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Mercury Deposition in the Great Lakes Region

Technical Report

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1 Executive Summary

This report examines the amounts and trends in wet and dry (litterfall) deposition of mercury in the Great Lakes region, along with the limited records of mercury concentrations in the atmosphere in this region. These records derive from data collected as part of the National Atmospheric Deposition Program (NADP). This report draws on findings from published research studies to interpret the trends.

While trends in atmospheric concentrations of mercury are difficult to discern based on the limited data available, there are clear patterns in the spatial distribution and trends in both wet and litterfall dry deposition of mercury in the Great Lakes region. Both wet and litterfall deposition are highest in the southern areas near the Ohio River Valley and lowest in the far northern parts of the region. However, these regional differences have decreased over time. Wet deposition of mercury is slightly increasing in the northern part of the region, likely due to increased precipitation, but strongly decreasing in the south, likely in response to decreased mercury emissions. Trends in litterfall deposition are unclear in the north but decreasing in the southern part of the region, and additional work is needed to better characterize dry deposition within the Great Lakes regions. This work supports the findings of other studies that local and regional emissions sources contribute to mercury deposition in this region, likely in combination with global sources.

2 Introduction

Mercury is a neurotoxin that be detrimental to human health, affecting brain, heart, kidney, lung and immune health (U.S. EPA, 2022). Mercury exposure can interfere with the development of the nervous system in babies and young children. In the environment, exposure to methylmercury can harm wildlife, with high levels of exposure impacting growth and development, reproduction, and even causing death (U.S. EPA, 2022). Humans are primarily exposed to mercury via consumption of fish and shellfish that have bioaccumulated high levels of methylmercury (U.S. EPA, 2022; Obrist et al., 2018).

Mercury is released to the atmosphere, waters, and soils from a range of anthropogenic and natural sources (Figure 1). The atmosphere is a crucial reservoir for mercury cycling that receives primary and secondary emissions and redistributes mercury via transport and deposition (Obrist et al., 2018). In the atmosphere, mercury exists as gaseous elemental mercury (GEM, or Hg^0), gaseous oxidized mercury (GOM, Hg^{2+}, or Hg^{II}), or as particle-bound mercury (PBM). While in the atmosphere, mercury can be oxidized or reduced (GEM $\leftrightarrow$ GOM), it can dissolve into water ($Hg^{2+}_{(g)} \rightarrow Hg^{2+}_{(aq)}$), and it can adsorb onto or desorb from particles (Obrist et al., 2018). Mercury leaves the atmosphere via wet or dry deposition onto surfaces, including plants, soils, and water. Wet deposition primarily removes GOM and PBM (Zhang et al., 2016a; Obrist et al., 2018), whereas dry deposition primarily removes GEM (Zhang et al., 2016b; Risch et al., 2017). Roughly 75% of dry deposition is estimated to occur via litterfall, and most of the mercury in leaf tissue subject to litterfall is found in the leaf tissue itself due to stomatal uptake rather than on the leaf surface due to simple attachment (Risch et al., 2017). Over land, dry deposition of GEM is now believed to be greater than wet deposition of GOM in many regions, with litterfall being the dominant GEM deposition mechanism, particularly in regions with less precipitation (Obrist et al., 2018). This understanding is a shift from the previous belief that wet deposition of GOM was always the dominant process.

There are large reservoirs of mercury in soils and in aquatic systems, resulting from both atmospheric deposition and from direct releases to these media (Figure 1). Mercury can undergo further chemical transformations in these reservoirs, most notably being converted into methylmercury. This form of mercury is particularly toxic and can bioaccumulate in the food web, reaching dangerous levels in fish that may be consumed by humans (Obrist et al., 2018; Brigham et al., 2021).

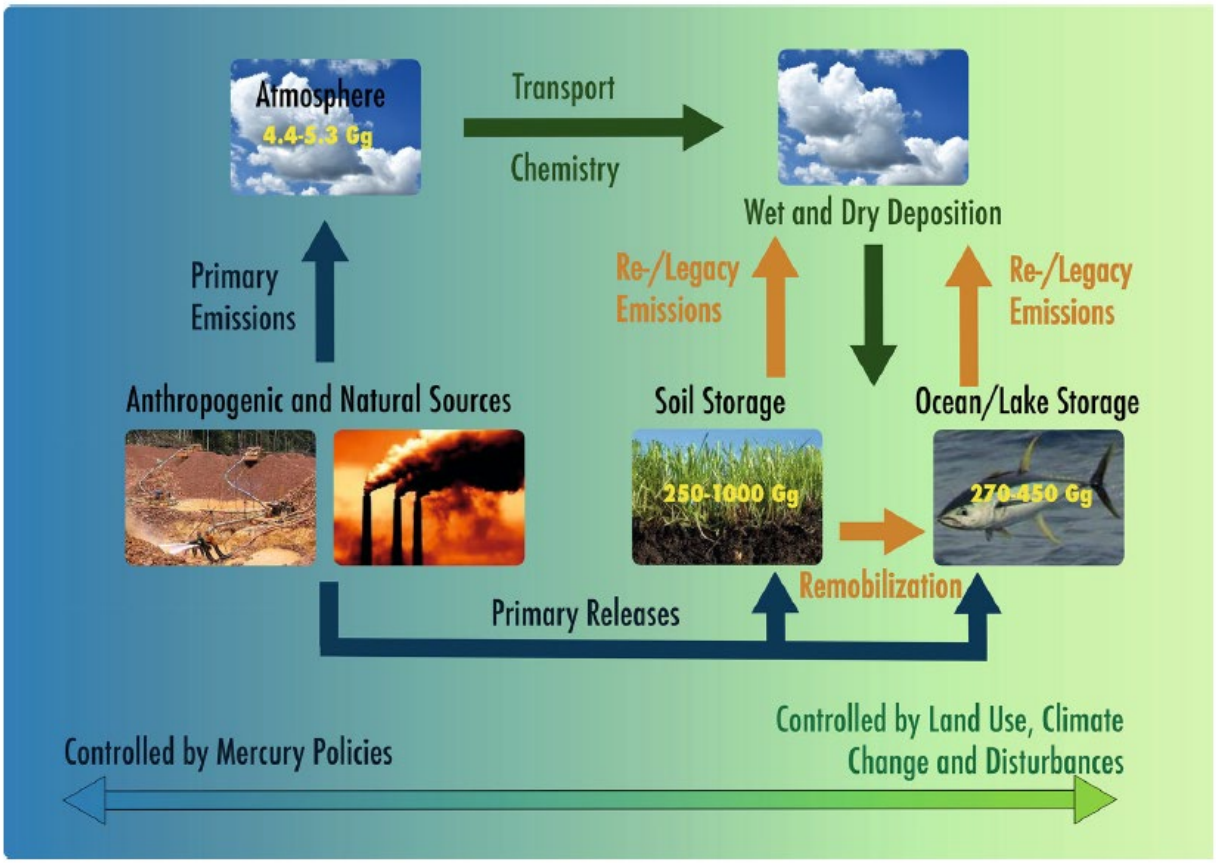

Figure 1. Overview of the global mercury cycle. Yellow numbers show the estimated amount of mercury in each global reservoir and arrows indicate exchange processes between reservoirs. From Obrist et al. (2018).

The National Atmospheric Deposition Program (NADP) has been monitoring levels of mercury in the atmosphere and in deposition reservoirs since the 1990s.[1] The most extensive NADP network for mercury measures wet deposition of GOM/PBM via the Mercury Deposition Network (MDN; Figure 2). NADP also operates the Mercury Litterfall Network (MLN) to measure dry deposition via litterfall and the Atmospheric Mercury Network (AMNet) to measure concentrations of GEM, GOM, and PBM in the air.

[1] https://nadp.slh.wisc.edu/.

Figure 2. Location of monitors in 2021 for the (left) Mercury Deposition Network (MDN), (middle) Mercury Litterfall Network (MLN), and (right) Atmospheric Mercury Network (AMNet) in the Great Lakes Region.

