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Spatial patterns and temporal trends in mercury concentrations, precipitation depths, and mercury wet deposition in the North American Great Lakes region, 2002–2008

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ABSTRACT

Annual and weekly mercury (Hg) concentrations, precipitation depths, and Hg wet deposition in the Great Lakes region were analyzed by using data from 5 monitoring networks in the USA and Canada for a 2002–2008 study period. High-resolution maps of calculated annual data, 7-year mean data, and net interannual change for the study period were prepared to assess spatial patterns. Areas with 7-year mean annual Hg concentrations higher than the 12 ng per liter water-quality criterion were mapped in 4 states. Temporal trends in measured weekly data were determined statistically. Monitoring sites with significant 7-year trends in weekly Hg wet deposition were spatially separated and were not sites with trends in weekly Hg concentration. During 2002–2008, Hg wet deposition was found to be unchanged in the Great Lakes region and its subregions. Any small decreases in Hg concentration apparently were offset by increases in precipitation.

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1. Introduction

Mercury (Hg) in aquatic ecosystems is a public-health concern and a threat to wildlife because it accumulates and magnifies to unsafe levels in aquatic food chains. Much of the Hg in aquatic ecosystems is introduced by atmospheric deposition, largely from Hg emissions to the atmosphere from human activity (Madison Declaration on Mercury Pollution, 2007). Currently, 100 percent of the Great Lakes and their connecting waters and the 8 USA states and 2 Canadian provinces in the North American Great Lakes region (hereafter, the Great Lakes region) have fish-consumption advisories because of unsafe Hg levels (Ontario Ministry of the Environment, 2009; Québec Ministère de l'Environnement, 2010; U.S. Environmental Protection Agency, 2009).

Atmospheric Hg can be transported to aquatic or terrestrial ecosystems in wet deposition through rainout from clouds and washout from the air. Mercury has been detected in precipitation throughout North America since monitoring began in 1996 (National Atmospheric Deposition Program, 2010; Prestbo and Gay, 2009; Sweet and Prestbo, 1999), and Hg concentrations in precipitation often exceed the water-quality criterion for a continuous freshwater concentration (12 ng per liter, ng/L; U.S. Environmental Protection Agency, 1999).

Previous investigations of Hg in precipitation in the USA and Canada have included monitoring sites in the Great Lakes region. At least 8 studies included Hg-monitoring data from sites in the Great Lakes region during 1993–2005. Sweet and Prestbo (1999) summarized data from as many as 30 sites in the Mercury Deposition Network (MDN) of the National Atmospheric Deposition Program (NADP) in North America for 1995–1998. Landis et al. (2002) investigated Hg wet deposition from 5 sites surrounding Lake Michigan as part of the Lake Michigan Mass Balance Study for

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1994–1995. Miller et al. (2005) estimated and mapped Hg wet deposition in northeastern North America with monitoring data from 27 sites for 1993–2002. VanArsdale et al. (2005) described patterns of Hg wet deposition and concentrations from 14 sites in northeastern North America for 1996–2002. Hall et al. (2005) described the relation of total and methyl-Hg concentrations in precipitation-sample data from 5 sites in the Great Lakes region for 1997–2003. Cohen et al. (2007) used Hg emissions data, back-trajectory modeling, and Hg-monitoring data from 5 MDN sites in the Great Lakes region to examine atmospheric transport, Hg deposition, and trends for 1996–2001. Butler et al. (2007) examined Hg-monitoring data from 33 MDN sites in the eastern USA for 1998–2005, including 15 sites used in our study. Prestbo and Gay (2009) summarized data from as many as 88 MDN sites for 1996–2005, including 30 sites used in our study.

At least 5 studies focused on data collected from sites within a single state in the Great Lakes region. Glass and Sorensen (1999) reported annual Hg wet deposition from 6 sites in Minnesota for 1990–1995. Keeler and Dvonch (2005) summarized atmospheric Hg observations from 3 sites in Michigan for 1994–2002. Lynch et al. (2005) described Hg-monitoring data from 8 MDN sites in Pennsylvania for 2003–2004. Keeler et al. (2006) summarized Hg-monitoring data for a site in eastern Ohio for 2003–2004. Risch (2007), Risch and Fowler (2008), and Risch et al. (2010) summarized Hg-monitoring data from 5 MDN sites in Indiana for 2001–2006.

Hg wet deposition is important because it is a primary loading to lakes and watersheds in the region. Other studies have demonstrated the relation between Hg loading and methyl-Hg levels in fish (Harris et al., 2007). The Great Lakes Commission (2007) identified long-term monitoring of Hg in precipitation as the source of information to indicate local or regional changes in the input of Hg to ecosystems. Hg wet deposition is computed as the product of Hg concentration and precipitation depth. Toward the goal of indicating changes in Hg loading, there was a need for available Hg concentration and precipitation-depth data in the Great Lakes region to be integrated to increase the number of data points with Hg wet-deposition estimates.

In this paper, we present a synthesis of spatial and temporal data related to Hg deposition in the Great Lakes region (the 8 states in the USA and 2 provinces in Canada shown in Fig. 1). Our study used data from 3 Hg-monitoring and 2 precipitation-monitoring networks in the Great Lakes region that previously had not been combined. We applied statistical and mapping techniques to utilize the monitoring data to its full extent. We analyzed the statistical significance, direction, and magnitude of temporal trends in weekly data from the Hg-monitoring sites. We used high-resolution maps to compute annual Hg wet deposition at precipitation-monitoring sites and to interpret spatial patterns in the region.

2. Methods

2.1. Mercury data

Hg data for the region were obtained from 3 Hg-monitoring networks that had collected observations for the 2002–2008 study period: the MDN of the NADP, the Michigan Mercury Monitoring Network of the Michigan Department of Environmental Quality, and the Integrated Atmospheric Deposition Network (IADN) of Environment Canada. These networks included urban, suburban, rural, and isolated site types.

We combined Hg data from the 3 networks because of their overall equivalence in collection and analysis of precipitation samples for Hg. All monitoring sites were equipped with automated wet-only precipitation collectors with trace-metals-clean sampling trains, and precipitation was recorded with co-located rain gages. The MDN and IADN sites collected weekly composite samples (removed on Tuesdays), and the Michigan sites collected daily precipitation-event-based samples (Landis and Keeler, 1997). For compilation in our analysis, Michigan data were converted to weekly values according to the Tuesday schedule. The networks used different laboratories, but each laboratory analyzed for Hg by cold-vapor atomic fluorescence spectroscopy, with reporting limits less than 1.0 ng/L. Equipment and methods used in the networks are described in the Supplementary Data.

