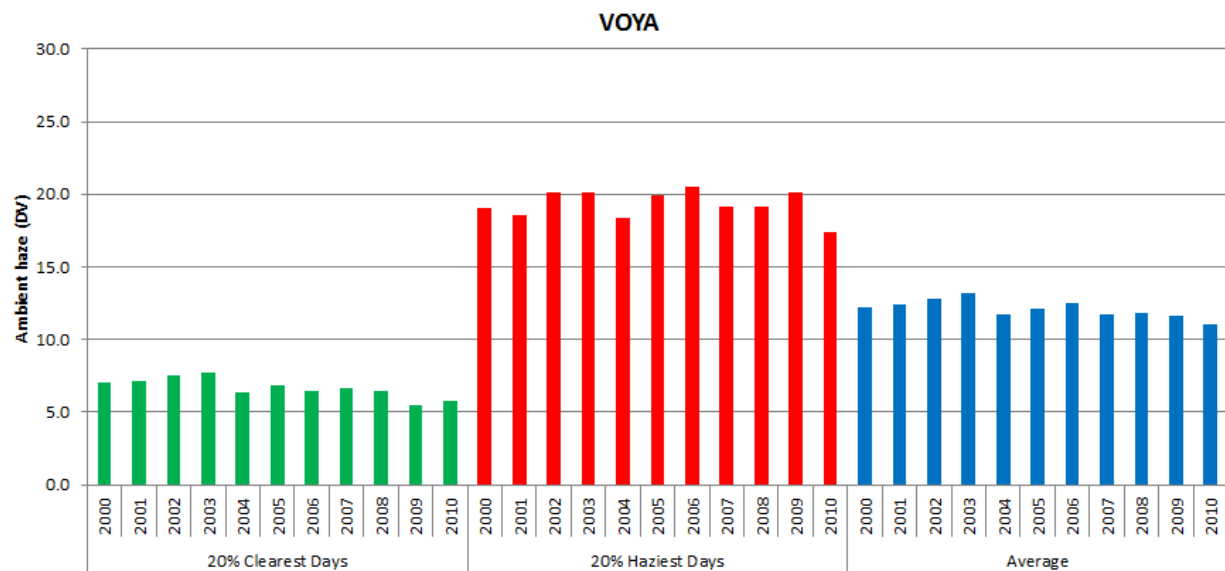


Figure 3c. Trends in ambient haze levels at VOYA, based on IMPROVE measurements on the 20% clearest, 20% haziest, and annual average visibility days over the monitoring period of record. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

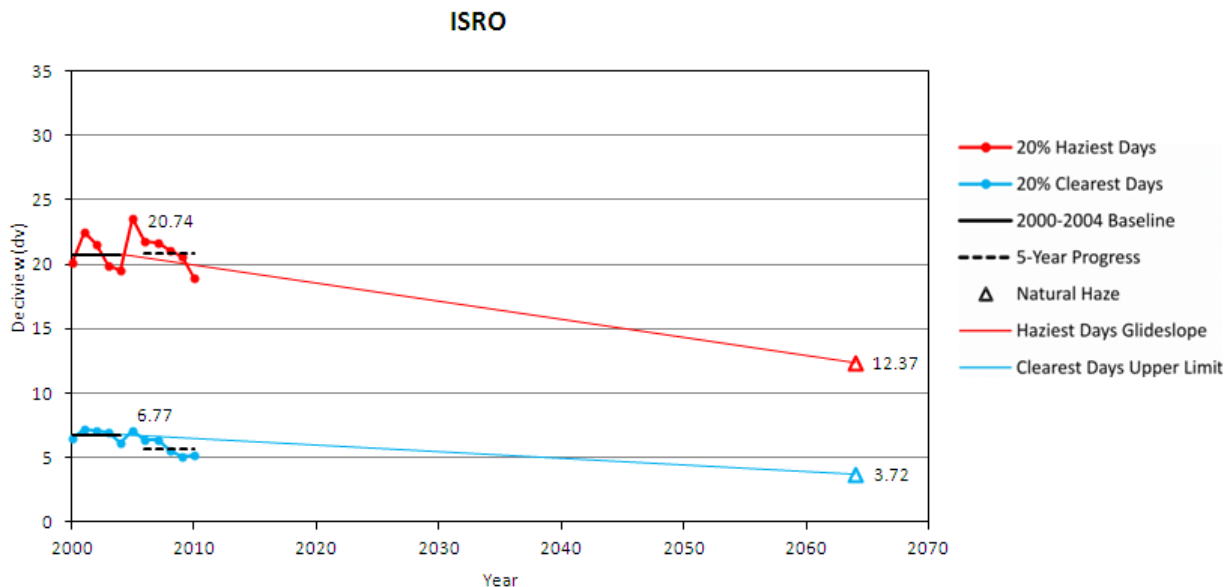


Figure 4a. Glideslopes to achieving natural visibility conditions in 2064 for the 20% haziest (red line) and the 20% clearest (blue line) days in ISRO. In the regional haze rule, the clearest days do not have a uniform rate of progress glideslope; the rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

