ONLINE SUPPLEMENTARY DATA

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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Methods for operation of Hg-monitoring networks

Mercury Deposition Network

The Mercury Deposition Network (MDN) collected weekly composite samples of liquid and frozen precipitation by using uniform procedures and equipment (National Atmospheric Deposition Program, 2010). In the MDN, each site had an automated collector that opened and closed when a sensor reacted to presence and absence of precipitation. The opened collector accumulated precipitation via a glass sampling train that included a bottle precharged with an acid preservative. The collector had a heater to melt frozen precipitation in the sampling train and a fan for ventilation in hot weather. An operator exchanged the sampling train on a weekly schedule, and samples were analyzed for total Hg at a central laboratory (Frontier Geosciences, Inc. in Seattle, Wash.). A rain gage at the site measured a continuous record of weekly precipitation. The Hg concentration in the sample, weekly precipitation amount, and computed weekly Hg wet deposition (concentration multiplied by precipitation) are archived in an online data base maintained by the NADP.

Michigan Mercury Monitoring Network

The Michigan Mercury Monitoring Network was operated for the Michigan Department of Environmental Quality by the University of Michigan Air Quality Laboratory (UMAQL). Samples of liquid and frozen precipitation were collected by an automated collector that opened when a sensor reacted to precipitation. The opened collector accumulated precipitation via a glass and Teflon sampling train until the precipitation ended. Frozen precipitation in the sampling train was melted by a heater in the base of the collector. A “daily-event-based sampling” method was used (Landis and Keeler, 1997; Keeler et al., 2006) in which an operator installed a new sampling train in the collector daily, using clean techniques, after each precipitation event. Samples were analyzed for total Hg at the UMAQL; analysis also included a suite of trace elements and major ions. A rain gage at the site measured a continuous record of precipitation.

Integrated Atmospheric Deposition Network

The IADN used methods similar to the MDN and collected weekly composite samples of liquid and frozen precipitation using uniform procedures and equipment. Each IADN site had an automated collector that opened and closed when a sensor reacted to precipitation. The opened collector accumulated precipitation through a glass sampling train that included a bottle pre-charged with an acid preservative. The collector had a heater to melt frozen precipitation in the sampling train and a fan for ventilation in hot weather. An operator exchanged the sampling train on a weekly schedule. Samples were analyzed for total Hg at Frontier Geosciences, Inc. (2002) and Flett Research Ltd. In Winnipeg, Manitoba (2003–2008); data were cross-checked at the Environment Canada National Laboratory for Environmental Testing in 2005–2006. A rain gage at the site measured a continuous record of weekly precipitation. The Hg concentration in the sample, weekly precipitation amount, and computed weekly Hg wet deposition (concentration multiplied by precipitation) are archived on a secure server.

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Methods for selection of Hg-monitoring sites for spatial and statistical analysis

In the Great Lakes region, more than 40 Hg-monitoring sites in the USA and Canada were operated before 2008. Generally, fewer than 15 sites operated annually before 2001 and approximately 30 or more sites operated annually after 2001. For this study, a selection method was used to include as many of these sites as possible while excluding incomplete annual data sets and sites with short-term records. The aim of site selection was spatial coverage of the entire Great Lakes region and an optimal representation of data from 2002–2008 at the sites. Candidate Hg-monitoring sites had to operate during 2002–2008. The annual data record for each site had to be at least 75 percent complete. The annual data for a site met the completeness criteria if valid samples were collected for 39 or more weeks in a year, whether or not precipitation was measured during those weeks. A site was used for spatial analysis of annual data if at least 5 of the 7 years during 2002–2008 had annual data records that were at least 75 percent complete. A site was used for statistical trends analysis if all 7 years during 2002–2008 had annual data records that were at least 75 percent complete. Samples with dry and trace precipitation and those with missing concentrations were excluded from these analyses.

Methods for calculating annual Hg concentrations

Annual Hg concentrations for the MDN sites were provided by the NADP. The NADP used weekly precipitation-volume-weighted mean Hg concentration in valid samples, as explained in Prestbo and Gay (2009) and National Atmospheric Deposition Program (2010). The precipitation-volume-weighted mean adjustment normalizes the bias from high Hg concentrations in samples with low sample volumes. Annual Hg concentrations for the Michigan Monitoring Network sites were calculated by the UMAQL, using a precipitation-volume-weighted mean procedure identical to that for the MDN. Annual Hg concentrations for the IADN sites were calculated as the annual sum of the precipitation-volume-weighted mean weekly Hg concentrations in valid samples.