In the Great Lakes region, more than 40 Hg-monitoring sites in the USA and Canada were operated before 2008. We selected 37 sites for our study that had complete data records for at least 5 of the 7 years during 2002–2008 (Fig. 1;

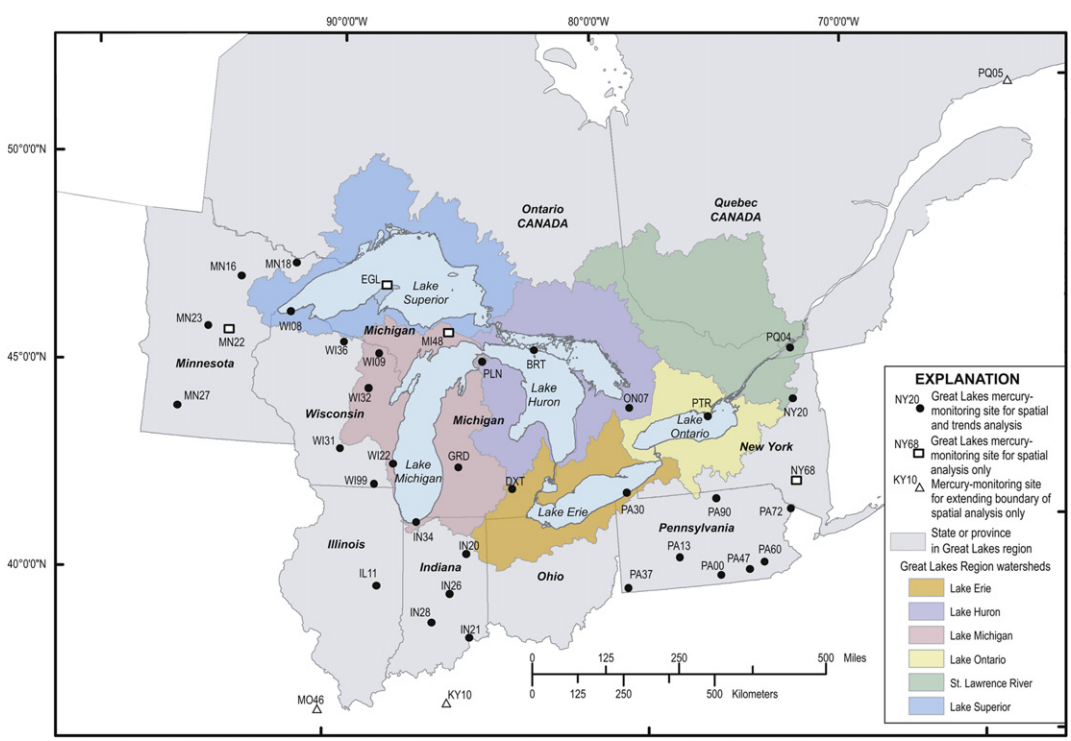

Fig. 1. Sites in the Great Lakes region with annual and weekly Hg concentration data for spatial and trends analysis, 2002–2008.

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Supplementary Data Table T1). The sites consist of 31 from the MDN, 4 from the Michigan network, and 2 from IADN. Among the 37 sites, 14 are in watersheds of tributaries draining to the Great Lakes, 15 are in watersheds tributary to the Mississippi River, and 8 are in watersheds of tributaries draining to the Atlantic Ocean. Annual precipitation-volume-weighted Hg concentrations (hereafter, annual Hg concentrations) were calculated with weekly data from the 37 sites. We selected 33 of the 37 sites that had complete annual records for all 7 years to use in the statistical analysis of temporal trends. Methods for site selection and annual Hg concentrations are described in the Supplementary Data.

2.2. Precipitation-depth data

Annual precipitation depths were calculated with daily values from sites in the cooperative observer networks of the U.S. National Weather Service and Environment Canada Meteorological Service, as well as from 37 sites in the Hg-monitoring networks. Cooperative observer data are daily precipitation depths measured at a fixed location by an observer using a stick gage and following standard procedures. Data for the cooperative observer sites in the USA were provided by the Midwest Region Climate Data Center at the University of Illinois, and data for the sites in Canada were provided by Environment Canada. Annual precipitation depths were calculated if more than 273 daily values were recorded (annual record more than 75 percent complete) in at least 5 of 7 years during 2002–2008. Annual precipitation depths were calculated for each of the 7 years in our study period with data from 96 to 99 percent of a total 1541 precipitation-monitoring sites (Fig. 2).

2.3. Isopleth maps

Isopleth maps were prepared with a map-grid technique in a geographic information system (ArcGIS 9.3; ESRI, 2009). An algorithm interpolated between the measured values at monitoring sites in some map-grid cells and assigned an estimated value to the rest of the cells. A contouring program was applied to the map grid of known and estimated values to geographically display ranges of values with a color scale. Annual Hg-concentration data from the 37 Hg-monitoring sites in the 8 states and 2 provinces were supplemented with data from 3 other MDN sites outside the region to extend the map-grid interpolations to the northern and southern edges of the study area (Fig. 1). Data from these 3 sites are not included in summary statistics for the region. The map grids of annual Hg concentrations and annual precipitation depths were used to make the isopleth maps of annual Hg wet deposition. The methods used to prepare isopleth maps of annual Hg concentrations, annual precipitation depths, and annual Hg wet deposition are described in the Supplementary Data.

The method we used for making high-resolution isopleth maps of annual Hg wet deposition in the Great Lakes region greatly increased the number of data points with Hg wet-deposition estimates beyond the diffuse array of 37 Hg-monitoring sites with annual Hg wet-deposition values. A map grid of annual Hg concentrations interpolated from the 37 Hg-monitoring sites was combined with the annual precipitation depths from the dense array of 1541 precipitation-monitoring sites in the region. The isopleth maps based on interpolation of annual Hg wet-deposition values computed for the precipitation-monitoring sites enabled us to attain a high resolution in the annual maps. This method was used to map Hg wet deposition in Indiana (Risch et al., 2007, 2010; Risch and Fowler, 2008). The approach used in our study to interpolate annual Hg concentrations between monitoring sites requires the assumption of a spatially consistent gradation between known values. Uncertainties in the interpolations are highest in parts of the region with few or nonexistent Hg-monitoring sites.

2.4. Statistical methods and net change

The nonparametric Kruskal–Wallis rank-sum test (KWRS) and Tukey multiple comparison of medians (Tukey) were used to minimize the effect of outliers in comparisons of annual data from different years and individual sites. A p-value less than 0.05 ($\alpha = 0.05$) was used to indicate a significant difference. The nonparametric Seasonal Kendall Trend Test (SKTT; Gilbert, 1987), a generalized Mann–Kendall test, was used to identify significance of temporal trends in weekly Hg concentrations, precipitation depths, and Hg wet deposition at Hg-monitoring sites. In our study, trends are reported at the 90-percent ($\alpha = 0.10$) and 95-percent ($\alpha = 0.05$) confidence levels. Observations were compared only within the same month (season) to account for the seasonal cycle of Hg wet deposition. The Seasonal Kendall Slope Estimator (SKSE; Gilbert, 1987) was used to determine the magnitude and direction of trends and to identify the most likely annual change for a site with a significant trend. The 7-year change for significant trends in this paper is 7 times the annual change. The statistical methods are described in the Supplementary Data.

The net change in annual Hg concentration, annual precipitation depth, and annual Hg wet deposition for Hg-monitoring or precipitation-monitoring sites during 2002–2008 was calculated with the interannual (year-to-year) differences. Interannual difference and net change provide a quantitative explanation and summary of comparisons between maps in a time series. An interannual difference was computed by subtracting the value in one year from the value in the preceding year, and was positive, negative, or zero. The net change was calculated as the sum of the 6 interannual differences, and was positive (a 7-year increase), negative (a 7-year decrease), or zero (unchanged in 7 years). For the equation used to calculate net change, see the Supplementary Data. The net change in annual Hg concentration was calculated with data from the 37 Hg-monitoring sites.