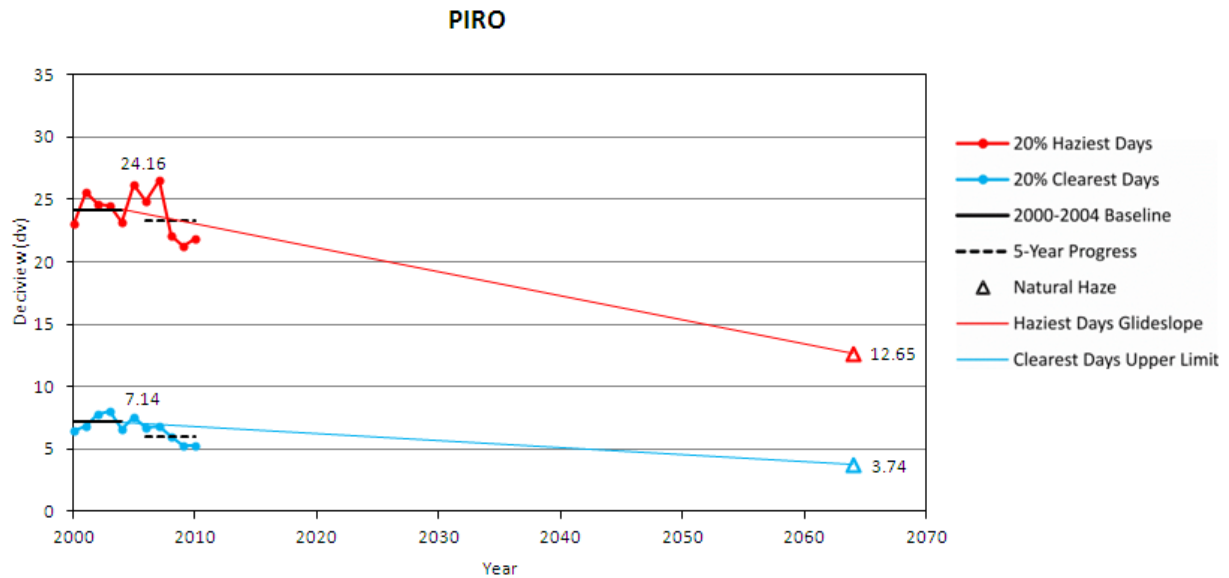


Figure 4b. Glideslopes to achieving natural visibility conditions in 2064 for the 20% hazeiest (red line) and the 20% clearest (blue line) days in Seney National Wildlife Refuge (representative of PIRO). In the regional haze rule, the clearest days do not have a uniform rate of progress glideslope; the rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Data for PIRO were taken from a nearby site (SENE1). Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm

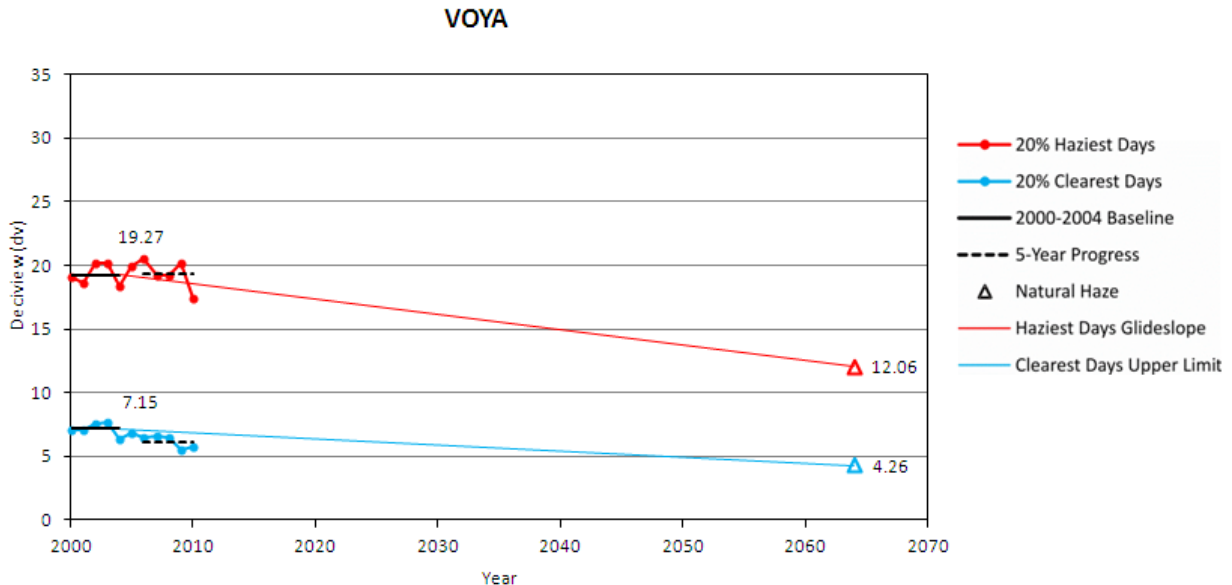
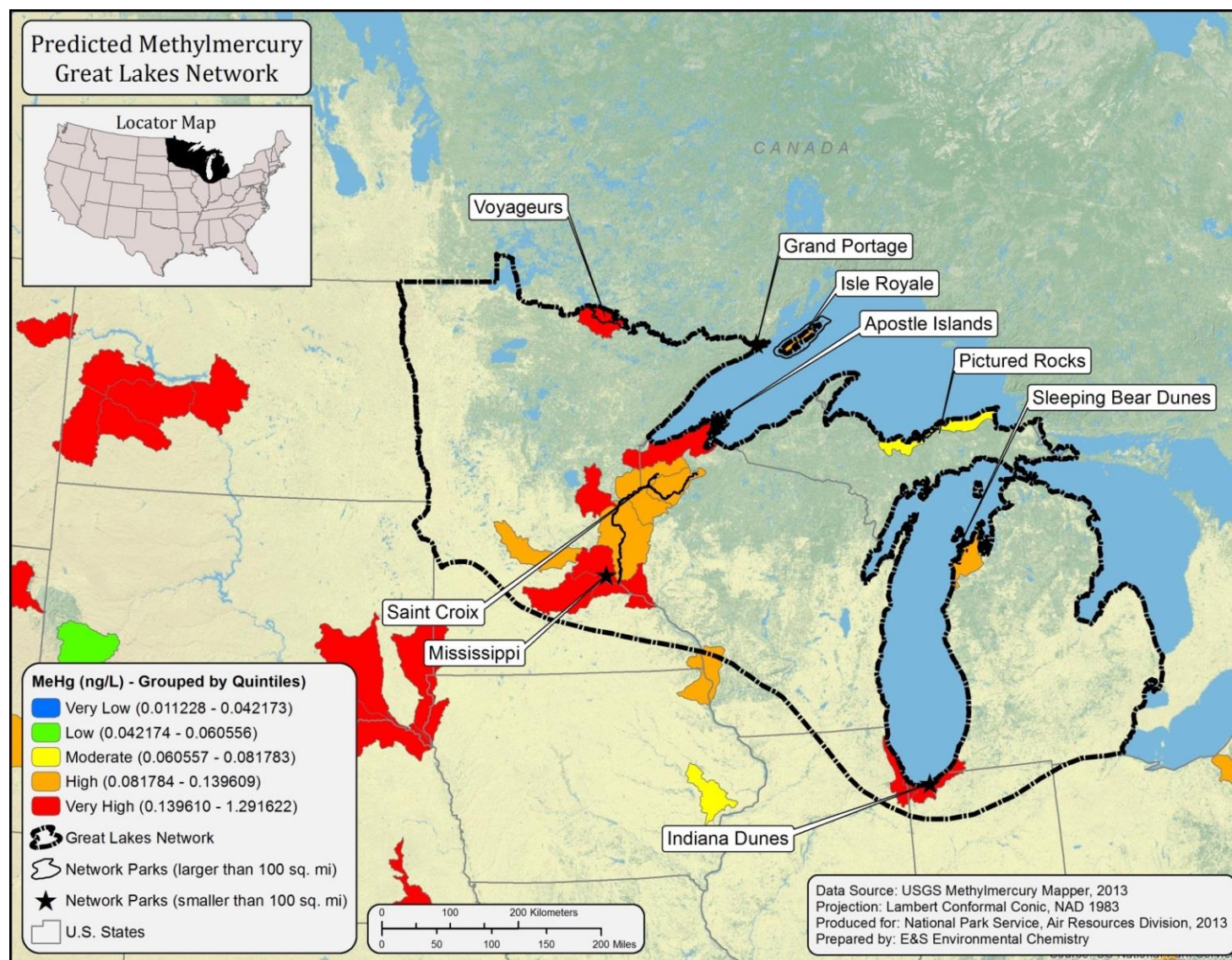