Methods for preparing isopleth maps

The following methods were used to prepare isopleth maps of annual Hg concentrations, annual precipitation depths, and annual Hg wet deposition in the Great Lakes region for 2002–2008. The software in a geographic information system (ArcGIS 9.3, ESRI, 2009) was used to analyze a map grid of the 8 states and 2 provinces in the Great Lakes region, with grid cells that were 5.5 km by 5.5 km. The software applied an algorithm that interpolated between the measured values at monitoring sites in some map-grid cells. Estimated (interpolated) values were assigned to the cells in the map grid that did not have measured values. The software used the inverse-distance-weighting (IDW) algorithm, which is a linearly weighted combination of sample points. The IDW used a variable search radius with a minimum of 12 points. The weight is a function of the inverse of the distance raised to a power. For the Hg-concentration IDW grid maps based on a maximum of 37 points, a power of 2 was used, which emphasizes nearer points and gives a less smooth interpolated surface. For precipitation-depth and Hg-deposition IDW grid maps based on approximately 1500 points, a power of 0.7 was used, which emphasizes points farther away and gives a smoother interpolated surface. An isopleth map was made from each IDW-interpolated map grid. Isopleth bands generated by the GIS software spatially connected grid cells that had the same value; homogeneity in the spatial distribution of values within isopleth regions of the grid is assumed. The range of values represented by each isopleth color band for a parameter (Hg concentration, precipitation depth, or Hg deposition) was applied consistently to all the maps for 2002–2008 and coordinated so that green shades indicate lower ranges of values, yellow are middle range, and orange to red shades are higher ranges of values.

Making an annual Hg wet-deposition map required six steps: (1) A map grid was made with the annual Hg concentration data. (2) A map grid was made with the annual precipitation depth data. (3) The Hg-concentration map grid was overlaid on the precipitation map grid, and a Hg concentration was assigned to every precipitation site. (4) For the cells with the known annual precipitation, the annual Hg concentration was multiplied by the annual precipitation to obtain the annual Hg wet deposition.

This calculation of annual Hg wet deposition applied to as many as 1541 precipitation-monitoring sites. (5) The inverse-distance-weighting algorithm was used to interpolate the annual Hg wet deposition for the rest of the cells in the new map grid of annual Hg wet deposition. (6) An isopleth map of wet deposition was made with the interpolated map grid from step 5. Isopleth bands generated by the software spatially connected grid cells that had the same value and represented different ranges of annual Hg wet deposition.

Statistical tests for determining temporal trends in weekly data

The nonparametric Seasonal Kendall Trend Test (SKTT; Gilbert, 1987) was used to identify significance of temporal trends in weekly data. The SKTT is a generalized Mann-Kendall test appropriate for data with seasonal differences. The SKTT is a nonparametric test that requires no assumptions about data distributions and is not greatly affected by outliers or missing data. The SKTT compares each sequential observation over time to all subsequent observations. It determines and scores whether the difference (change) in values is an increase (score +1), a decrease (score –1), or no change (score 0). Observations are compared only within the same season to account for seasonal differences. In the analysis for this paper, months signified separate seasons, so all the weekly data from January of any year were compared only to data from January of other years. Once the observations are scored, the results are summed over all months and years. Determinations of statistical significance in trends over time are a test of the sum of changes compared to no changes. In this study, trends are reported at the 90-percent ($\alpha = 0.10$) and 95-percent ($\alpha = 0.05$) confidence levels.

The magnitude of trends was determined by using the Seasonal Kendall Slope Estimator (SKSE; Gilbert, 1987). The SKSE trend is the median of all the individual SKTT changes, and the direction is indicated by the sign (negative is a decrease; positive is an increase). When all changes are calculated and annualized for a site, they are ranked highest to lowest. The median for all seasons and years is identified as the most likely annual rate of change for a site.

Calculation of net change in annual data

The net change in annual Hg concentration, annual precipitation depth, or annual Hg wet deposition is the sum of the interannual (year-to-year) differences and was calculated for each site by means of the following equation. If the net change was a positive number, an increase was indicated. If the net change was a negative number, a decrease was indicated.

$$\textit{Net Change} = \sum_{x=0}^{x=5} y_{2002+(x+1)} - y_{2002+x}$$

y = value of annual Hg concentration, annual Hg wet deposition, or annual precipitation for year indicated

Table T1. Characteristics of mercury-monitoring sites in the Great Lakes Region, 2002–2008.