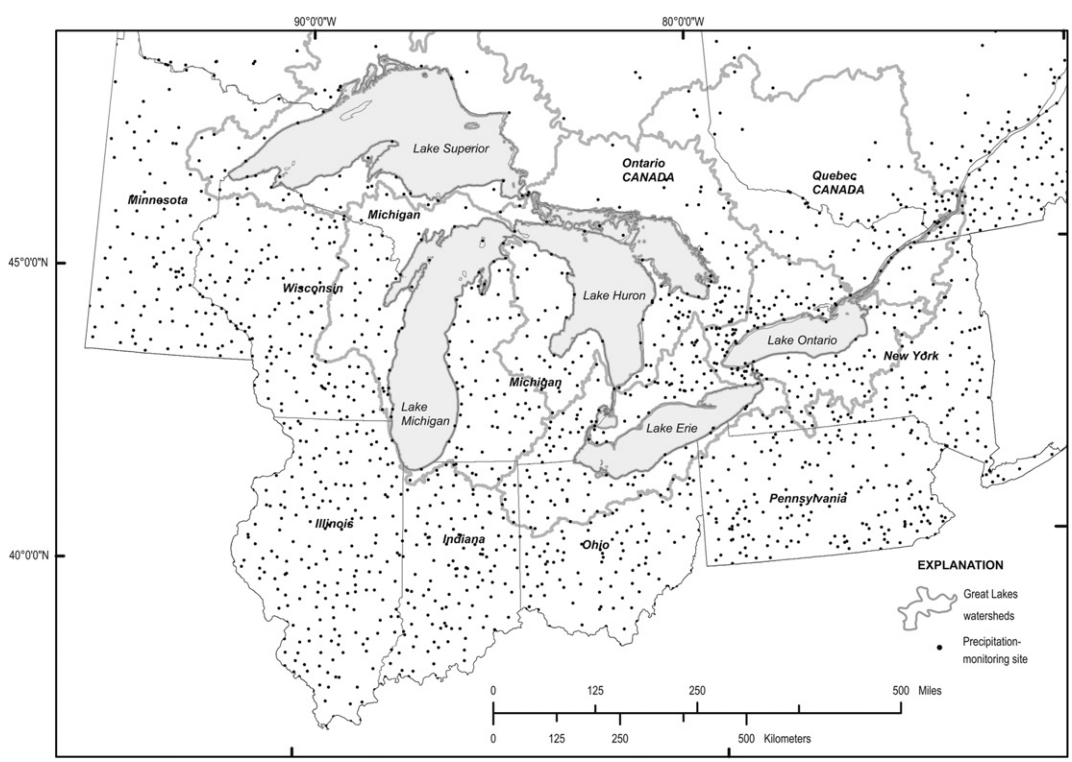

Fig. 2. Sites in the Great Lakes region with annual precipitation data for spatial analysis, 2002–2008.

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(Wetherbee et al. (2007) noted that measurement variability between co-located samplers in the MDN could resolve Hg concentrations to 2 ng/L, thus limiting the certainty of net changes in annual Hg concentrations less than 2 ng/L) The net change in annual precipitation depth was computed with data from 1532 of the 1541 precipitation-monitoring sites that had values for at least 5 successive years. The net change in annual Hg wet deposition was computed with the Hg deposition calculated for these precipitation-monitoring sites. If an interannual difference substantially contributed to the net change, it was identified in the Results and discussion section.

3. Results and discussion

This section is organized with Hg concentrations and precipitation depths presented first because their annual spatial patterns and weekly temporal trends are the components that affect Hg wet deposition. Hg wet deposition, which constitutes the atmospheric Hg loading to watersheds and ecosystems, is presented next. Finally, we integrate the patterns and trends for Hg concentrations, precipitation depths, and Hg wet deposition at regional, subregional, and local scales, each having implications for Hg monitoring or policy decisions.

3.1. Mercury concentrations

3.1.1. Spatial patterns in annual Hg concentrations

Annual Hg concentrations were significantly different among the individual Hg-monitoring sites (KWRS, $p < 0.001$). The annual Hg concentrations at GRD, IN21, and MN27 statistically exceeded those at 7 or 8 other sites (Tukey). The 7-year mean annual Hg concentrations at the 37 sites ranged from 5.8 ng/L at NY20 to 13.6 ng/L at MN27 and were higher than 12 ng/L at 5 sites in 4 states – MN27, MN22, WI22, GRD, and IN21 (Figs. 1 and 3). In 6 of the 7 years, areas with annual Hg concentrations higher than the 12 ng/L water-quality criterion (U.S. Environmental Protection Agency, 1999) were mapped in western Michigan, southeastern Indiana, and southwestern Minnesota.

The median of all annual Hg concentrations for all years in the region (the group of 37 Hg-monitoring sites) was 9.6 ng/L, and the range was 5.0–17.1 ng/L. The annual median concentrations were 11.1 ng/L in 2002, 10.2 ng/L in 2003, and lower in subsequent years (Table 1). The median of the 2002–2008 net change in annual Hg concentrations for the region was −0.4 ng/L, and the range was −6.1 to +4.9 ng/L (Fig. 4). Net changes in most of the area around Lake Michigan, including eastern Wisconsin, northern Illinois, northern Indiana, and Michigan, were −2 to −4 ng/L. Single interannual differences at individual sites in this area were −3 to −4 ng/L but did not occur between the same pairs of years. The +2 to +4 ng/L net change in central Indiana included a +5 ng/L difference near IN26 between 2007 and 2008. Half of the net changes in annual Hg concentrations in the region were between −2.1 and +0.56 ng/L. Large distances between monitoring sites with known values result in greater uncertainty associated with the interpolated values. Parts of the region with the highest uncertainty in the annual Hg concentration maps include Ohio, western Illinois, Ontario, and Québec (Figs. 3 and 4).

3.1.2. Temporal trends in weekly Hg concentrations

Significant temporal trends in weekly Hg concentration during 2002–2008 were identified at the 90-percent confidence level for 14 of 33 sites (Fig. 5), and trends for 9 of these 14 sites were significant at the 95-percent confidence level. Sites showing these trends were in all 3 networks. Trends of decreasing Hg concentration were determined for 8 sites, including a cluster of 6 sites in southern Wisconsin, southern Michigan, and northern Indiana, which showed a 7-year change of −2.1 to −4.1 ng/L (Table 2). The trends at these 6 sites are consistent with the spatial pattern of −2 to −4 ng/L net change in annual Hg concentration for that area (Fig. 4). Significant temporal trends in weekly precipitation depths were identified at 4 of these sites and are discussed further in the section "Localized Conditions". The 7-year median weekly Hg concentrations at these 6 sites were 9.7–13.6 ng/L (Table 2), which are consistent with the spatial pattern around southern Lake Michigan that has 7-year mean annual Hg concentrations of 10–13 ng/L (Fig. 3).