Figure 4c. Glideslopes to achieving natural visibility conditions in 2064 for the 20% hazeiest (red line) and the 20% clearest (blue line) days in VOYA. In the regional haze rule, the clearest days do not have a uniform rate of progress glideslope; the rule only requires that the clearest days do not get any worse than the baseline period. Also shown are measured values during the period 2000 to 2010. Data Source: http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm



Map 10. Predicted MeHg concentrations in surface waters by HUCs that contain national parklands in the Great Lakes Network. Estimates were generated by USGS (2012). Rankings are based on quintile distributions across all I&M parks having estimates by USGS.

Swackhamer and Hornbuckle (2004) assessed air quality and air pollutant impacts in two of the principal parks within this network (ISRO and VOYA) in a report to the NPS. They concluded that the air pollutants of most concern in these two parks were Hg and persistent organic pollutants (POPs), such as dioxins, PCBs, chlorinated pesticides, and brominated flame retardants. Exposure of wildlife to these chemicals occurs largely through fish consumption, and may be linked to reproductive, neurological, and developmental problems. Inputs of these toxic substances to park ecosystems are primarily atmospheric, attributable mostly to long range transport.

The NPS and USGS have monitored lichen species in parks of the GLKN for decades (Bennett 2007). INDU has the fewest species (69) of the park lands studied; it is also furthest south and most heavily influenced by anthropogenic emissions. The parks south of 46°N latitude average 180 lichen species per park. Parks north of 46°N latitude average more than twice as many lichen species per park (Bennett 2007). Elements associated with human activities (i.e., copper, lead, sulfur, zinc) increase in lichen tissue from west to east, with increasing proximity to human population centers.

Research on Hg contamination in the Great Lakes region has been extensive (see reviews by Wiener et al. (2012b) and Evers et al. (2011a)). Mercury biomagnification research in the region has focused largely on piscivorous fish (Sandheinrich et al. 2011, Wiener et al. 2006). Route et al. (2011) investigated spatial patterns of POPs in bald eagle (*Haliaeetus leucocephalus*) nestlings in and adjacent to APIS, MISS, and SACN. Blood plasma and feather samples were analyzed from 288 birds for total Hg, lead (Pb), dichlorodiphenyltrichloroethane (DDT) and metabolites, total PCBs, PBDEs, and perfluorinated chemicals (PFCs). The geometric mean Hg concentration in feathers ranged from 2.69 µg/g in nestlings on pools of the Mississippi River in 2008 to 7.96 µg/g on the Upper St. Croix Riverway in 2006. Mean Pb levels in feathers were lowest in APIS in 2006 and highest in the lower St. Croix River in 2006. In general, Pb concentrations were highest in the lower St. Croix River and along the Mississippi River and lowest on the Apostle Islands and the upper St. Croix Riverway (Route et al. 2011). The POPs that are most commonly associated with industry and municipal waste (PCBs, PBDEs, and PFCs) were highest in bald eagle nestlings near large population centers. However, some industrial contaminants were also high in nestlings on remote islands in Lake Superior.

Rutkiewicz et al. (2011) evaluated Hg exposure in several tissues of bald eagles collected across five Great Lakes states (Iowa, Michigan, Minnesota, Ohio, and Wisconsin) between 2002 and 2010. Total Hg concentrations in brain tissue were highest in Michigan. The researchers concluded that bald eagles in the Great Lakes region are exposed to Hg at levels that might be capable of causing subclinical neurological damage.

Possible effects of atmospherically deposited toxic metals have been the focus of research interest at ISRO for several decades (cf., Bennett 1995). Subtle patterns of slightly elevated elements in two lichen species collected in ISRO suggested potential impacts from atmospheric deposition. Lichens collected from areas having higher exposures were found to have higher element concentrations of S, Mn, Se, and other heavy metals (Bennett 1995).

Trends in contaminant concentrations in bald eagles along the southern shore of Lake Superior decreased substantially between 1989 and 2008 (Dykstra et al. 2010). The concentrations of DDE in eagle nestling blood plasma collected along Lake Superior decreased an average of 3% annually over the 10-year period. Total PCBs decreased 4% annually. Mercury in nestling feathers decreased from 1991 to 2008 by 2.4% per year. With the possible exception of Hg concentration in the upper St. Croix River, mean concentrations in 2006-2008 of all three of these contaminants were below levels expected to cause significant impairment of eagle reproduction at all monitoring sites. In addition, the eagle reproduction rate averaged more than 1.2 young per occupied territory, a level suggestive of a healthy population (Dykstra et al. 2010).

The importance of atmospheric deposition of Hg as a source of aquatic contamination in the upper Midwest was further established when a study of lake sediments illustrated that wet atmospheric Hg deposition could explain most of the observed sediment Hg loadings (Glass and Sorensen 1999, Sorensen et al. 1990). Analyses of lake sediment cores reported by Swain et al. (1992) suggested that the rate of Hg accumulation in lake sediments in the Upper Midwest had nearly tripled since preindustrial time. Rolfhus et al. (2011) reported MeHg data for two shallow (~ 2 m) lagoons on Stockton and Outer Islands in APIS, in southern Lake Superior. These lagoons contained some of the highest water column MeHg concentrations in a semi-remote temperate forest ecosystem in the GLKN (Rolfhus et al. (2011).