Site identification	Abbreviated site name	State/Province	Latitude (decimal degrees)	Longitude (decimal degrees)	Elevation (meters)	Network[a]	Annual maps	Temporal trends[b]	Great Lakes subregion	Watershed
IL11	Bondville	Illinois	40.0528	-88.3719	212	MDN	x	x	Southern	Mississippi River
IN20	Roush Lake	Indiana	40.8401	-85.4639	244	MDN	x	x	Southern	Mississippi River
IN21	Clifty Falls	Indiana	38.7622	-85.4202	256	MDN	x	x	Southern	Mississippi River
IN26	Fort Harrison	Indiana	39.8583	-86.0208	260	MDN	x	x	Southern	Mississippi River
IN28	Bloomington	Indiana	39.1464	-86.6133	256	MDN	x	x	Southern	Mississippi River
IN34	Indiana Dunes	Indiana	41.6318	-87.0881	208	MDN	x	x	Southern	Lake Michigan
DXT	Dexter	Michigan	42.4000	83.9000	267	MMMN	x	x	Eastern	Lake Erie
EGL	Eagle Harbor	Michigan	47.4631	88.1497	185	MMMN	x			Lake Superior
GRD	Grand Rapids	Michigan	47.5592	93.4667	617	MMMN	x	x	Eastern	Lake Michigan
MI48	Seney Refuge	Michigan	46.2875	-85.9541	216	MDN	x			Lake Michigan
PLN	Pellston	Michigan	45.5525	84.7844	238	MMMN	x	x	Eastern	Lake Huron
MN16	Marcell Forest	Minnesota	47.5311	-93.4686	431	MDN	x	x	Western	Mississippi River
MN18	Fernberg	Minnesota	47.9464	-91.4961	524	MDN	x	x	Western	Mississippi River
MN22	Mille Lacs	Minnesota	46.2053	-93.7589	384	MDN	x			Mississippi River
MN23	Camp Ripley	Minnesota	46.2494	-94.4972	410	MDN	x	x	Western	Mississippi River
MN27	Lamberton	Minnesota	44.2369	-95.3010	343	MDN	x	x	Western	Mississippi River
NY20	Huntington	New York	43.9731	-74.2231	500	MDN	x	x	Eastern	St. Lawrence River
NY68	Biscuit Brook	New York	41.9936	-74.5031	634	MDN	x			Hudson River
BRT	Burnt Island	Ontario	45.8000	-82.9500	184	IADN	x	x	Eastern	Lake Huron
ON07	Egbert	Ontario	44.2333	-79.7833	251	MDN	x	x	Eastern	Lake Huron
PTR	Point Petre	Ontario	43.8300	-77.1500	78	IADN	x	x	Eastern	Lake Ontario
PA00	Arendtsville	Pennsylvania	39.9231	-77.3078	269	MDN	x	x	Eastern	Susquehanna River
PA13	Allegheny Portage	Pennsylvania	40.4570	-78.5600	739	MDN	x	x	Eastern	Mississippi River
PA30	Erie	Pennsylvania	42.1558	-80.1134	177	MDN	x	x	Eastern	Lake Erie
PA37	Holbrook	Pennsylvania	39.8161	-80.2850	452	MDN	x	x	Eastern	Mississippi River

Table T1. Characteristics of mercury-monitoring sites in the Great Lakes Region, 2002–2008--continued.

Site identification	Abbreviated site name	State/Province	Latitude (decimal degrees)	Longitude (decimal degrees)	Elevation (meters)	Network[a]	Annual maps	Temporal trends[b]	Great Lakes subregion	Watershed
PA47	Millersville	Pennsylvania	39.9900	-76.3862	85	MDN	x	x	Eastern	Susquehanna River
PA60	Valley Forge	Pennsylvania	40.1166	-75.8833	46	MDN	x	x	Eastern	Delaware River
PA72	Milford	Pennsylvania	41.3273	-74.8199	212	MDN	x	x	Eastern	Delaware River
PA90	Hills Creek	Pennsylvania	41.8043	-77.1903	476	MDN	x	x	Eastern	Susquehanna River
PQ04	St. Anicet	Québec	45.2000	-74.0333	49	MDN	x	x	Eastern	St. Lawrence River
WI08	Brule River	Wisconsin	46.7466	-91.6055	207	MDN	x	x	Western	Lake Superior
WI09	Popple River	Wisconsin	45.7964	-88.3994	421	MDN	x	x	Western	Lake Michigan
WI22	Milwaukee	Wisconsin	43.0752	-87.8843	206	MDN	x	x	Western	Lake Michigan
WI31	Devil's Lake	Wisconsin	43.4352	-89.6801	389	MDN	x	x	Western	Mississippi River
WI32	Middle Village	Wisconsin	44.9308	-88.7550	319	MDN	x	x	Western	Lake Michigan
WI36	Trout Lake	Wisconsin	46.0528	-89.6531	501	MDN	x	x	Western	Mississippi River
WI99	Lake Geneva	Wisconsin	42.5792	-88.5006	288	MDN	x	x	Western	Mississippi River