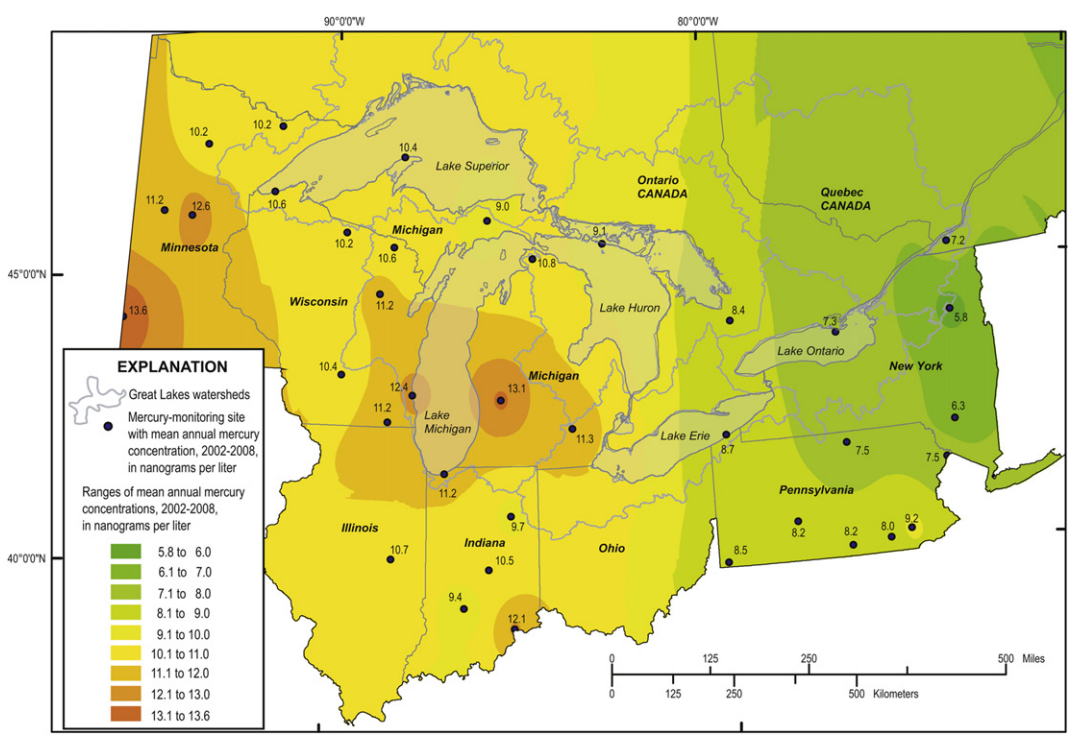

Fig. 3. Seven-year mean annual Hg concentrations in the Great Lakes region, 2002–2008.

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Table 1
Annual summary data for Hg-monitoring sites in the Great Lakes region, 2002–2008.

Year	Minimum Hg concentration (ng/L)	Median Hg concentration (ng/L)	Maximum Hg concentration (ng/L)	Median precipitation depth (cm)	Median Hg wet deposition (μg/m^2)
2002	4.4	11.1	17.1	84.4	9.1
2003	4.3	10.2	16.6	86.3	8.8
2004	5.3	9.3	14.3	96.5	9.6
2005	5.1	9.6	15.4	77.2	8.0
2006	5.0	9.3	16.0	98.9	8.7
2007	5.3	9.7	15.6	91.7	8.1
2008	5.0	9.2	14.2	104.0	9.2
7 years	5.0	9.6	17.1	89.4	8.6

Trends of increasing concentration were determined for 6 sites, including a group of 4 sites in Pennsylvania, which showed a 7-year change of +1.5 to +2.0 ng/L (Table 2). The trends at these 4 sites are consistent with the spatial pattern of +1 ng/L net change in annual Hg concentration (Fig. 4), but are below the limits of measurement variability determined by Wetherbee et al. (2007). Temporal trends in weekly Hg concentration were not shown for 19 of 33 sites, including 2 sites with the highest 7-year mean annual Hg concentrations in the region—MN27 and IN21 (Fig. 3).

The median −0.4 ng/L net change in annual Hg concentrations for the region is 4 percent of the 9.6 ng/L median. Prestbo and Gay (2009) reported either no trend or decreasing Hg concentrations during 1996–2005 at many MDN sites. We observed similar decreasing Hg concentrations in southern Wisconsin and Michigan and northern Indiana (Fig. 4) for 2002–2008 but trends of increasing Hg concentrations at 4 sites in eastern Pennsylvania. Butler et al. (2007) reported a trend with a 3-percent decrease in Hg concentrations during 1998–2005 for a group of sites in their study that included the Great Lakes region. This observation is generally consistent with the pattern of decreasing Hg concentrations we observed for 2002–2008. The absence of trends in Hg concentration for sites in Minnesota and western Wisconsin we observed for 2002–2008 also was identified for 1996–2005 by Butler et al. (2007) and by Prestbo and Gay (2009), who noted decreasing precipitation depths in the region.

3.2. Precipitation depth

3.2.1. Spatial patterns in annual precipitation depths

The median of the 2002–2008 annual precipitation depth for the 1541 precipitation-monitoring sites in the region was 99 cm, and the range was 22–218 cm. Isopleth maps of annual precipitation depths during 2002–2008 indicate gradients of increasing precipitation depth from north to south and from west to east, with one or sometimes both gradients exhibited. The 7-year mean annual precipitation depths in the region ranged from 44 to 183 cm (Fig. 6). The highest (120–140 cm) were in southern Indiana, eastern Pennsylvania, New York, and Québec; the lowest (60–80 cm) were in northern Wisconsin, northern Michigan, and most of Minnesota. The median net change in annual precipitation depth at the monitoring sites was +15 cm, and the range was −99 to +98 cm. Net changes in most of the region were between zero and +40 cm (Fig. 7). The highest increases (+40 to +60 cm net change) were near southern Lake Michigan, including a +40 cm difference from 2002 to 2003 and 2007 to 2008. The greatest decreases (−20 to −60 cm net change) were in northern Wisconsin,

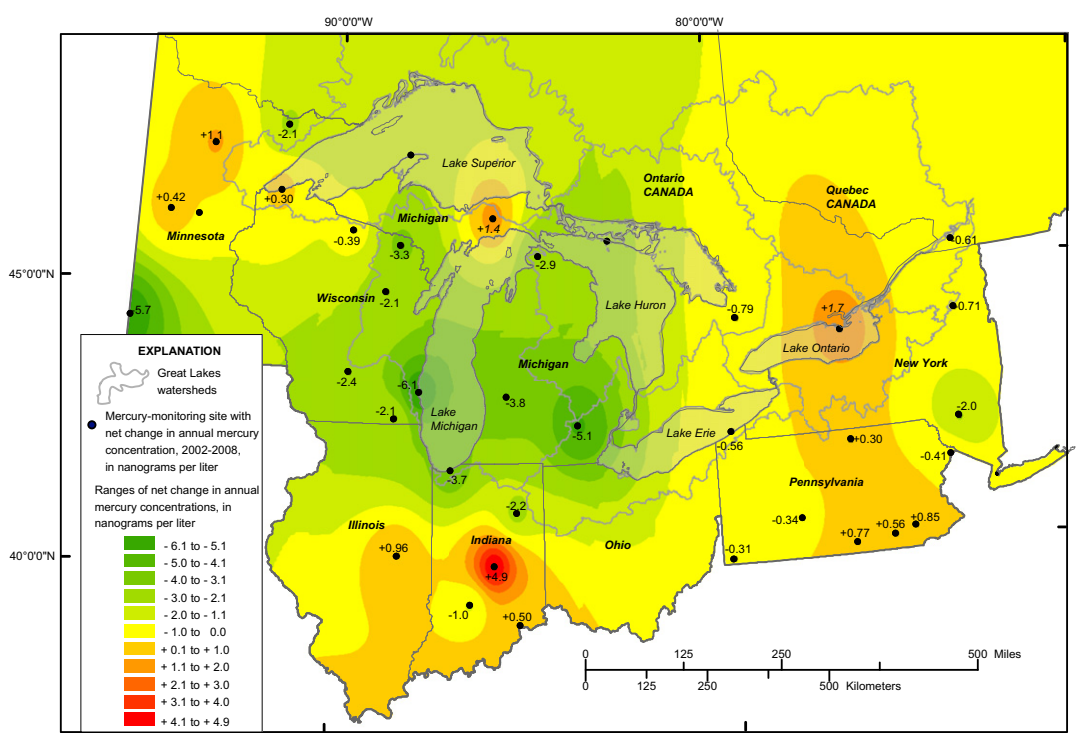

Fig. 4. Net changes in annual Hg concentrations in the Great Lakes region, 2002–2008.