Stratigraphic data from eight lakes in rural Minnesota indicate that atmospheric Hg deposition in this region peaked in the 1960s and 1970s, followed by decreases attributable to decreased emissions from regional sources (Engstrom and Swain 1997). Based on comparison with data from remote lakes in southeastern Alaska, the authors estimated that global Hg emissions in the Northern Hemisphere could account for about 7.4 $\mu\text{g}/\text{m}^2$ of annual Hg deposition in rural Minnesota. The remaining deposition (about 5.1 $\mu\text{g}/\text{m}^2$, or 40% of the total) was estimated to derive mainly from regional anthropogenic Hg sources in the upper Midwest and eastern United States. It has been estimated that about 60% of the Hg in lake sediments in VOYA was derived from atmospheric sources (Sorensen et al. 2005, Wiener et al. 2006). Some of that deposited Hg probably originated in Asia (Pittman et al. 2011).

Mercury binds to organic matter. As a consequence, DOC is an important parameter affecting Hg bioavailability and transport through watersheds (Grigal 2002). Methylation is critical to the effects of Hg on aquatic biota. Methylating bacteria typically require SO_4^{2-} to carry on their metabolic activities. Therefore, increased S deposition has been shown to increase rates of Hg methylation in fresh water wetlands (Galloway and Branfireun 2004, ICF International 2006, Jeremiason et al. 2006). Methylation is also correlated with water acid-base chemistry (Driscoll et al. 2007, Wiener et al. 2006).

The northern Great Lakes region, and eastward into northern New York, is especially sensitive to Hg bioaccumulation, due in part to relatively high Hg deposition and in particular due to watershed and lake characteristics that exacerbate Hg transport, methylation, and bioaccumulation (Evers et al. 2011a). The distribution and magnitude of the impacts of Hg contamination of natural ecosystems in the Great Lakes region is more substantial than previously recognized, with concentrations of Hg

exceeding risk thresholds in many species of fish and wildlife across the region (Evers et al. 2011a). Many species of fish in the inland waters of the Great Lakes region have average Hg concentration in fillets above the general risk threshold for piscivorous wildlife (0.27 ppm; Sandheinrich and Wiener 2011).

The Hg that has accumulated historically in lake sediments provides an index of changes over time in Hg inputs from atmospheric deposition and other sources. Drevnick et al. (2012) analyzed 91 sediment cores collected from relatively undisturbed inland lakes in the Great Lakes region. Inferred rates of Hg accumulation in these lakes increased about 7-fold from pre-industrial times to a peak in about the 1980s. Over the past two decades, inferred inputs declined about 20%. This recent decrease in sediment Hg is consistent with documented trends in Hg deposition (Drevnick et al. 2012).

Methylation

Much of the research that has been conducted on Hg methylation, the influence of SO_4^{2-} on methylation rates, and controls on Hg transport within watersheds in the United States has been conducted in the GLKN region (cf., Hrabik and Watras 2002, Watras et al. 1998, Watras et al. 2000, Wiener et al. 2006) and the Northeast (cf., Chen et al. 2005, Driscoll et al. 2007, Evers 2005, Evers et al. 2005, Evers et al. 2007, Evers et al. 2008, Kamman et al. 2005). Some additional work has been conducted in Florida (cf., Gilmour et al. 1998) and the mid-Atlantic region (cf., Lazorchak et al. 2003).

Wetlands act as important sources of MeHg to fresh water ecosystems. This is likely due in large part to two characteristics of wetlands: 1) high availability of DOC, and 2) anaerobic conditions in sediments. Both enhance methylation rates, and DOC also enhances the transport of MeHg to downstream receiving waters. As a consequence of these wetland influences on Hg methylation and transport, the percentage of wetland areas within watersheds is commonly correlated with MeHg flux (Grigal 2002). The MeHg produced in wetlands can bind with organic matter and be transported to hydrologically connected lakes (Grigal 2002, Sellers et al. 2001, St. Louis et al. 1996).

Hg in Fish

Wiener et al. (2012b) synthesized data on 6,400 yellow perch (*Perca flavescens*) from the Great Lakes and associated inland lakes and reservoirs in and around the GLKN. Yellow perch from 6.5% of the waters examined had average whole fish concentrations of Hg high enough to cause adverse effects on piscivorous fish. Concentrations of Hg were higher in fish at higher trophic levels. Fish consumption advisories due to high Hg content were extended to include all lakes in Minnesota and Michigan (Glass and Sorensen 1999).

Mercury loads in fish collected in the Great Lakes region tended to be higher in inland waters (e.g., median Hg in yellow perch fillets 0.14 ppm [ww]) than in the Great Lakes themselves (median Hg in yellow perch fillets 0.09 ppm [ww]; Wiener et al. 2012b). Similarly, Hg concentrations in fish from the Great Lakes were about 55% lower for walleye and 25% lower for largemouth bass (Monson et al. 2011) as compared with concentrations in fish collected from inland waters within the region.

Gorski et al. (2003) investigated bioaccumulation of Hg in northern pike in two inland lakes in ISRO: one Hg advisory lake (Sargent Lake) and one non-advisory lake (Lake Richie). Concentrations of total and MeHg were analyzed in water, zooplankton, macroinvertebrates, and fish. Although concentrations of total Hg were significantly higher in pike collected from Sargent Lake, concentrations in open water were slightly higher in Lake Richie. Analyses of stable isotopes of C and N in biota indicated that pike from the two lakes were positioned at approximately the same trophic level (4.2 and 4.3). However, the food web in Sargent Lake was more pelagic-based, whereas in Lake Richie it was more benthic-based. Gorski et al. (2003) speculated that the pelagic food web in Sargent Lake may enhance bioaccumulation. For example, Campbell et al. (2000) showed by ^{13}C analysis that organochlorines can bioaccumulate to a greater extent in pelagic food webs. It remains difficult to identify *a priori* lakes in ISRO where Hg concentrations in fish will exceed health thresholds for humans or wildlife without direct measurement of Hg content in fish.