This report examines atmospheric mercury concentrations and wet and dry deposition of mercury within the Great Lakes states to better understand the sources of and trends in mercury concentrations and deposition in this region. This report includes new analyses of NADP mercury monitoring data, as well as a non-exhaustive review of the scientific literature. The report first examines trends in mercury emissions before looking at concentrations of gaseous and particle-bound mercury in the atmosphere. We then examine mercury amounts and trends in wet and dry deposition in the region and explore the factors influencing the trends. Finally, we discuss the insights that these studies provide into the sources of atmospheric mercury in the Great Lakes region.

3 Mercury Emissions

Total atmospheric emissions of mercury from U.S. sources decreased by 87% from 1990 to 2017, with similar reductions in the Canadian provinces of Manitoba and Ontario (Figure 3, Brigham et al., 2021). These emissions reductions resulted from decreases from a variety of types of sources. Mercury emissions from waste incineration and chlor-alkali plants decreased by more than 95% prior to 2002 (Weiss-Penzias et al., 2016). Mercury emissions from U.S. coal combustion decreased by 75% from 2005 to 2015, mainly due to co-benefits from controls on other pollutants (Zhang et al., 2016b). From 2010 to 2017, mercury emissions from electric generating units (EGUs) decreased by 86%, due in part to implementation of the Mercury and Air Toxics Standard (MATS), which was finalized in 2012 with implementation required by 2016 (U.S. EPA, 2022b). While North American emissions of mercury have decreased dramatically over the last several decades, global mercury emissions may have increased

through at least 2013, although there is no consensus on the direction or magnitude of the trend (Weiss-Penzias et al., 2016).

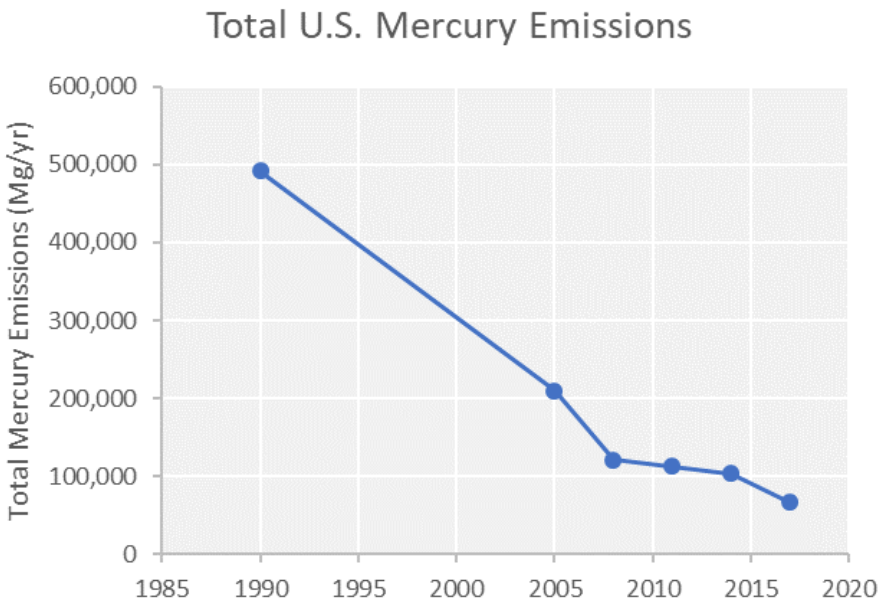

Figure 3. Trends in total U.S. mercury emissions. Data from the National Emissions Inventory (NEI) as reported in Brigham et al. (2021).

Mercury emissions from anthropogenic sources in the Great Lakes states decreased by amounts ranging from 21% in Indiana to 75% in Wisconsin from 2008 to 2017 (Figure 4). EGUs had the largest reductions in all states, with mercury emissions from EGUs decreasing by 58% in Illinois to 87% in Wisconsin. There were smaller reductions in the Industrial-Metals category in most states, with changes ranging from a 128% increase in Indiana to a 62% reduction in Michigan. Emissions from waste disposal sources increased in all states over this time.

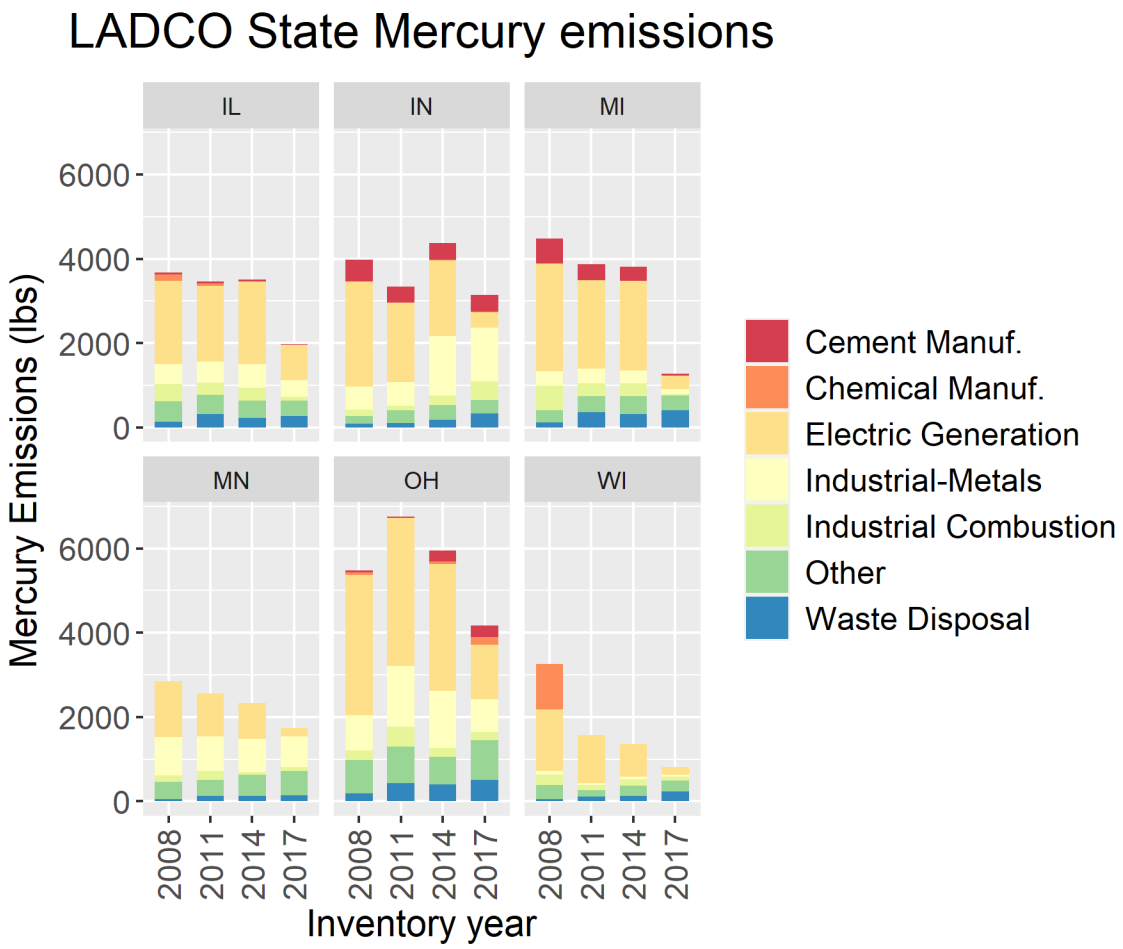

Figure 4. Annual mercury emissions (lbs) from sources in the Great Lakes states. Only source sectors accounting for at least 2% of the total emissions are shown individually; smaller sectors are grouped into the "other" category, which also includes categories labelled "not elsewhere classified" by the NEI. Data is from the NEI.[2]

Figure 5 shows the changes in the relative importance of different mercury emissions sources from 2008 to 2017 as a result of the emissions changes described above. In 2008, over half of the mercury emissions in the six Great Lakes states came from EGUs, whereas this source accounted for less than a quarter of emissions in 2017. In contrast, emissions from Industrial-Metals sources increased from 14% to 26% in this time, and waste disposal increased from just 3% to 14%. The map of mercury emissions from point sources in 2021 shown in Figure 5 illustrates the continuing and growing importance of metal mining and processing as a source of mercury emissions in the region. Almost all of the largest point sources of mercury in the six Great Lakes states (e.g., those sources that emitted more than 100 lbs of

[2] https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei.

mercury in 2021) were involved in metal mining or processing. These sources included steel mills, taconite processing facilities, and other metal processing facilities, as well as one coking plant.[3] Mercury emissions from EGUs fell into a second emissions tier, with lower emissions than the metals processing facilities as a result of existing regulatory programs for EGU emissions and a large number of EGU shutdowns.