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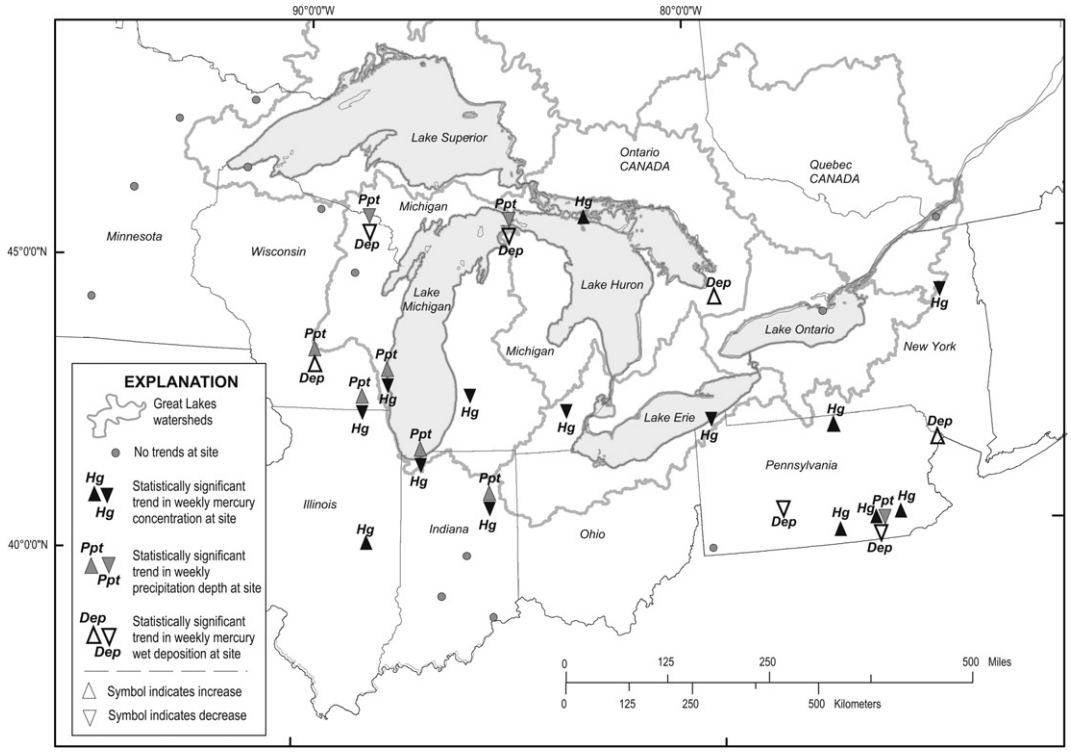

Fig. 5. Trends in weekly Hg concentrations, precipitation depths, and Hg wet deposition at monitoring sites in the Great Lakes region, 2002–2008.

the Upper Peninsula of Michigan, and eastern Minnesota, including a −40 cm difference from 2002 to 2003 and 2004 to 2005.

The 2002–2008 increases in annual precipitation depths for most of the region are consistent with a historical increase reported by2 data reviews for the Great Lakes. Hodgkins et al. (2007) found that precipitation depths increased during the 90 years preceding 2004 in the Great Lakes Basin of the USA. Using the average of 37 Historical Climatology Network stations in the USA in their analysis, they noted an increase of 10.7 cm from 1955 to 2004. They stated that most of the increase observed in their study period was after 1970. In another review, a net increase in annual precipitation depths for 1895–2006 was reported for states in the Great Lakes region (Midwestern Regional Climate Center, 2010). The largest statewide increases in annual precipitation depths for the 112 years were 11.4 cm for Indiana and 10.4 cm for Michigan.

3.2.2. Temporal trends in weekly precipitation depths

Significant temporal trends in weekly Hg precipitation depths during 2002–2008 were identified at the 95-percent confidence level for 8 of 33 sites (Fig. 5). Sites showing these trends were in the MDN and UMAQL networks. Trends of increasing precipitation depths were determined for a cluster of 5 sites near the southern end of Lake Michigan: 3 sites in southern Wisconsin and 2 sites in northern Indiana. Decreasing trends in Hg concentration were determined at 4 of these 5 sites and are discussed further in the section "Localized Conditions".

Table 2
Temporal trends data for weekly Hg concentrations at selected Hg-monitoring sites in the Great Lakes region, 2002–2008.

Monitoring site ID/statistical group	Statistically significant trend[a]	Confidence level[a](percent)	7-year median Hg concentration (ng/L)	Median annual change[b] (ng/L)	7-year[c] change (ng/L)
DXT	Decrease	95	11.6	−0.58	−4.1
IN34	Decrease	95	10.5	−0.50	−3.5
GRD	Decrease	95	13.6	−0.50	−3.5
WI22	Decrease	95	11.7	−0.46	−3.2
IN20	Decrease	95	9.7	−0.33	−2.3
WI99	Decrease	90	10.2	−0.30	−2.1
NY20	Decrease	95	5.6	−0.21	−1.5
PA30	Decrease	90	9.1	−0.16	−1.1
PA60	Increase	90	10.5	0.22	+1.5
PA90	Increase	95	7.5	0.22	+1.5
PA00	Increase	90	9.1	0.23	+1.6
IL11	Increase	90	11.3	0.28	+1.9
PA47	Increase	95	8.9	0.29	+2.0
BRT	Increase	95	7.7	0.42	+2.9
Southern subregion	Decrease	90	10.5	−0.15	−1.1
Great Lakes region	Decrease	90	9.4	< −0.01	< −0.1

[a] Significant trends determined with Seasonal Kendall Trend Test (Gilbert, 1987).
[b] Median annual change determined with Seasonal Kendall Slope Estimator (Gilbert, 1987).
[c] 7-year change computed as 7 times median annual rate of change.

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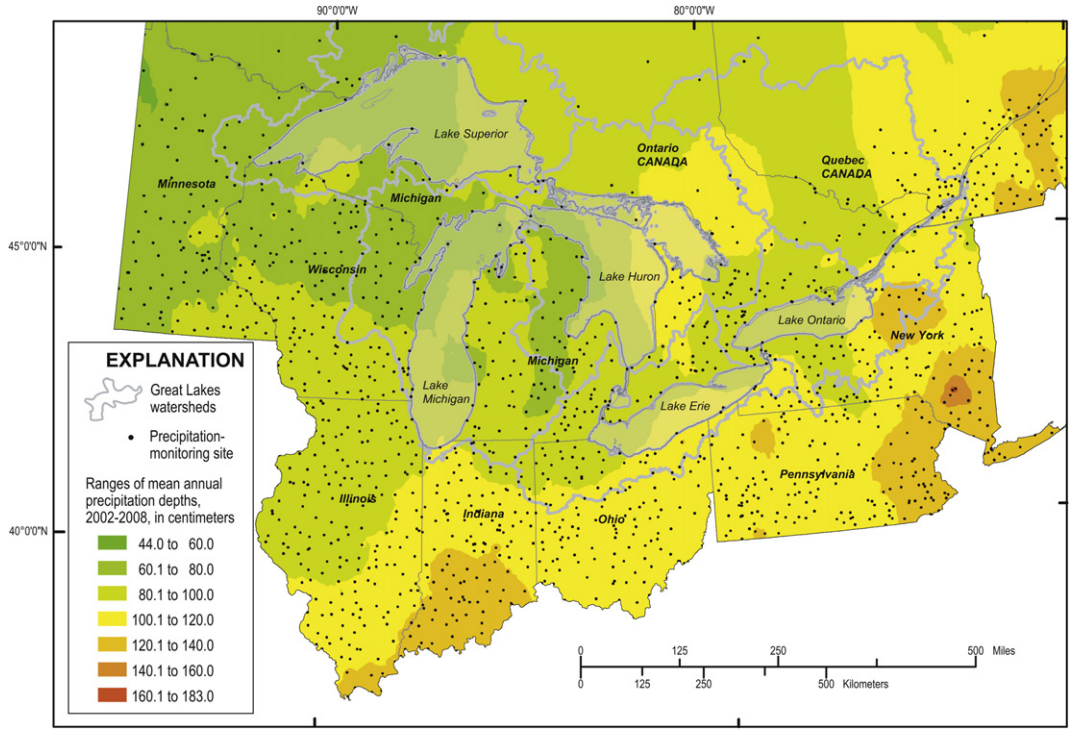

Fig. 6. Seven-year mean annual precipitation depths in the Great Lakes region, 2002–2008.