[a]MDN, Mercury Deposition Network; MMMN, Michigan Mercury Monitoring Network; IADN, Integrated Atmospheric Deposition Network

[b]Four sites included in the annual maps were excluded from temporal trends analysis because data were not available for all 7 years, 2002–2008 (EGL, MI48, MN22, and NY68).

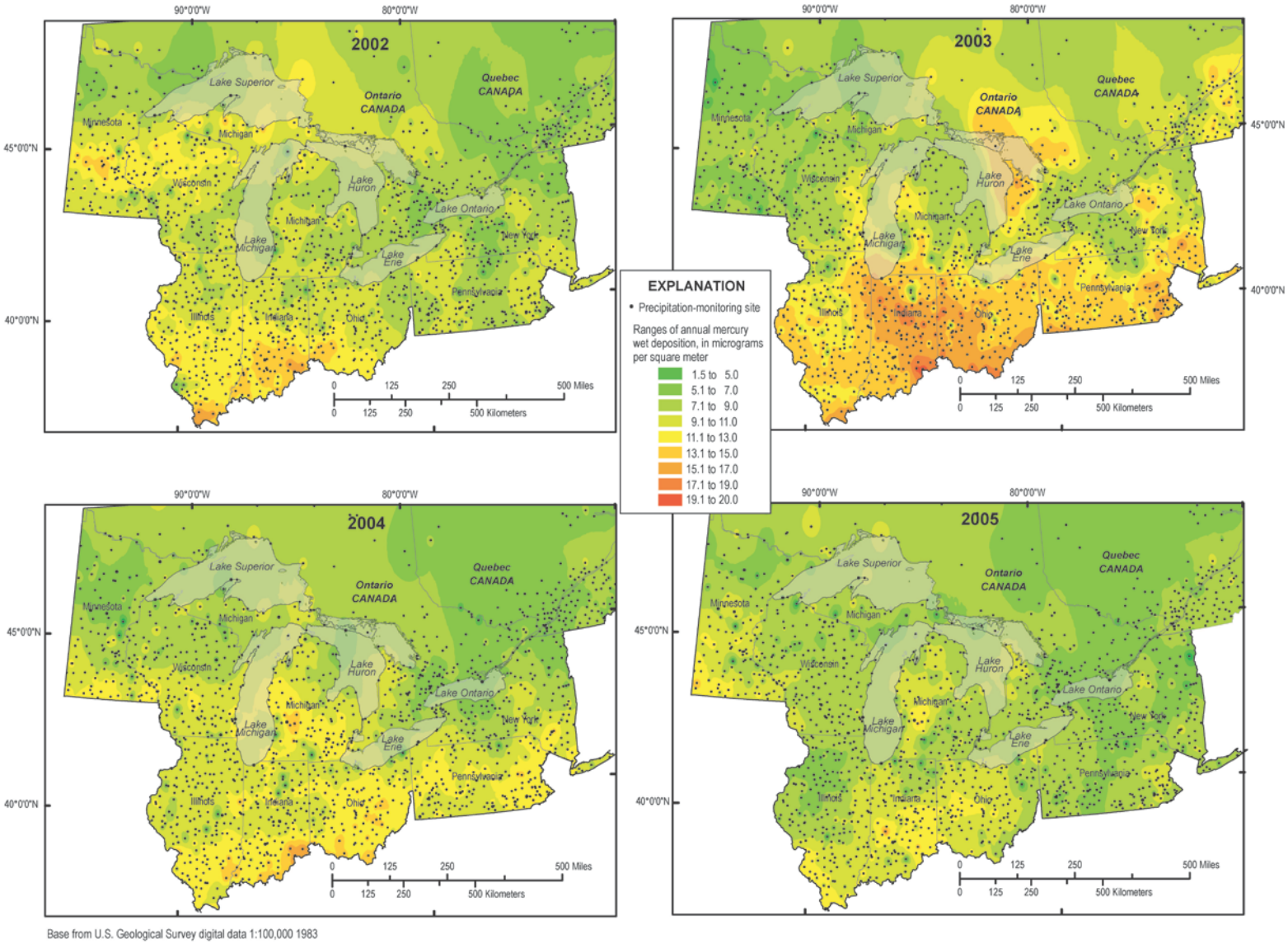

Figure F1. Annual Hg wet deposition in the Great Lakes region, 2002–2008.