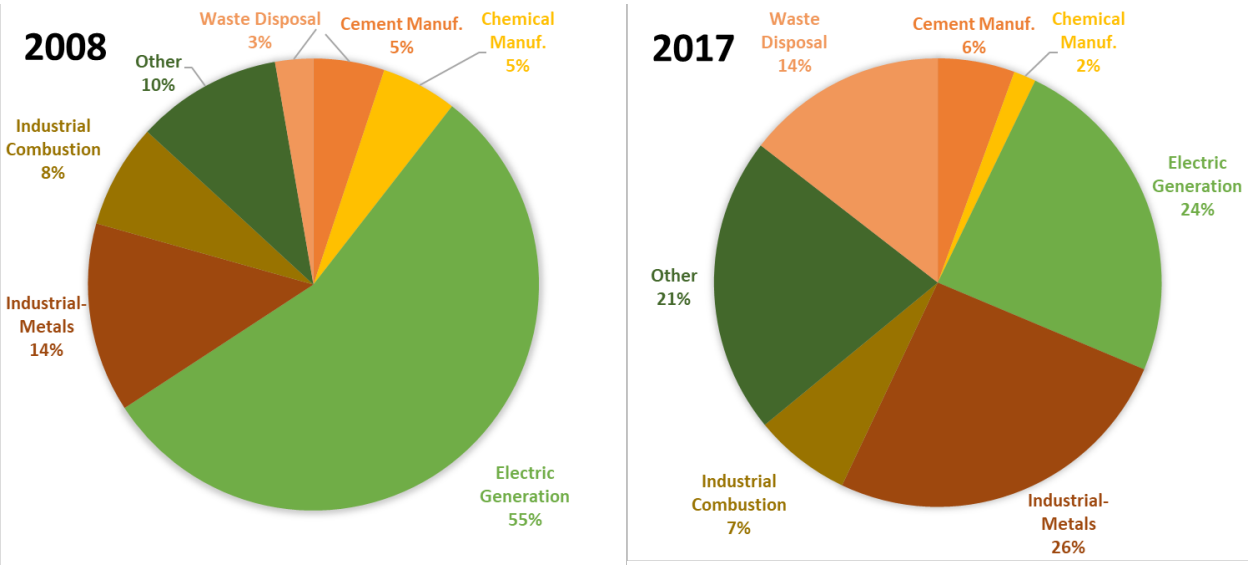

Figure 5. Comparison of mercury emissions source categories in (left) 2008 and (right) 2017 from the Great Lakes states. Data sources as described in Figure 4.

[3] Note that the map is missing a taconite facility in northern Michigan because these facilities were not included in EPA's Toxic Release Inventory.

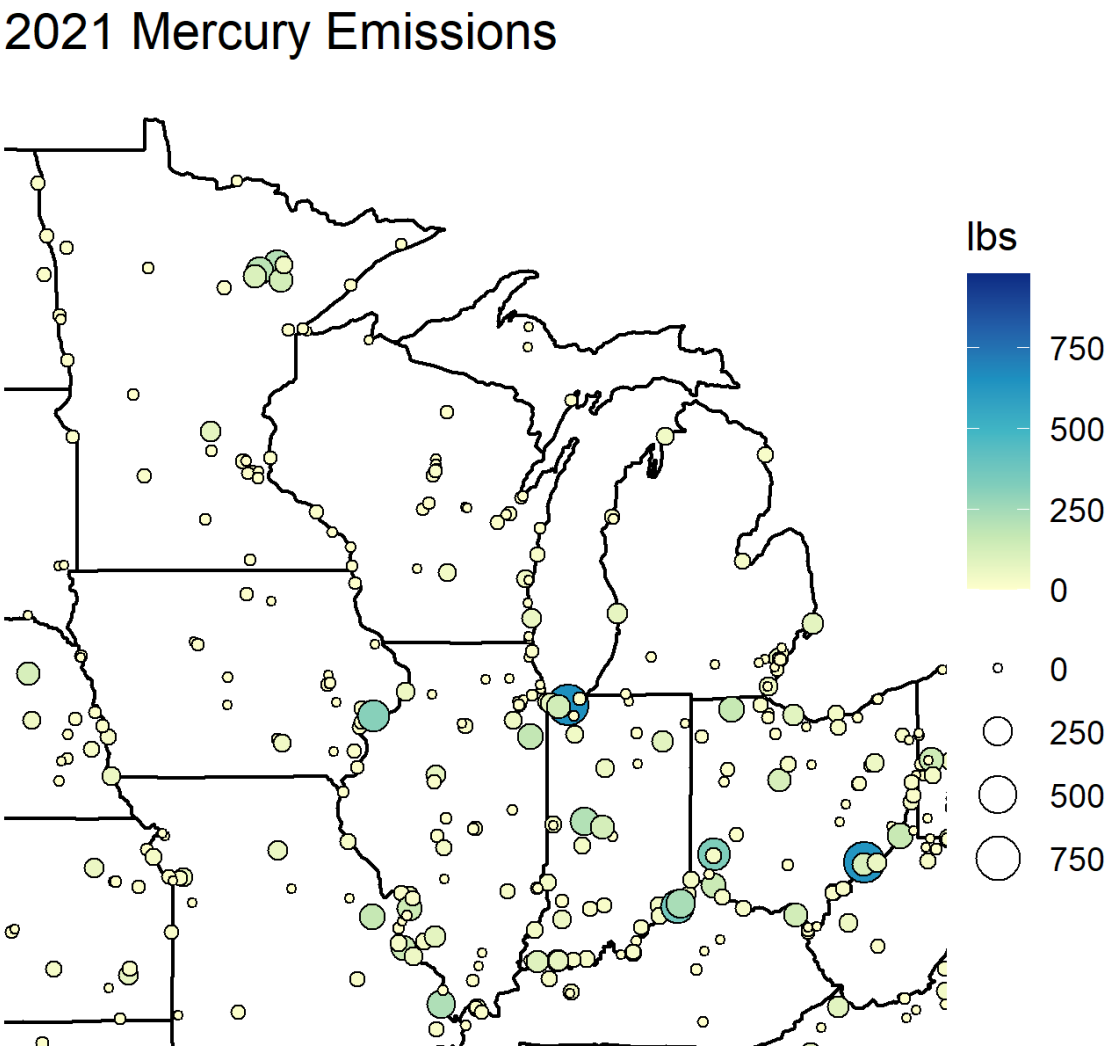

Figure 6. Map of mercury emissions (lbs) from point sources in 2021. Data for most states comes from EPA's Toxic Release Inventory (TRI)[4], and emissions for Minnesota come from Minnesota's point source air emissions inventory[5] and show only sources that emitted more than 1 lb of mercury.