3.3. Mercury wet deposition

3.3.1. Spatial patterns in Hg wet deposition (hereafter, Hg deposition)

The median annual Hg deposition for the individual Hg-monitoring sites was 8.6 μg per square meter (μg/m^2), and the range was 4.3 μg/m^2 at PTR in 2004 to 19.7 μg/m^2 at IN26 in 2008. Annual Hg deposition was significantly different among the 37 monitoring sites (KWRS, $p < 0.001$). The annual Hg deposition at IN21 (7-year median, 15.4 μg/m^2) statistically exceeded that for 13 other sites (Tukey). For the group of 37 sites, the annual median Hg deposition ranged from 8.0 μg/m^2 in 2005 to 9.6 μg/m^2 in 2004

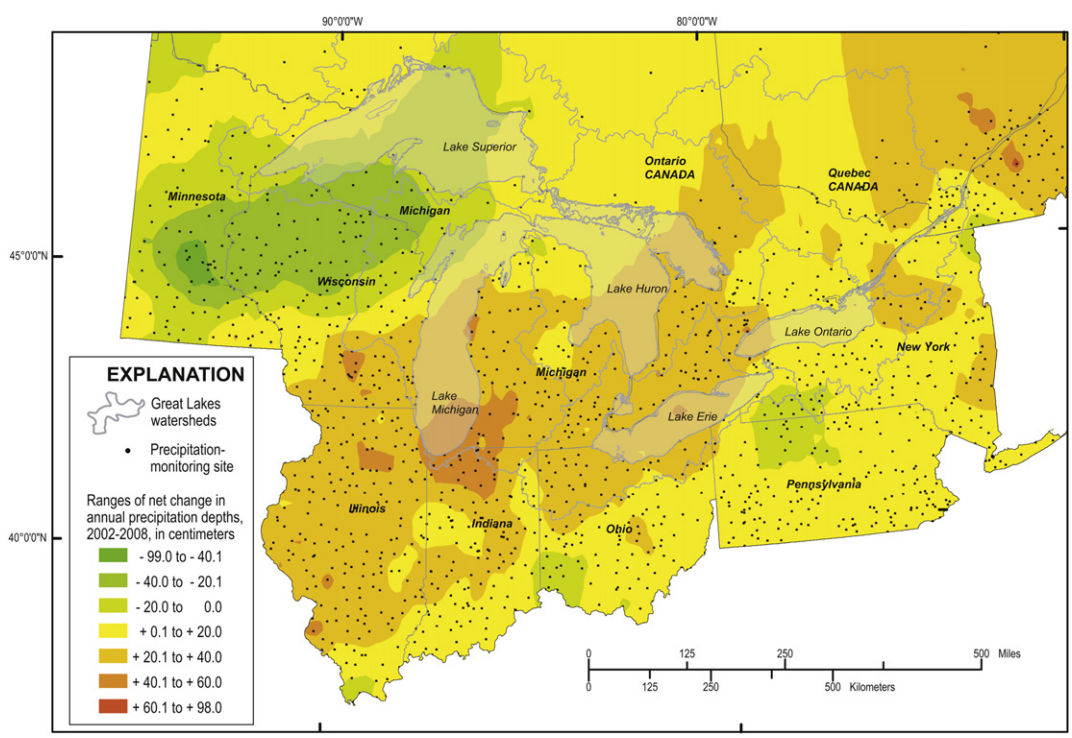

Fig. 7. Net changes in annual precipitation depths in the Great Lakes region, 2002–2008.

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(Table 1). The median of the annual Hg deposition calculated for precipitation-monitoring sites with the high-resolution maps was 9.2 μg/m^2, and values ranged as high as 20 μg/m^2.

The 7-year mean annual Hg deposition calculated for precipitation-monitoring sites with the high-resolution maps ranged from 4.3 to 15.9 μg/m^2 (Fig. 8). The highest mean annual Hg deposition was in much of Indiana and southern Illinois (12–14 μg/m^2), and the lowest was in northern Minnesota, eastern Ontario, Québec, and parts of New York (4.3–6 μg/m^2). In 5 of the 7 years, an area with 15–20 μg/m^2 annual Hg deposition was mapped in southeastern Indiana (Supplemental Data Fig. F1). In 2003, this area extended into central Indiana and most of southern Ohio. In 2008, this area extended into central Indiana and most of southern Illinois.

The area in southeastern Indiana with statistically and spatially high annual Hg deposition is consistent with reports by Risch (2007), Risch and Fowler (2008), and Risch et al. (2010), who found that annual Hg deposition at IN21 was significantly higher than at 4 other MDN sites in Indiana for 2001–2006. In addition, they indicated that Hg deposition in southeastern Indiana, unlike the rest of the state, may exhibit a greater influence from annual Hg concentrations than from annual precipitation depths.

The median net change in annual Hg deposition at the monitoring sites was +0.7 μg/m^2, and the range was −11 to +13 μg/m^2. Net changes in annual Hg deposition in most of the region were between −2 and +2 μg/m^2 (Fig. 9). The highest increases (+4 to +6 μg/m^2 net change) were in central Indiana and central to southwestern Illinois, including a +6 μg/m^2 difference from 2007 to 2008. The greatest decreases (−4 to −6 μg/m^2 net change) were in northern Wisconsin, northern Michigan, and central Minnesota, including a −6 μg/m^2 difference from 2002 to 2003.

3.3.2. Temporal trends in weekly Hg deposition

Significant temporal trends in weekly Hg deposition during 2002–2008 were identified at the 90-percent confidence level for 7 of 33 sites (Fig. 5), and trends for 4 of these 7 sites were significant at the 95-percent confidence level. Sites showing these trends were in all 3 networks. Trends of decreasing Hg deposition were determined for 4 sites, and trends of increasing Hg deposition were determined for 3 sites. A geographic cluster was not apparent. At 6 of the 7 sites with trends in Hg deposition, no trends in Hg concentration were identified. One site showed trends of decreasing Hg deposition and increasing Hg concentration. At 4 of the 7 sites with trends in Hg deposition, trends in precipitation depths were identified. At 3 sites, Hg deposition and precipitation depths were decreasing; at 1 site, both were increasing. Temporal trends in weekly Hg deposition were not evident for 26 of 33 sites. The absence of trends in Hg deposition for sites in Minnesota and western Wisconsin corresponds with an absence of trends in Hg concentrations at these sites.

The temporal trends in Hg concentrations, precipitation depths, and Hg deposition that we identified for 2002–2008 were different from those determined by Prestbo and Gay (2009) for 1996–2005 at most of the sites in our study area. The inconsistency may be due, in part, to the different time periods examined for trends. Prestbo and Gay mentioned the complication of precipitation trends affecting Hg deposition trends, something we also observed. For the region during 2002–2008, we computed median net changes of +0.7 μg/m^2 in annual Hg deposition, −0.4 ng/L in annual Hg concentrations, and +15 cm in annual precipitation depths. Our findings are somewhat different from those of Butler et al. (2007) for 1998–2005, who reported a 3-percent statistical decrease in Hg deposition and Hg concentration for their group of sites that included the Great Lakes region. Butler et al. acknowledged that trends in regional Hg emissions appear to play a significant role in the Hg deposition trends, which is something we did not test.