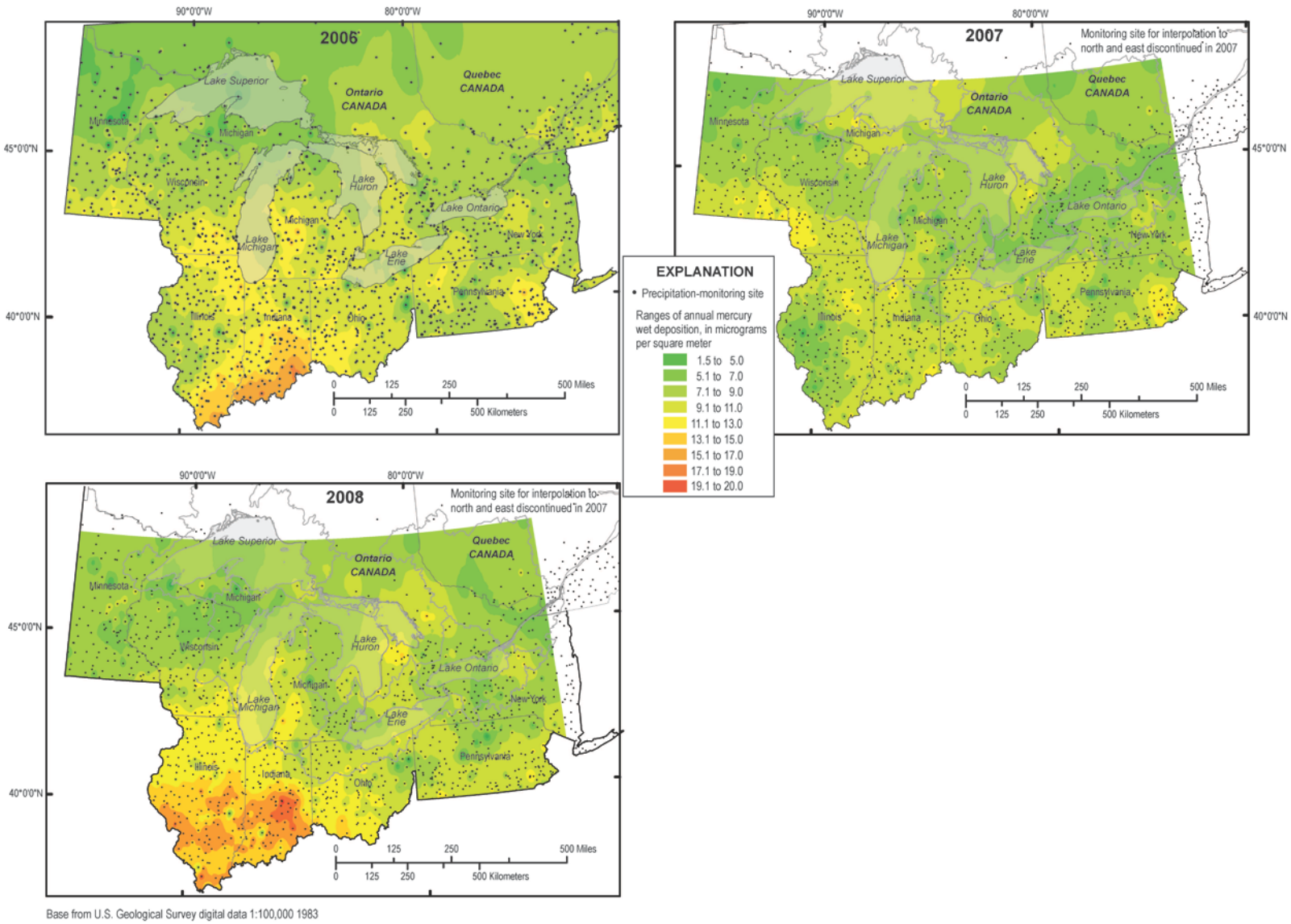

Figure F1. Annual Hg wet deposition in the Great Lakes region, 2002–2008—continued.