4 Concentrations of Mercury in the Atmosphere

Atmospheric concentrations of GEM decreased by 1.2 to 2.1 % per year in the northern midlatitudes from 1990 to 2013 (Figure 7, Zhang et al., 2016b). In contrast, atmospheric mercury concentrations have been increasing in East Asia (Obrist et al., 2018). Figure 8 shows trends in GEM, GOM, and PBM concentrations at the few sites with routine monitoring in the Great Lakes region. Mercury

[4] https://edap.epa.gov/public/extensions/TRIToxicsTracker/TRIToxicsTracker.html

[5] https://public.tableau.com/app/profile/mpca.data.services/viz/Pointsourceairemissionsdata_v10_5-11130/Byfacility. We used a different data source for Minnesota because the TRI did not include the largest sources in the state: the taconite facilities in the northeast. The TRI also does not include a taconite facility in the Upper Peninsula of Michigan.

concentrations were measured at very few sites and for very few years at most of these sites. Many of the years contained incomplete data, making annual average concentrations less representative of the full-year concentrations. These limitations must be considered in interpreting this data. Based on the available data, GEM concentrations are similar at all sites and do not show any clear patterns for this time period, in contrast with the longer-term trends apparent in Figure 7. This may be because the decreases shown in Figure 7 have slowed in recent years or may be a fluke of the characteristics of the two sampling sites with somewhat complete records (WI07 and OH02). GOM concentrations were lower at the WI07 site than at the OH02 site, and concentrations appeared to decrease at both sites. There were no clear spatial differences in concentrations of PBM between sites, and trends in PBM concentrations aren't clear.

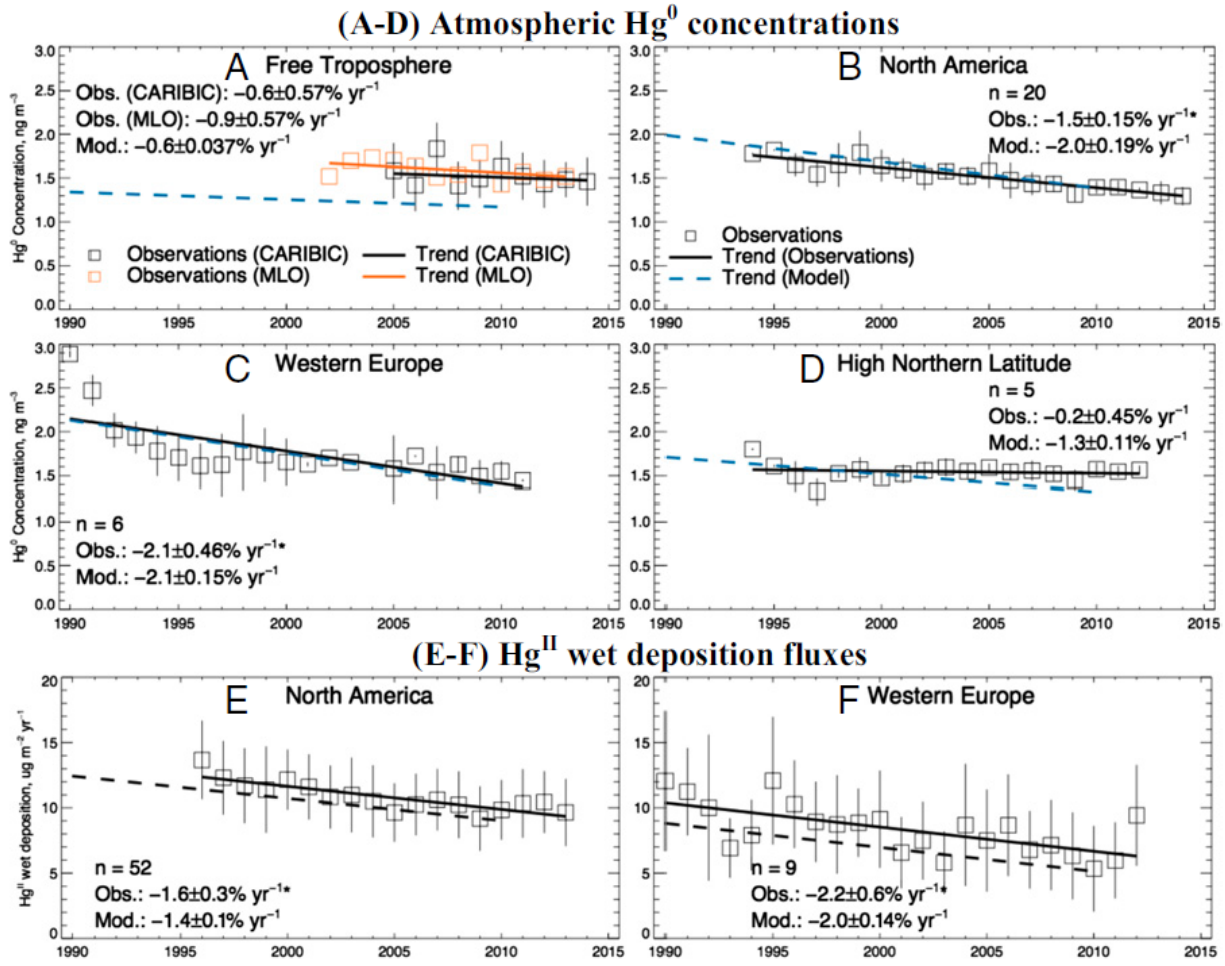

Figure 7. Trends in (top) atmospheric GEM (Hg^0) concentrations and (bottom) wet deposition of GOM (Hg^{II}) for different regions for 1990 through 2013 from Zhang et al. (2016b).