Other investigators have commented about the episodic nature of Hg wet deposition. High Hg concentrations have been reported to be associated with high-intensity or short-duration precipitation events (Keeler et al., 2005, 2006; Mason et al., 1997). The number of

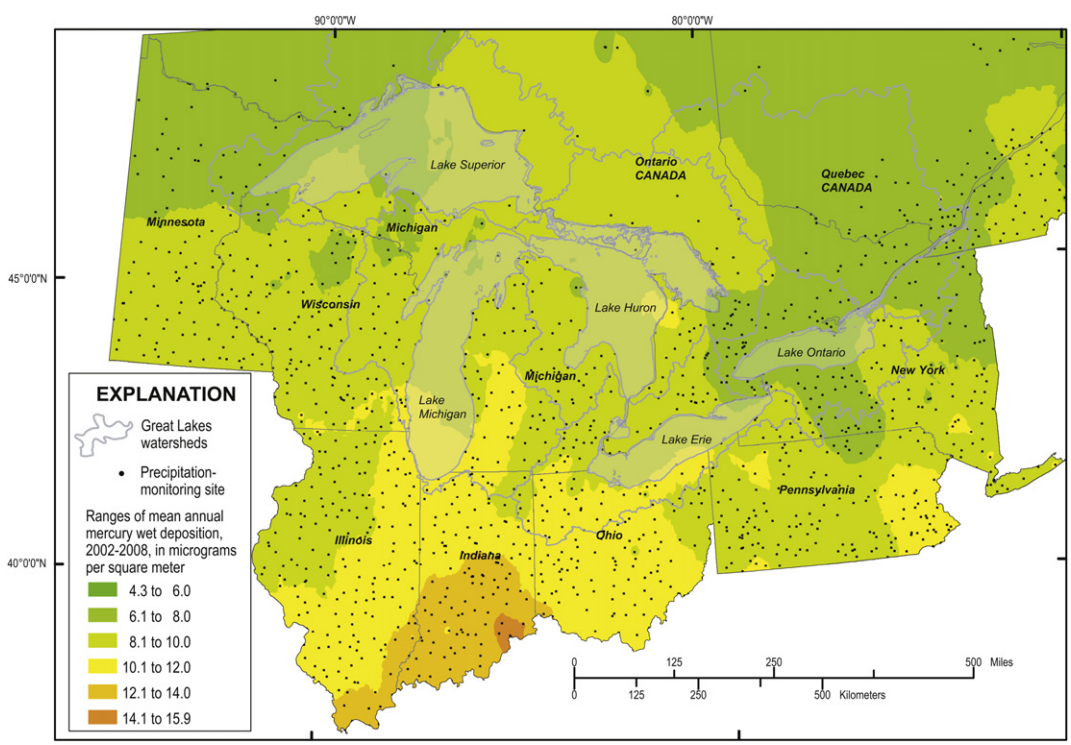

Fig. 8. Seven-year mean annual Hg wet deposition in the Great Lakes region, 2002–2008.

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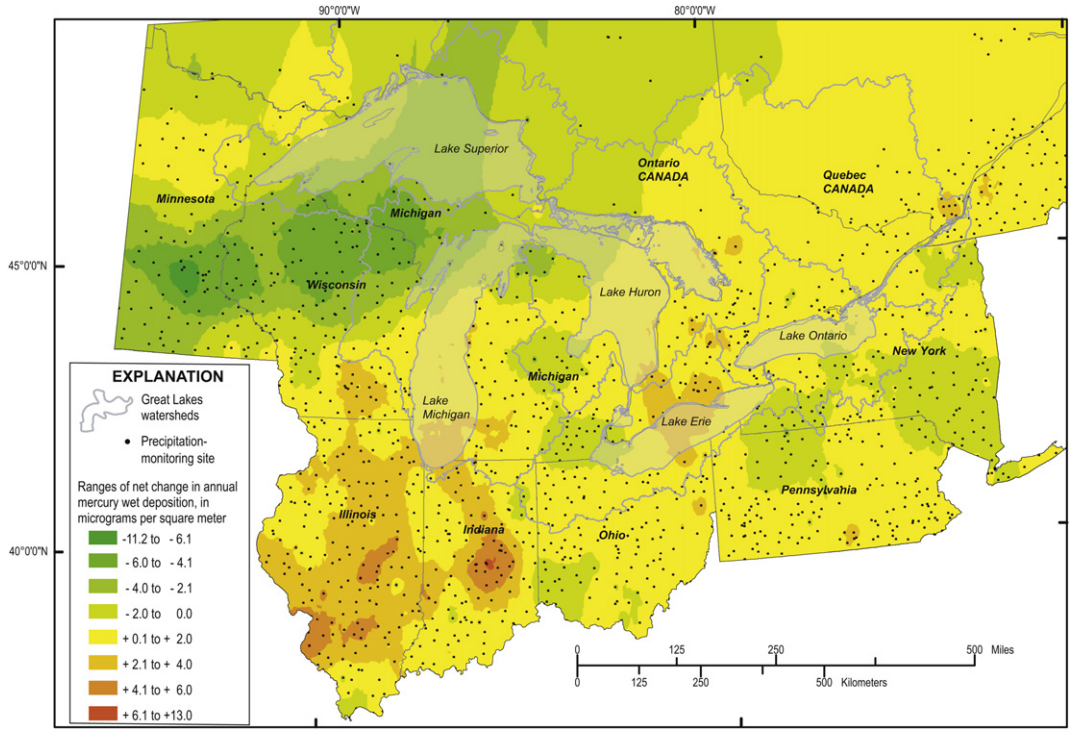

Fig. 9. Net changes in annual Hg wet deposition in the Great Lakes region, 2002–2008.

episodes of high Hg deposition affects annual Hg deposition at sites in a network (VanArsdale et al., 2005). Episodes of high Hg deposition typically have high Hg concentrations and high precipitation depths (Keeler et al., 2006; Risch and Fowler, 2008), and they can contribute approximately 10–15 percent of the long-term annual Hg deposition at a site (Keeler et al., 2005; Risch and Fowler, 2008). The location of precipitation events with respect to major Hg emissions sources can influence Hg concentrations and Hg deposition at a monitoring site too. In our study, we did not examine episodes of high Hg deposition or the effects of precipitation events on Hg deposition.

3.4. Spatial patterns and temporal trends

3.4.1. Regional and subregional

Tests for temporal trends in Hg concentrations, precipitation depths, and Hg deposition within the entire Great Lakes region were made by using the combined weekly data from the 33 Hg-monitoring sites. Tests for temporal trends in geographic subregions of our study area were made by subjectively dividing the 33 Hg-monitoring sites into 3 groups—western, eastern, and southern. The 11 western sites are in Minnesota and Wisconsin; the 16 eastern sites are in Michigan, Pennsylvania, New York, Ontario, and Québec; and the 6 southern sites are in Indiana and Illinois (Supplemental Data Table T1).

A significant temporal trend of decreasing weekly Hg concentrations was determined for the entire region at a 90-percent confidence level, but the 7-year change was small (Table 2) and below the limits of measurement variability determined by Wetherbee et al. (2007). Significant trends in weekly precipitation depths or Hg deposition were not observed for the entire region. Two trends were determined for the southern subregion – decreasing weekly Hg concentrations and increasing weekly precipitation depths, both at the 95-percent confidence level. The 7-year change in Hg concentrations for this subregion was −1.1 ng/L (Table 2), again below the limits of measurement variability. Significant trends in Hg concentrations, precipitation depths, or Hg deposition were not observed for the eastern and western subregions. Trends in these same measurements were not identified for 7 of the 11 sites in the western subregion or for 3 of the 6 sites in the southern subregion (Fig. 5).