The concentration of Hg in fish tissue is often positively correlated with lake and/or watershed area, and negatively correlated with pH, ANC, and zooplankton density (Chen et al. 2005, Driscoll et al. 2007). Lake types that are generally associated with the most Hg bioaccumulation are poorly buffered, low in pH and productivity, and have forested watersheds with little human development (Chen et al. 2005). Such lakes and watersheds are common in the GLKN. Lake pH, SO_4^{2-} concentration, and extent of wetland connectivity were the major factors identified by Wiener et al. (2006) controlling Hg bioaccumulation in predatory fish within VOYA. Low-ANC, low-pH lakes are common in VOYA. Such lakes are prone to having high levels of Hg in fish (Swain and Helwig 1989, Wiener and Spry 1996). The review of Evers (2005) classified Hg-sensitive surface waters as those having:

- high SO_4^{2-} concentrations,
- low pH and ANC,
- extensive wetlands,
- large watershed area relative to lake area,
- fluctuating water level, and
- low nutrient concentration

The USGS sampled 20 lakes in VOYA during the period 2000-2002 and analyzed the water and fish for Hg. Near-surface water samples had MeHg concentrations ranging from below the method detection level of 0.04 ng/L to concentrations that were more than an order of magnitude higher. In near-by Ontario, Scheuhammer and Blancher (1994) estimated that 30% of studied lakes had prey-size fish that had Hg concentrations sufficiently high to cause reproductive impairment in common loons (*Gavia immer*) that consumed those fish.

Changes in atmospheric Hg deposition have been shown to have an important influence on Hg concentrations in fish. Hrabik and Watras (2002) found approximately a 30% reduction in fish Hg concentrations between 1994 and 2000 in a Wisconsin seepage lake in response to decreased atmospheric Hg deposition of about 10% per year between 1995 and 1999 (Watras et al. 2000). It must be noted, however, that seepage lakes, such as the lake studied by Hrabik and Watras (2002),

might be expected to respond more markedly and quickly to decreased atmospheric Hg loading (Harris et al. 2007), compared with drainage lakes that typically receive a large portion of their Hg input via the watershed.

VOYA contains many lakes that vary in size, productivity, and fish Hg content (Sorensen et al. 2005, Wiener et al. 2006). Within VOYA, lakes with extremely low and extremely high fish Hg content are situated within a few kilometers of each other. Fish collected from Ryan Lake and Mukooda Lake in VOYA had some of the highest and lowest Hg concentrations recorded in Minnesota for northern pike (Rolfhus et al. 2011). These two lakes receive nearly identical Hg inputs in atmospheric deposition (Rolfhus et al. 2011, Wiener et al. 2006). Thus, lake- and watershed-specific factors have large influence on Hg bioaccumulation.

Within the Great Lakes region, walleye and largemouth bass exhibited increasing Hg concentrations from south to north and from west to east. Portions of the region having highest concentrations were forested and contained substantial wetland area (Evers et al. 2011a).

Sorensen et al. (2005) reported results of a monitoring study of Hg concentrations in young-of-the-year (YOY) yellow perch in the context of water level fluctuations in 14 lakes in northeastern Minnesota, including 6 lakes in or adjacent to VOYA. Twelve years of monitoring data were collected for Sand Point Lake, and three years for each of the other lakes. Over the three-year period of record across all lakes, mean fish Hg concentrations varied in each lake by nearly a factor of 2, on average. For the 12-year monitoring period at Sand Point Lake, values ranged from 38 ng/g (ww) in 1998 to 200 ng/g (ww) in 2001. Annual water level fluctuation was correlated with Hg concentrations in YOY perch. Because the Hg concentration measurements were made on YOY fish at the end of each growing season, they represented water conditions and bioaccumulation for each year individually. The researchers concluded that annual water level fluctuations in the reservoir systems in VOYA have significant influence on Hg bioaccumulation in perch. This relationship provides a management opportunity for controlling Hg bioaccumulation in VOYA.

Bioaccumulation of Hg and the factors that control it have been topics of considerable research in VOYA. Results of a key study were reported by Wiener et al. (2006), who studied Hg concentrations and bioaccumulation in 17 lakes in the park. They assessed the importance of atmospheric and geologic sources of Hg to interior lakes and their watersheds and identified factors associated with lake-to-lake variation in MeHg contamination of lacustrine food webs. Geologic sources were judged to be small. Most Hg found in the upper O and A soil horizons was of atmospheric origin, primarily from anthropogenic sources. The most important factors influencing MeHg concentrations in lake water and fish were identified as lake pH, SO_4^{2-} concentration in lake water, and total organic C in lake water, which largely reflects wetland influence. The area of connected wetlands adjoining the 17 study lake watersheds represented from 3.5 to 20% of total watershed area (Wiener et al. 2006).

Northern pike from some lakes in VOYA have contained the highest concentrations of Hg reported in Minnesota (Wiener et al. 2006). Concentrations of Hg in northern pike collected in VOYA varied almost 10-fold among the small lakes in the park (Wiener et al. 2006). This reflects the importance of lake and watershed characteristics, in addition to atmospheric deposition, as controlling factors in the

cycling and bioaccumulation of Hg. There was no indication in the deposition measurements or distribution of local Hg emissions sources that the atmospheric loading of Hg would explain these spatial differences.

Mean concentrations of total Hg in one-year-old yellow perch ($n = 612$) varied more than 5-fold across the 17 study lakes of Wiener et al. (2006; 182 ng/g [dw]) in Mukooda Lake to 942 ng/g [dw] in Ryan Lake). A model with pH and lake SO_4^{2-} concentration explained 53% of the variation in total Hg concentration in yellow perch. A model with SO_4^{2-} concentration, TOC, and $[\text{TOC}]^2$ explained 60% of the variation in total Hg. The model judged best, based on the Akaike Information Criteria (AIC), for predicting MeHg concentration in lake water included SO_4^{2-} , TOC and $[\text{TOC}]^2$, and explained 79% of the variation in MeHg concentration in water (Wiener et al. 2006).

Ryan and Tooth lakes had both the highest concentrations of Hg in yellow perch and the highest concentrations of lake SO_4^{2-} (up to 74 $\mu\text{eq/L}$) among the studied lakes. Fish Hg concentrations were lowest in the three lakes (Little Trout, Mukooda, O'Leary) that had $\text{pH} > 7.0$ (Wiener et al. 2006), a pattern observed previously (Grieb et al. 1990, Spry and Wiener 1991).

Piscivorous Wildlife

Relatively high levels of Hg have been documented in many species of bird, mammal, and fish at multiple trophic positions in a variety of habitats across the Great Lakes region (Evers et al. 2011a). Fish constitute an important pathway for transferring MeHg to wild mammals and birds. Monitoring of fish for Hg in the GLKN has often focused on both small prey fish and large, older piscivorous fish. The former are expected to respond quickly to changes in Hg exposure and reflect trophic transport of contaminants in food webs (Wiener et al. 2007). The latter respond more gradually to Hg bioavailability, and are influenced by such factors as fish age, fish size, nutrient input, and inter-species competition (Mason et al. 2005). Thus, fish monitoring is often targeted at both the mid-trophic level omnivorous prey fish and the higher-trophic level predatory fish in order to capture the full range of fish Hg conditions (Kamman et al. 2005).