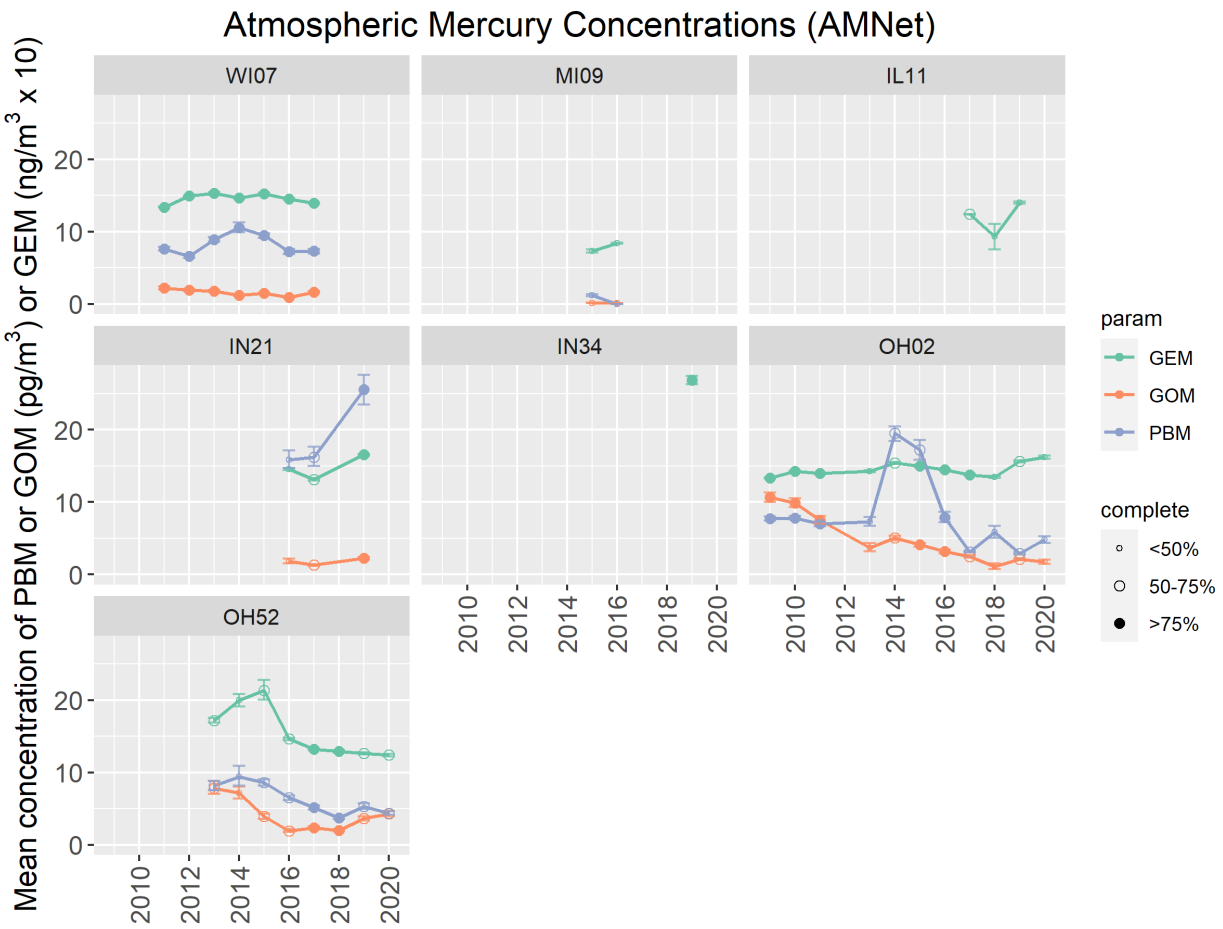

Figure 8. Timeseries of GEM (ng/m^3 x 10), GOM (pg/m^3), and PBM (pg/m^3) at all AMNet monitors in the Great Lakes states from 2009 through 2020. The point size and fill indicate the data completeness[6] for a year. The error bars show the 95th percentile confidence interval for the annual averages. Note the different units for the different parameters and that the GEM concentrations are shown multiplied by 10 to better visualize the trends. See Figure 16 in the Appendix for site locations.

5 Wet Deposition of Mercury

Wet deposition of GOM/PBM was monitored at a larger number of sites in the Great Lakes region for a longer time period than were atmospheric concentrations (Figure 9 and Figure 10). A spatial gradient in mercury wet deposition is apparent, with the highest deposition in the southern parts of the region and the lowest amounts in the northern parts (Figure 9). Risch and Kenski (2018) found that spatial patterns in wet deposition were driven primarily by differences in precipitation. Figure 17 in the Appendix shows

[6] Data completeness is determined as the percentage of days with valid data available for each year. Annual mean concentrations for years with more complete records should be given more weight than those with less complete records.

that precipitation was higher in the southern part of this region, suggesting that this is the main driver of these spatial patterns.

In the northern states of Minnesota, Wisconsin, and Michigan, mercury wet deposition has been flat to increasing, with the most consistent increases in Minnesota (Figure 10). These increases have been accompanied by increases in precipitation at many sites and in many years, with the clearest trends in Minnesota (Figure 19 and Figure 20 in the Appendix). In contrast, mercury concentrations at most sites decreased through 2012-16, with mixed trends into 2017-2021. Another study examined trends in wet deposition at two northern Minnesota sites (MN16 and MN18) through 2018 and found decreases in wet deposition at these sites through 2009 (Brigham et al., 2021). They concluded that these decreases were due to reductions in mercury emissions. Brigham et al. (2021) found that mercury deposition at these two sites was fairly steady from 2009 through 2018. The current study finds small but consistent increases in mercury wet deposition through 2021, accompanied by increases in precipitation and decreases in mercury concentrations. These findings suggest that over the last 15 or so years, wet deposition has been increasing due to increases in precipitation in northern states. One impact of climate change on these states has been an increase in precipitation (Kunkel et al., 2022), and this increased precipitation appears to be increasing wet deposition of mercury in these northern states.

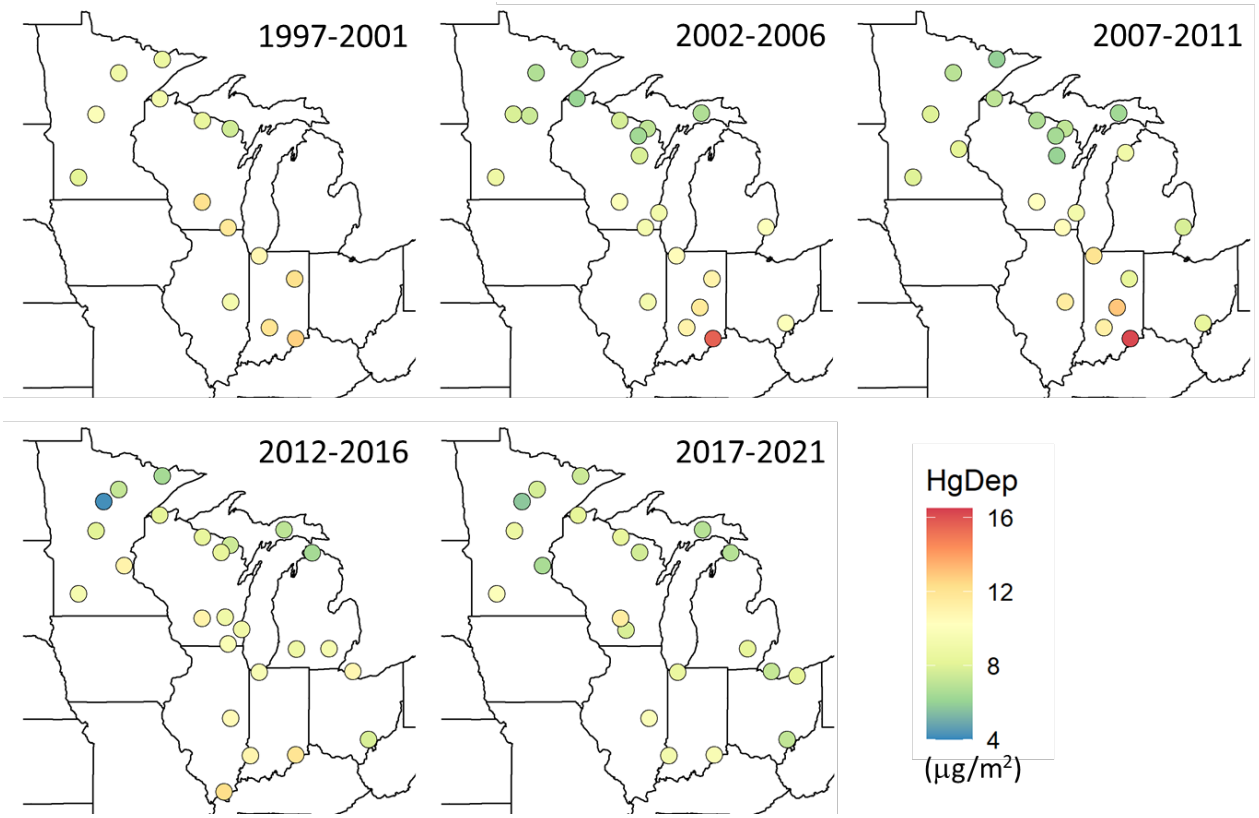

Figure 9. Maps of wet deposition of mercury (μg/m^2) measured at MDN sites around the region. Data are shown as 5-year averages.