3.4.2. Localized conditions

Five localized conditions were identified with respect to the spatial patterns and temporal trends for Hg concentration, precipitation depth, and Hg deposition in the region during 2002–2008.

(1) *Local relations of Hg concentrations and precipitation depths to Hg deposition.* Mean annual Hg concentrations higher than the 12 ng/L water-quality criterion and mean annual precipitation depths that ranged 120–140 cm resulted in mean annual Hg deposition higher than 14 μg/m^2 in southeastern Indiana (Figs. 3 and 6, and 8). Where mean annual precipitation depths ranged 120–140 cm and mean annual Hg concentrations were 8–9 ng/L, mean annual Hg deposition was 10–12 μg/m^2 in eastern Pennsylvania (Figs. 3 and 6, and 8). Where mean annual Hg concentrations were higher than 12 ng/L and mean annual precipitation depths ranged 80–100 cm, mean annual Hg deposition was 10–12 μg/m^2 in central Michigan (Figs. 3 and 6, and 8). In southwestern Indiana and southern Illinois, mean annual Hg deposition was 10–12 μg/m^2, but there are no monitoring sites to measure Hg concentrations, leading to more uncertainty about annual Hg deposition in this part of the region. This limitation was described by Risch and Fowler (2008).

(2) *Local increases in Hg concentrations, precipitation depths, and Hg deposition.* An increase in annual Hg concentrations (+2 to +4 ng/L net change) and an increase in annual precipitation depths (+20 to +40 cm) resulted in an increase in annual Hg

deposition (+4 to +6 μg/m^2 net change) in central Indiana (Figs. 4 and 7, and 9). No temporal trends were identified in weekly data for IN26 in central Indiana. An increase in annual Hg concentration (+1 to +2 ng/L net change) and an increase in annual precipitation (+20 to +40 cm) resulted in an increase in annual Hg deposition (+4 to +6 μg/m^2 net change) in central Illinois (Figs. 4 and 7, and 9). A significant trend in weekly Hg concentrations was determined for IL11 in central Illinois, with a 7-year change of +1.9 ng/L (Fig. 5, Table 2). Trends in weekly precipitation depths or Hg deposition were not identified at IL11.

(3) *Local trends of increasing Hg concentrations.* Significant trends in weekly Hg concentrations were identified for 4 sites in eastern Pennsylvania (PA00, PA47, PA60, and PA90), with 7-year changes of +1.5 to +2 ng/L (Fig. 5, Table 2). A significant trend in weekly Hg deposition and precipitation depth was not identified at 3 of these sites; a trend of decreasing weekly Hg deposition and precipitation depth was determined for PA47. Relatively small increases or no changes were observed in annual Hg concentrations, annual precipitation depths, and annual Hg deposition in eastern Pennsylvania (Figs. 4 and 7, and 9).

(4) *Local trends of decreasing Hg concentrations and increasing precipitation depths.* Significant trends of decreasing weekly Hg concentrations with 7-year changes of −2.1 to −4.1 ng/L were determined for 6 sites—WI99, WI22, GRD, DXT, IN34, and IN20 (Fig. 5, Table 2). Significant trends of increasing weekly precipitation depths were determined for 4 of these 6 sites—WI99, WI22, IN34, and IN20, and for another nearby site, WI31 (Fig. 5). No significant trends in weekly Hg deposition were identified for the first 6 sites, even though a trend of increasing weekly Hg deposition was identified for WI31. These sites are in an area around Lake Michigan in southeastern Wisconsin, northeastern Illinois, northwestern Indiana, and southern Michigan that showed a decrease in annual Hg concentrations (−2 to −4 ng/L net change) and an increase in annual precipitation depth (+40 to +60 cm net change), while annual Hg deposition showed a relatively small increase or was unchanged (Figs. 4 and 7, and 9). One potential explanation for this condition around Lake Michigan is that increased precipitation depths caused the decreased Hg concentrations through a dilution effect. A decrease in annual Hg concentration associated with increased annual precipitation depths was reported by Prestbo and Gay (2009) for MDN sites in this area for 1996–2005.

The site PA30 on southern Lake Erie showed a trend of decreasing Hg concentration with a 7-year change of −1.1 ng/L, but no trend in precipitation depth was apparent (Fig. 5). The area around Lake Erie showed a decrease in annual Hg concentrations (−1 to −2 ng/L net change, Fig. 4) and an increase in annual precipitation depths (+20 to +40 cm, Fig. 7). Because the decreases in Hg concentration were below the limits of measurement uncertainty, these data cannot resolve whether the area with decreasing Hg concentration and increasing precipitation depths around southern Lake Michigan extends eastward to include the area around Lake Erie.

(5) *Local decreases in annual Hg concentrations, precipitation depths and Hg deposition.* A decrease in annual Hg concentrations (−2 to −3 ng/L net change) and annual precipitation depths (−20 to −40 cm net change) resulted in a decrease in annual Hg deposition (−4 to −6 μg/m^2 net change) in northern Wisconsin, eastern Minnesota, and the Upper Peninsula of Michigan (Figs. 4 and 7, and 9). Two sites in this area (WI09 and PLN) showed significant trends of decreasing weekly Hg deposition and precipitation depth but no trend in weekly Hg concentrations. None of the Hg-monitoring sites showed spatially coincident trends of decreasing weekly Hg concentrations and weekly Hg deposition, although Prestbo and Gay (2009) did report this kind of trend for MDN sites in the northeastern USA during 1996–2005.

4. Conclusions

Data from 3 Hg wet-deposition-monitoring networks and 2 precipitation-monitoring networks in the USA and Canada, for 2002–2008, were combined to assess spatial patterns and temporal trends in 8 states and 2 provinces in the Great Lakes Region. Spatial patterns of annual Hg wet deposition were examined by generating high-resolution maps based on annual Hg concentrations at 37 sites and annual precipitation depths at 1541 sites. Temporal trends in weekly data at 33 sites were determined by means of statistical techniques.

Areas in southern Indiana and Illinois, eastern Pennsylvania, and central Michigan had mean annual Hg wet deposition of 10–14 μg/m^2 related to annual Hg concentrations higher than 12 ng/L, annual precipitation depths of 120–140 cm, or both. Locally, changing annual Hg concentrations and precipitation depths increased Hg deposition +4 to +6 μg/m^2 in central Indiana and Illinois and decreased Hg deposition −4 to −6 μg/m^2 in northern Wisconsin, eastern Minnesota and the Upper Peninsula of Michigan. A spatial pattern of decreasing annual Hg concentrations and increasing annual precipitation depths near Lake Michigan in southern Wisconsin, southern Michigan, northern Illinois and northern Indiana included 6 sites with significant 7-year temporal trends of decreasing weekly Hg concentrations and increasing precipitation depths.

During 2002–2008, Hg wet deposition was found to be unchanged in the Great Lakes region and its subregions. Significant 7-year trends in weekly Hg wet deposition did not spatially coincide with trends in weekly Hg concentrations. Generally, any small decreases in Hg concentrations apparently were offset by increases in precipitation depths. Although Hg emissions data were not analyzed in our study, 7 years of monitoring data indicated that atmospheric Hg continues to be deposited to Great Lakes ecosystems without a long-term downward trend. Continued monitoring could detect whether these observations are consistent over a longer time period.

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The authors dedicate this paper to the fond memory and lasting scientific legacy of our friend and colleague from the University of Michigan, Dr. Gerald Jerry Keeler (1960–2011). The mercury tribe is small and we have lost an elder of the tribe who will be truly missed.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2011.05.030.

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