In the southern portions of the Great Lakes region, agricultural land uses predominate and nutrient inputs from fertilizer use and livestock waste have contributed to increased algal populations. The abundant algae biodilute MeHg in the food web, resulting in lower concentrations in fish and wildlife at higher trophic levels (Evers et al. 2011a).

Analyses of soil, bedrock, and lake sediments indicated that atmospheric deposition was the primary source of Hg to 17 study lakes in VOYA (Wiener et al. 2006). Bedrock and lower soil horizon material contained much lower Hg concentrations than upper A and O soil horizons. Within the A horizon, Hg concentration was positively correlated with organic content ($r^2 = 0.82$). Lake sediment cores showed patterns of low background concentration in sediments deposited before 1860 (47 to 167 ng/g [dw]) to maximum values in the late 20th century (102 to 364 ng/g [dw]). Sediment Hg concentrations were lowest in the lake cores that exhibited the highest sedimentation rates, suggesting dilution of sediment Hg concentration by sediment flux. The ratio of recent Hg concentration in sediment divided by preindustrial Hg concentration was relatively consistent among lakes (mean $\pm$ SD: 2.1 ± 0.1). Measured Hg fluxes represented in lake sediment cores collected from

five lakes were not controlled mainly by atmospheric Hg deposition. Rather, they were strongly influenced by sedimentation patterns within the lakes and watershed characteristics that control runoff, including watershed-to-lake area ratio and the percent of the watershed covered by wetlands. Analyses conducted by Wiener et al. (2006) confirmed that both watershed and in-lake processes affect the concentrations of Hg in lacustrine food webs in the GLKN. The concentration of SO_4^{2-} , TOC, and pH in water are robust indicators of the sensitivity of lake watersheds to Hg inputs in landscapes affected by atmospheric Hg deposition.

Elevated MeHg accumulation in fish-eating birds in both Wisconsin in the GLKN region and in the northeastern United States has been linked to lake acidification (Evers et al. 2007, Hrabik and Watras 2002, Meyer et al. 1995). This form of Hg accumulates in top predators to levels of concern for both human health and the environment (Evers et al. 2007). Several piscivorous bird and mammal species have been suggested as biomonitors of Hg bioaccumulation in the Northeast and the GLKN (Wolfe et al. 2007). The common loon and bald eagle (*Haliaeetus leucocephalus*) are especially good indicators of Hg risk to wildlife (Evers 2006). Increased concentrations of Hg have been found to be associated with behavioral, physiological, and reproductive effects on these bird species (Burgess and Meyer 2008, Evers et al. 2008). The common loon has become established as one of the main avian indicators for evaluating the exposure and effects of MeHg in the United States (Evers et al. 2009, Evers 2006, Evers et al. 2008, Evers et al. 2011b).

Acidic deposition might contribute to Hg toxicity in fish-eating birds in the GLKN because SO_4^{2-} addition to wetland environments could stimulate the production of MeHg, thereby increasing lake water concentrations of MeHg (Jeremiason et al. 2006). Kramar et al. (2005) determined that the extent of wetland located in close proximity (less than 150 m) to loon territory was positively correlated with Hg concentrations in loon blood.

The lowest observed adverse effect level (LOAEL) provides a benchmark for quantifying potential injury to wildlife from Hg exposure. For example, the LOAEL for the common loon has been established as 3.0 $\mu\text{g/g}$ of Hg in adult loon blood (Evers et al. 2007, Evers et al. 2008). This level of Hg is associated with reproductive effects such as reduced fledgling success (Burgess and Meyer 2008). However, loon Hg exposure data can include either sex; different ages, locations, and time periods; and can be derived from analysis of blood, tissue or eggs. It has therefore been difficult to standardize the data regarding MeHg availability. Evers et al. (2011b) developed linkages among loon Hg measurements in eggs, blood, and fish prey in the Great Lakes region. Data were normalized into standard loon tissue units. Use of a standard unit of measure that combines multiple tissues of a high profile species and its principal prey items facilitates examination of spatial gradients in pollution effects (Evers et al. 2011b). Based on analysis of over 8,000 male loon units (MLUs), seven biological Hg hotspots were identified in the region. The average MLU concentration across the Great Lakes region was 1.8 $\mu\text{g/g}$; 82% were above 1 $\mu\text{g/g}$ and 9.8% were above the LOAEL of 3 $\mu\text{g/g}$.

At a given lake, MLUs tend to have higher Hg concentration than female loon units (FLUs) because male loons are typically 21% larger than female loons (Evers et al. 2010) and therefore eat larger fish (Barr 1996). These larger fish tend to have higher Hg concentration (Sandheinrich and Wiener 2011).

Evers et al. (2011b) identified two biological Hg hotspots within the GLKN for which rationales were well described for the observed high concentrations of Hg in loons: northeastern Minnesota and northern Wisconsin/upper Michigan. Both were characterized by mixed deciduous and coniferous forest (79% and 61%, respectively) interspersed with scrub-shrub and emergent wetland (12% and 20%, respectively). In the northeastern Minnesota hotspot, high MLUs were further associated with reservoir impoundments characterized by fluctuating water levels and with small natural lakes having low pH and high SO_4^{2-} and DOC concentration. Some of these high MLU lakes were located in VOYA (Wiener et al. 2006) and nearby Superior National Forest. In northern Wisconsin/upper Michigan, high MLUs were associated with low lake ANC (Cope et al. 1990, Meyer et al. 1995, Meyer et al. 1998) and interactions with SO_4^{2-} and DOC (Watras and Morrison 2008).

The loon Hg biological hotspot in northeastern Minnesota identified by Evers et al. (2011b) included reservoirs as an important landscape feature. Continuing water level fluctuations are likely important for increasing MeHg bioavailability. More than one-fourth of the MLUs that were higher than 3 $\mu\text{g/g}$ (ww) were found in reservoirs. Within the northern Wisconsin/upper Michigan loon Hg hotspot, reservoirs were less common, but nevertheless were often the water bodies having high MLUs (Evers et al. 2011b).

Myers et al. (2007) proposed a national map showing the relative sensitivity of aquatic ecosystems to Hg contamination. Areas showing the highest estimated sensitivity were mainly confined to the East Coast, Gulf Coast, and the region in and around the GLKN, with scattered small areas in other regions.