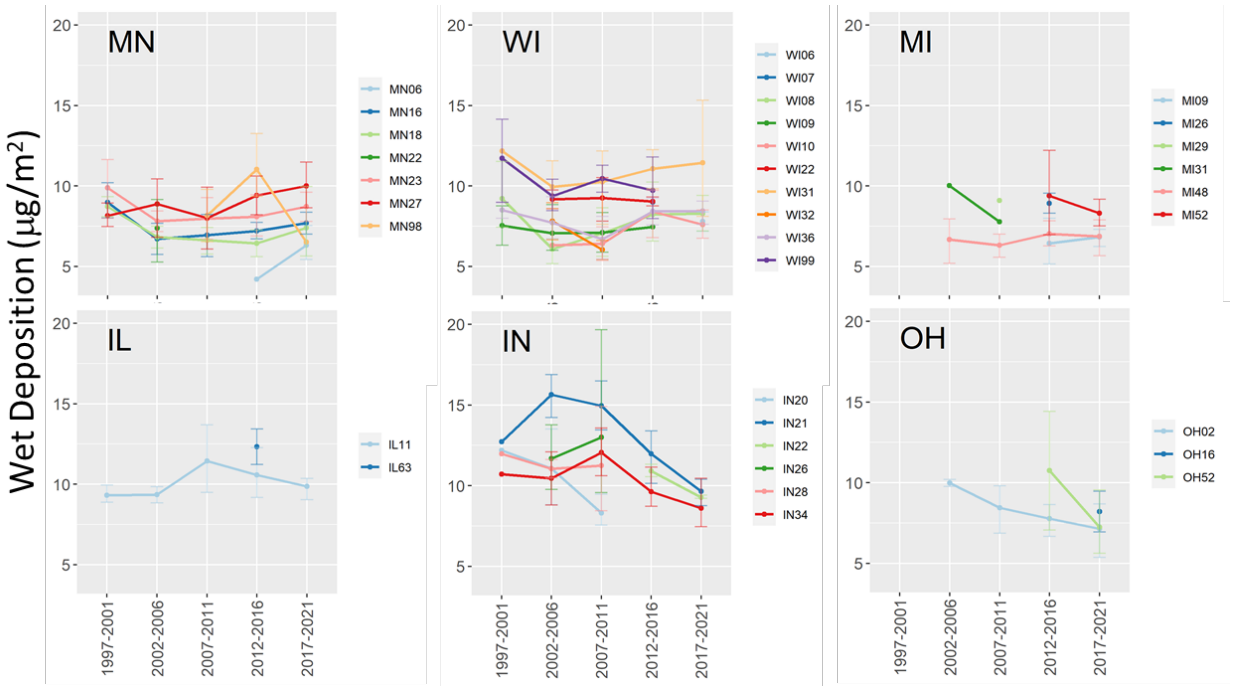

Figure 10. Timeseries of wet deposition of mercury (µg/m²) measured at MDN sites around the region. Sites are organized by state, lines are color-coded by site, and data are shown as 5-year averages. The error bars show the 95th percentile confidence interval for the 5-year averages.[7] See Figure 16 in the Appendix for site locations. Figures 18-20 in the Appendix show timeseries of precipitation and mercury concentrations.

In contrast to the observations for the northern states, mercury wet deposition in the southern states of Illinois, Indiana, and Ohio has been decreasing over the last 15 or more years, with the largest reductions at the IN21 site in the Ohio River Valley (Figure 10). Wet deposition had increased at several sites during the first part of the study-. Mercury concentrations at these sites showed clear decreases over the whole 25-year time period, particularly in Indiana and Ohio, and trends in precipitation were less clear in these states than in the northern states (Figure 20 and Figure 21 in the Appendix). In these states, it appears that mercury concentration reductions are driving the decrease in mercury wet deposition. This is consistent with the conclusions of Risch and Kenski (2018) that decreases in wet deposition from 2001-2013 to 2014-2016 were due to decreased mercury concentrations in the southern part of the region, not to changes in precipitation. As seen in Figure 6, these southern states include most of the large point sources of mercury, and mercury emissions from these states were generally larger than from the northern states (Figure 4). The observed decreases in mercury

[7] NADP does not report any uncertainty in the annual values. Missing error bars indicate that only one year of data was present for that site during that set of years.

concentrations and wet deposition therefore likely reflects reductions in emissions from these local and regional emissions sources.

A previous study found that wet deposition in the U.S. generally decreased from 1997 to 2013, but that many sites had increasing wet deposition from 2008 to 2013 (Weiss-Penzias et al., 2016). These increases were particularly notable in the Upper Midwest region (MN, WI, and northern MI), but were also apparent in the Lower Midwest (IL, IN, and KY). The authors found that significant positive trends in mercury concentrations in the Upper Midwest accompanied by reductions in precipitation during this time period. They concluded that a combination of factors was driving mercury wet deposition in this region. These increases in deposition during this earlier time period are also apparent in our data, although we have grouped the years differently so direct comparisons are difficult (Figure 10).

6 Litterfall Dry Deposition of Mercury

Monitoring of litterfall dry deposition of mercury only began in 2007, so these monitoring records are not available for as long a time period as for wet deposition. Litterfall deposition is also measured at fewer sites than is wet deposition (Figure 11), although the spatial coverage is better than that for atmospheric concentrations. As found for wet deposition, there is a gradient in litterfall deposition rates, from the highest levels in the southern part of the region to lower levels in the north (Figure 11). Litterfall mercury deposition at the northern sites appears to be fairly steady over time, although only a few sites have long-term records (Figure 12). Litterfall mass and mercury concentrations in the litterfall are also fairly constant at these sites (Figure 22 and Figure 23 in the Appendix).

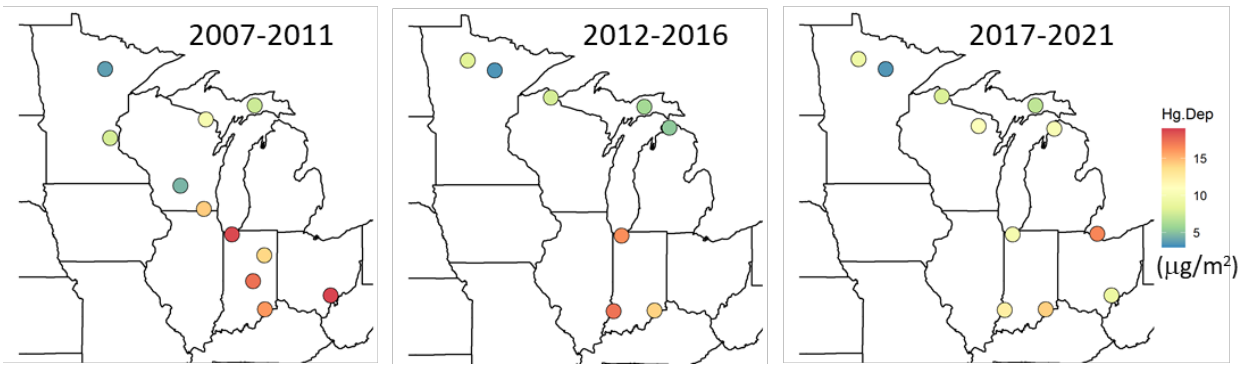

Figure 11. Maps of litterfall deposition of mercury (µg/m^2) measured at MLN sites around the region. Data are shown as 5-year averages.

In contrast, litterfall deposition decreased over time at all of the southern sites, accompanied by decreases in mercury concentrations in litterfall at these sites (Figure 12 and Figure 23 and Figure 24 in

the Appendix). Litterfall mass also decreased at many sites during this time. It is likely that these reductions were driven by reductions in mercury emissions from local and regional sources, as found for wet deposition in these states. This finding is consistent with the conclusions of Risch et al. (2017) who found that litterfall mercury deposition in forests decreased from 2007-2009 to 2012-2014, potentially due to emissions reductions. In contrast, Risch and Kenski (2018) did not find a statistically significant trend in litterfall in this region from 2007-2009 to 2012-2016. However, the reductions in deposition through 2017-2021 were even larger than those from the previous period at most sites, making it more likely that these reductions would be significant through the latest time period.

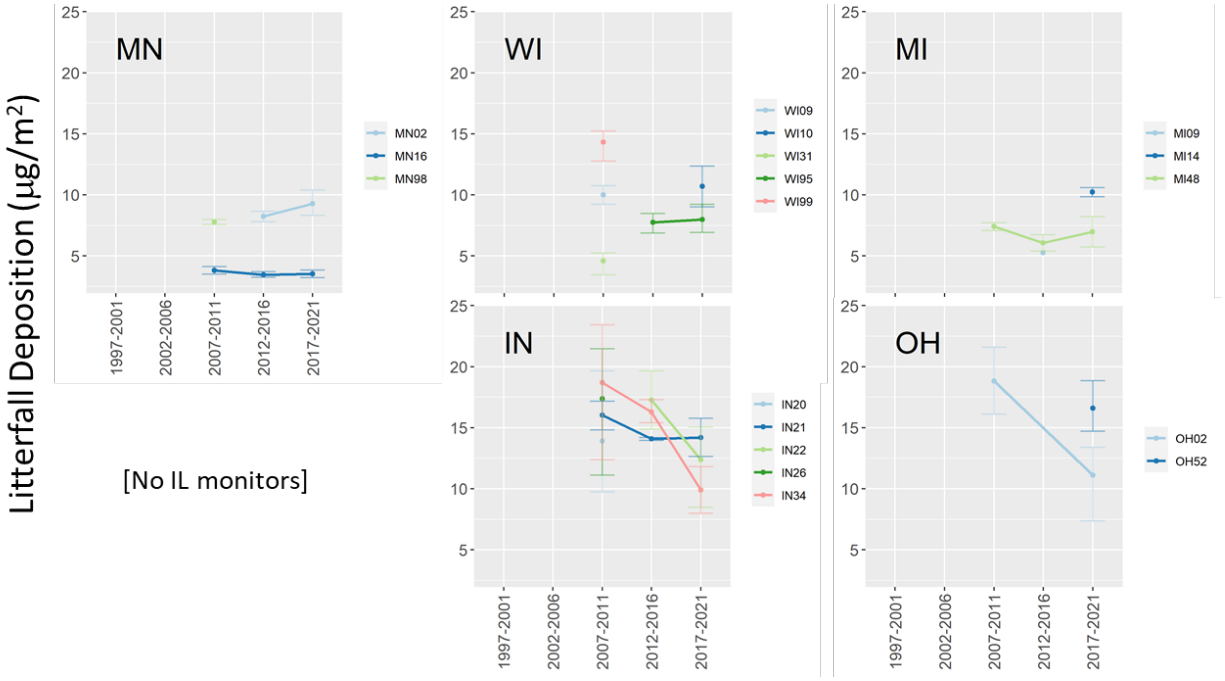

Figure 12. Timeseries of litterfall deposition of mercury (µg/m²) measured at MLN sites around the region. Sites are organized by state, lines are color-coded by site, and data are shown as 5-year averages. The error bars show the 95th percentile confidence interval for the 5-year averages.[7] See Figure 16 in the Appendix for site locations. Figures 22 and 23 in the appendix show trendlines for litterfall mass, mercury and methylmercury concentrations, and methylmercury deposition.

Methylmercury concentrations in litterfall were a small portion of the total (around 1% or less; Figure 23 and Figure 24 in the Appendix). This is consistent with the findings of Risch et al. (2017) that methylmercury comprised less than 1% of total mercury in litterfall. Methylmercury deposition did not show clear trends in northern states but showed inconsistent decreases in the southern states; given the low concentrations of methylmercury, trends will be difficult to observe.

7 Combined Wet and Dry Deposition of Mercury

Both wet and dry deposited mercury can end up in soils and in water bodies, where it can be methylated and passed up the food chain. Examining trends in mercury in lake sediments provides long-term records of total mercury deposition. However, these records are also impacted by more local factors such as changes in sediment inputs to the lake and bioturbation of the sediments. These factors may mute the sedimentary signals from changes in atmospheric deposition (e.g., Lepak et al. (2019). Engstrom et al. (2007) found that mercury levels in urban lake sediments in Minneapolis-St. Paul, MN decreased by more than half from the 1970s through 1997. They concluded that this resulted from a combination of decreased emissions of mercury and decreased erosional inputs to the lakes. This finding supports that of Brigham et al. (2021) that mercury deposition in Minnesota has decreased in the past in response to decreased emissions. Lepak et al. (2019) similarly concluded that reductions in U.S. mercury emissions due to regulatory actions were apparent in the mercury isotopic signature of fish in Lake Michigan.

Figure 13 shows the split between wet and litterfall dry deposition of mercury at sites in the region that measured both. In general, there were roughly equal proportions of the two types of deposition around the region. Both types of deposition clearly play an important role in mercury cycling in the Great Lakes states. Some sites had relatively more wet deposition, whereas others had relatively more dry deposition. In general, litterfall deposition seemed to be more important at most southern sites, whereas wet deposition was more important at two northern sites (MN16 and WI31). These findings are consistent with those from other studies. Zhang et al. (2016a) found that averaged over a year, wet and dry deposition had similar magnitudes, with slightly more dry deposition than wet deposition. However, dry deposition was more important in all seasons except the summer. Risch et al. (2012 and 2017) found that litterfall deposition was similar to or more important than wet deposition at 70% of the years and sites studied. Zhang et al. (2016a) also found that dry GEM deposition was greatest over forests due to the large leaf area index (LAI). In the Great Lakes states' records, the changes in the relative importance of the two types of deposition over time are not consistent, with the contributions from litterfall increasing at some sites whereas at others, wet deposition became relatively more important (Figure 13).

Figure 14 shows the geographic distribution of both litterfall and wet deposition of mercury, with sites grouped by quartile. Using this approach to distinguish areas of high, medium, and low deposition, Risch et al. (2017) found Illinois, Indiana, Kentucky and areas nearby had the highest levels of both wet and

litterfall mercury deposition from 2007 to 2014. In contrast, northern parts of the Great Lakes region had the lowest levels of both kinds of deposition, along with the northeastern U.S. Other parts of the region had moderate levels. These findings are consistent with the distributions found through 2017-2021 (Figure 9 and Figure 11), except that amounts of wet deposition in the "high" area have decreased enough to mute the distinctions between the "high" and "low" areas. Several factors likely drive these geographic trends. As mentioned above, Risch and Kenski (2018) state the spatial trends in wet deposition are primarily driven by precipitation differences, with precipitation being highest in the southern part of the region. In addition, the largest emission sources are located in the southern part of the region (Figure 4 and Figure 6), which is likely to increase deposition of mercury in these areas. Finally, studies have found that forests take up more mercury than do barren lands or shrublands (Olson et al., 2022). Forest cover is greatest in the northern and southern portions of the Great Lakes region, so high forest cover might have contributed to high mercury deposition along the Ohio River Valley but would not have contributed at the other Indiana sites.