Although the common loon has been well studied as an example of Hg bioaccumulation in wildlife, this species is actually relatively insensitive (LC 50 of MeHg injected into eggs > 1 ppm (ww)) to adverse effects of Hg compared with other avian species. For example, American kestrel (*Falco sparverius*), white ibis (*Eudocimus albus*), snowy egret (*Egretta thula*), osprey (*Pandion haliaetus*), and tricolored heron (*Egretta tricolor*) are all thought to be much more sensitive (LC 50 of MeHg injected into eggs < 0.25 ppm (ww)), based on research by Heinz et al. (2009) and Kenow et al. (2011).

The NPS is monitoring environmental contaminants in bald eagle nestlings at APIS, MISS, and SACN in the GLKN (Route et al. 2011). Monitoring includes heavy metals, agricultural pesticides, and industrial chemicals. Contaminant levels in 288 eaglets were associated with proximity to municipal and industrial waste. Mercury was highest where wetlands influenced water chemistry.

Total Hg concentrations in mink in the Great Lakes region have been in many cases high enough to suggest the likelihood of subclinical effects (Basu et al. 2007). In one survey, Hg concentrations in mink were highest in wetlands along impounded rivers that had fluctuating water levels and that were downstream of large historical point sources (Hamilton et al. 2011). Similarly, bald eagles in this region accumulated sufficient Hg as to suggest subclinical neurological damage. An estimated 14% to 27% of the eagles studied had Hg tissue concentration above the proposed risk threshold for liver toxicity of 16.7 ppm (Rutkiewicz et al. 2011, Zillioux et al. 1993). Dykstra et al (2010) showed

declines in bald eagle nestlings in GLKN study areas. Much of this observed decrease can likely be attributed to decreases in Hg deposition.

In spite of the multidecadal decline in Hg concentrations in fish and wildlife of the Great Lakes region, there has also been evidence of a more recent increase in Hg concentrations for some species at some locations (Figure 7). This has been shown for walleye from Ontario, walleye and northern pike from Minnesota (Monson 2009, Monson et al. 2011), walleye from Lake Erie (Bhavsar et al. 2010, Zananski et al. 2011), loon blood from northern Wisconsin (Meyer et al. 2011), and bald eagles from VOYA (Pittman et al. 2011). The cause of this recent increase in Hg concentrations in fish and wildlife is not known, but may be related to lower water levels and increased exposed shoreline associated with changing climatic conditions (Meyer et al. 2011), effects of introduced exotic species (Monson et al. 2011), or decreased nutrient loading (Zananski et al. 2011).

Rolfhus et al. (2011) evaluated the results of ten studies in the western Great Lakes region to document the trophic transfer efficiency of MeHg in the pelagic food webs of lakes. The largest increases in MeHg (largest biomagnification) was found at the base of the food web, between water and suspended particles. The observed similarity in the efficiency of trophic transfer suggested that the aqueous supply of MeHg controls much of the bioaccumulation in pelagic food webs in this region.

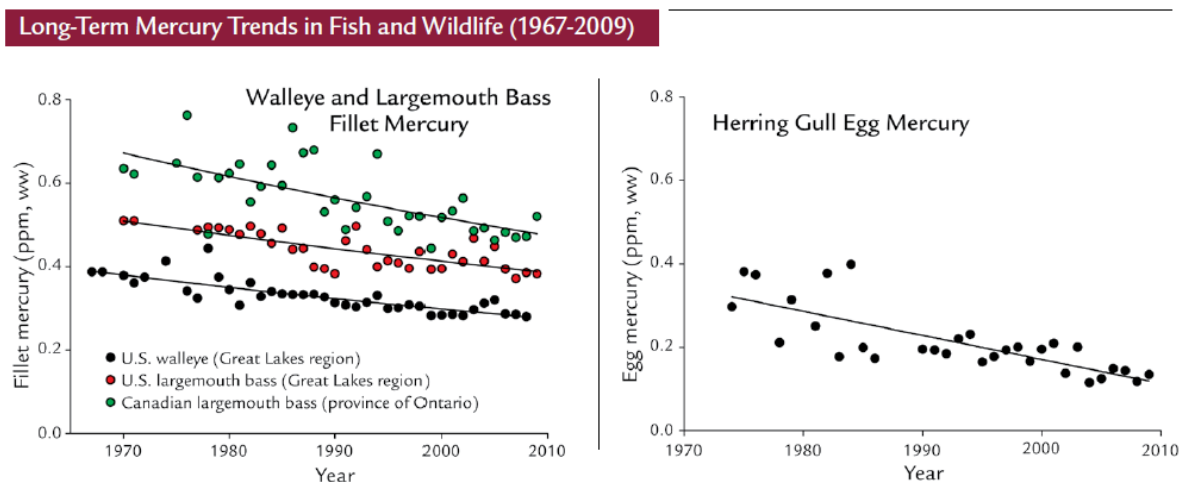


Figure 5. Temporal trends in herring gull egg mercury concentrations (averaged by year across multiple sites in the Great Lakes region; Weseloh et al. 2011) and fish fillet mercury concentrations (walleye and largemouth bass, averaged by year across multiple sites in the Great Lakes and inland water bodies in the U.S. Great Lakes states and the province of Ontario; Monson et al. 2011). These data are characteristic of the regional trend of decreasing mercury concentrations in fish and wildlife in recent decades. Much of this decrease has been attributed to reductions in regional mercury emissions, although there may be other contributing factors as well (Weseloh et al. 2011). (Source: Evers et al. 2011a)

Feathers from nestling bald eagles in VOYA have been collected over the past two decades and analyzed for Hg content. This monitoring has focused on nesting sites near three impoundments: Rainy, Kabetogama, and Namakan (included together with Crane and Sand Pointe) lakes. The

VOYA environment has high potential for Hg methylation because wetlands are abundant (Grim and Kallemeyn 1995). Since 1999, the water levels of these impoundments have been stabilized to more closely match natural conditions. The lake level stabilization was ordered by the International Joint Commission because research had shown that large changes in lake stage can increase MeHg concentrations in lake water (Rudd 1995, Sorensen et al. 2005, St. Louis et al. 2004). In response to this control order, the annual geometric mean of Hg concentrations in bald eagle nestling feathers decreased 74.4% from 1989 to 2010 (Pittman et al. 2011).

Bald eagles in the United States have commonly been found to contain substantial amounts of Hg in feathers, eggs, liver, and brain (cf., Bechard et al. 2007, Scheuhammer et al. 2008, Wood et al. 1996). Impacts of Hg toxicity on eagle reproduction and survival can affect individual and population condition. It is therefore important to identify markers of subclinical effects of Hg on the brain of eagles and other piscivorous bird species as early warning signals. Rutkiewicz et al. (2011) evaluated Hg exposure to bald eagles collected in Iowa, Michigan, Minnesota, Ohio, and Wisconsin. Levels of Hg in eagle brains were associated with neurochemical receptors and enzymes. Results suggested that bald eagles in this region are exposed to Hg at levels high enough to cause subclinical neurological damage (Rutkiewicz et al. 2011). The concentrations of total Hg in bald eagle brain and liver tissues were lowest in Ohio and Wisconsin, and highest in Michigan, Iowa, and Minnesota.

Weiner et al. (2013) investigated contaminant bioaccumulation in fish and larval dragonflies (Insecta, Odonata) in six national park units in the GLKN (GRPO, INDU, ISRO, PIRO, SLBE, and VOYA) during 2008 and 2009. Objectives of the study were to assess spatial patterns of contamination of aquatic biota to identify locations where contaminant concentrations may pose a risk to aquatic biota, and to document temporal trends. The investigated contaminants included total and methyl Hg, Pb, the insecticide DDT and its metabolites, PCBs, PFCs, and PBDEs. Adult piscivorous fish, prey fish, and larval dragonflies were sampled and analyzed. The concentration of Hg in adult piscivorous fish from several water bodies exceeded the EPA tissue residue criterion for MeHg (0.3 ppm), which was established to protect human health. In some predatory fish, the concentrations of Hg were high enough to adversely impact fish health and reproduction. One or more fish collected in ISRO, PIRO, SLBE, and VOYA exceeded 0.5 ppm (ww), a level associated with impaired fish reproduction and other health effects. Concentrations of Hg in prey fish were also considered high enough to impact piscivorous fish or birds. Levels of Hg contamination at INDU were lower.

In contrast to results for Hg contamination, levels of legacy pollutants (DDT and its metabolites, PCBs, Pb) and emerging contaminants (PBDEs and PFCs) were generally low or below the detection limit. Measured levels of these contaminants were not considered harmful (Wiener et al. 2013). The average Hg concentrations in predatory fish were closely correlated with the average concentrations in larval dragonflies of the genus *Gomphus* in lakes of ISRO, PIRO, SLBE, and VOTA (<http://science.nature.nps.gov/im/units/GLKN/monitor/contaminants/contaminants.cfm>).

Other Hg bioindicators

Dragonfly larvae (family Gomphidae) were found to be useful indicators of Hg accumulation in GLKN lakes. In larvae taken from lakes in ISRO, PIRO, SLBE, and VOYA, mean concentrations of

total Hg and methyl Hg were positively correlated with mean methyl Hg concentrations in unfiltered lake water and with mean total Hg in coexisting prey fish and game fish (Haro et al. 2013).

In 2012, NPS staff in VOYA, working in collaboration with USGS and the University of Wisconsin-LaCrosse, began a project to assess Hg concentrations in the eggs of songbirds in Hg methylating environments in VOYA. Eggs of red-winged blackbirds (*Agelaius phoeniceus*) and tree swallows (*Tachycineta bicolor*) were collected and analyzed. Nearly all (96%) of the total Hg was in the methyl form. Concentrations in red-winged blackbird eggs averaged 37 ng/g (ww), with concentrations in individual eggs as high as 77 ng/g (ww) (Weiner et al. 2013). These values were well below the LC₅₀ documented for MeHg in eggs of common grackle (*Quiscalus quiscula*; 210 ng/g [ww]; Heinz et al. 2009).

Vucetich et al. (2001) investigated variation in terrestrial ecosystem Hg exposure throughout ISRO based on Hg concentrations in the livers of deer mice (*Peromyscus maniculatus*). Concentrations of Hg were lower outside the Sargent Lake watershed (100 ng/g, dry tissue) as compared with inside (36 ng/g, dry tissue; $p = 0.06$) the watershed. The authors speculated that there was cause for concern because any Hg exposure in deer mice represents a path for biomagnification in the terrestrial food web.

Research on the Hg content of moose (*Alces alces*) teeth collected before and after 1980 in the upper Peninsula of Michigan in the vicinity of ISRO (Peterson et al. 2002) provided definitive evidence that biological uptake of Hg in terrestrial food chains has begun to decline.

Persistent Organic Pollutants

In addition to the substantial Hg research conducted within the GLKN region, there has also been considerable work in this region on atmospheric inputs of other toxic compounds. Hites (2006) provided a comprehensive summary, with chapters covering PCBs, pesticides, PAHs, PFCs, and others. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) are lipophilic environmental contaminants that are emitted into the atmosphere via combustion of municipal and industrial waste (Czuczwa et al. 1984, Czuczwa and Hites 1986). They deposit readily from the atmosphere and accumulate in lake sediments. Cores of undisturbed lake sediment can produce a record of changes in atmospheric inputs of these contaminants over time for lakes lacking substantial non-atmospheric inputs. This approach has been applied to sediment cores collected from Siskiwit Lake, a remote lake on Isle Royale (Baker and Hites 2000, Czuczwa and Hites 1986). Sediment inferred lake concentrations of PCDD/F were near zero prior to about 1930, increasing to peak concentrations about 1970, and subsequently declining by about 50% (Baker and Hites 2000).

Brominated flame retardants, including PBDEs, are added to various commercial products to reduce flammability. Their usage increased markedly after about 1980 and are now ubiquitous in the environment (Hites 2004). Venier et al. (2010) reported concentrations of PBDEs in the plasma of nestling bald eagles sampled throughout the Great Lakes region. The effects of these atmospherically deposited contaminants on the health and reproduction of bald eagles, or other wildlife, is not known.

Great Lake POP contaminants have affected the health of several bird species, including herring gull (*Larus argentatus*), ring-billed gull (*Larus delawarensis*), and double-crested cormorant (*Phalacrocorax auritus*). Birth deformities, endocrine disruption, and reproductive problems have been documented, although improvements have been noted since the 1980s (Environment Canada 1995).

Control programs for POPs have shown evidence of effectiveness, based on monitoring contaminant concentrations in wildlife. Measurements of POPs in archived herring gull eggs from the Great Lakes showed 75% to 80% decreases in PCB concentrations between 1971 and 1982 (Hebert et al. 1999).

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