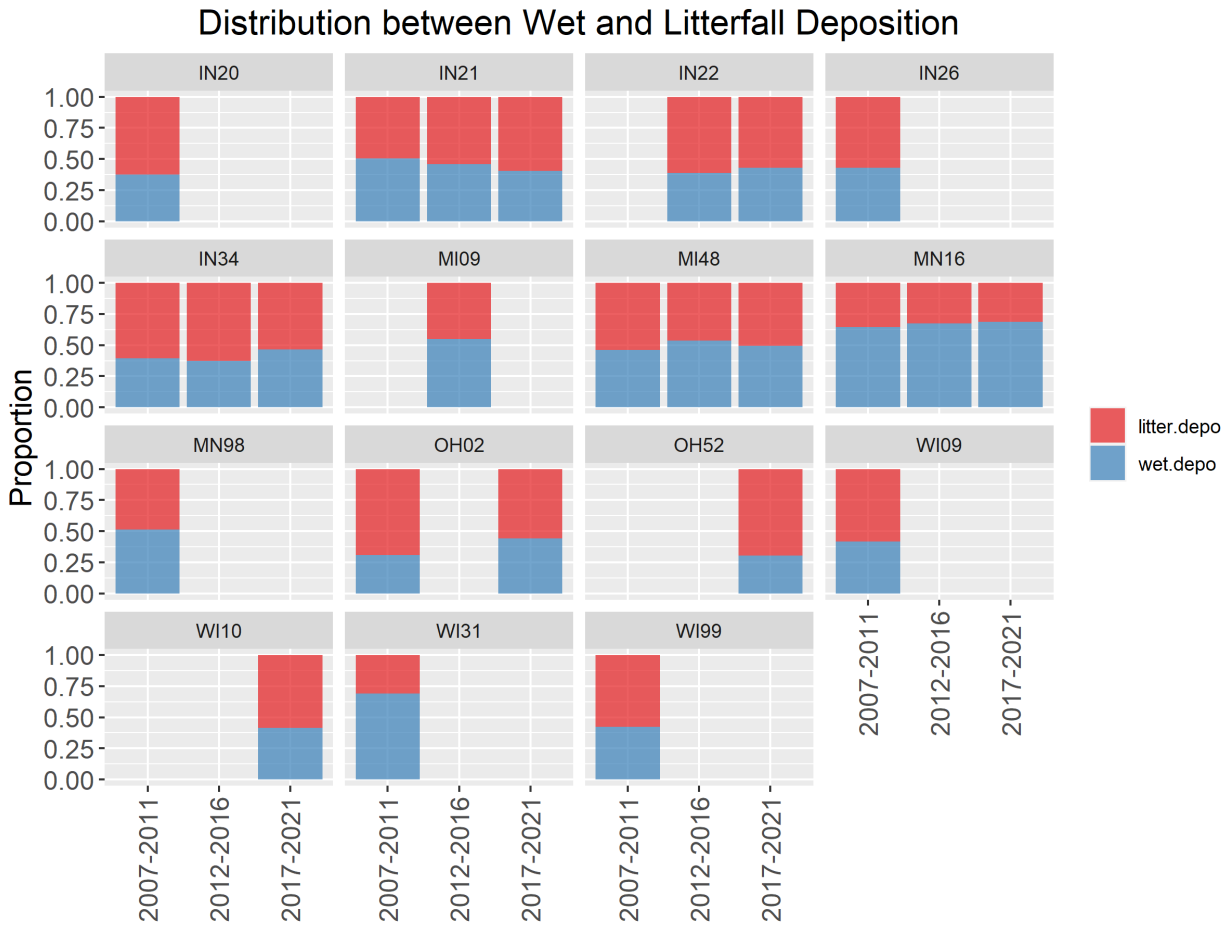

Figure 13. Distribution of total deposition between wet deposition and litterfall dry deposition at monitoring locations with both measurements.

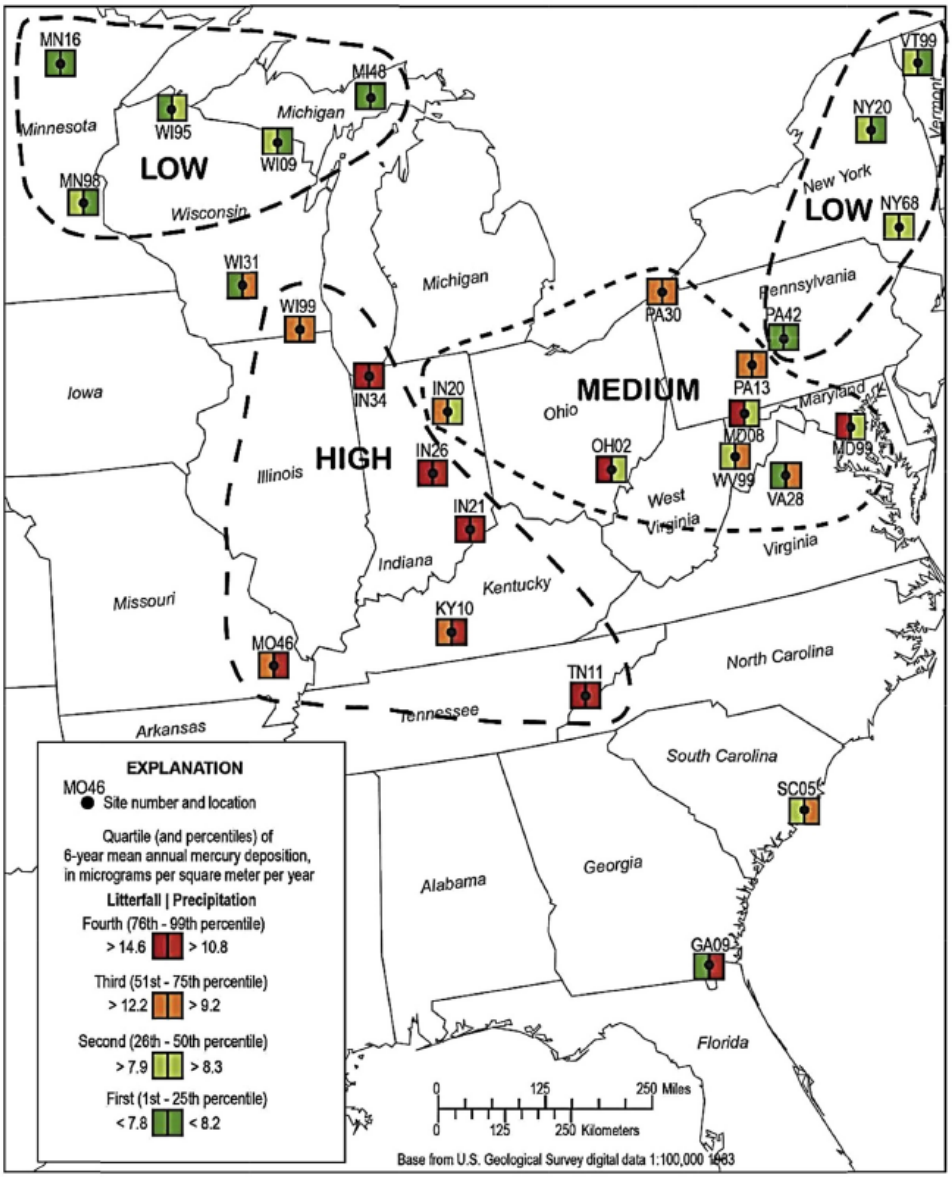

Figure 14. Comparison of the quartile distribution of litterfall and wet deposition of mercury at sites in the eastern U.S. for 2007-2014, from Risch et al. (2017).

8 Insights into Sources of Mercury in the Region

A general consensus has developed over the last decade or two that local, regional, and continental-scale emissions all contribute significantly to mercury deposition in the U.S., in addition to global emissions (e.g., Risch and Kenski, 2018; Cohen et al., 2016; Brigham et al., 2021) The primary evidence for this conclusion is the observations of significant decreases in mercury concentrations and deposition in many media and locations at a time when global emissions have remained constant or increased but emissions within and near the U.S. have decreased (e.g., Zhou et al., 2016; Lepak et al., 2019; Brigham et

al., 2021) . These decreases suggest that mercury levels are responding to emissions on a local to continental scale in addition to global emissions. For example, Zhang et al. (2016b) compared decreases in mercury concentrations in the free troposphere to those in North America and Europe and concluded that surface sites are more influenced by regional emissions sources than by global sources. The current study's observations of the large decreases in wet and litterfall deposition in the southern portion of the region (Figure 10 and Figure 12) also support this conclusion. These large reductions occurred in the area of greatest emissions at a time when major emissions sources (e.g., EGUs) were installing control equipment or shutting down, leading to decreased mercury emissions. The finding that the greatest reductions in deposition were observed closest to the decreasing emissions sources suggests that local and regional emissions were important sources of mercury deposited in this region.

In the northern part of the Great Lakes region, there is evidence that mercury levels are impacted by a combination of local, regional, and global sources. Several studies concluded that local and regional sources drove decreases in mercury deposition in this region. Brigham et al. (2021) found evidence from trends in deposition, lake water, and biota that regional- to continental-scale emissions reductions of mercury and sulfate contributed to decreased mercury deposition to lakes in northern Minnesota. Similarly, decreases in mercury deposition in northeastern Minnesota through 1997 seem to have derived from emissions reductions at nearby paper mills and at a coal-fired boiler (Engstrom et al., 2007). This same study also observed the impacts of local emissions sources on mercury in lake sediments in the Minneapolis-St. Paul area (Engstrom et al., 2007). In contrast, Weiss-Penzias et al. (2016) speculated that the increase in mercury wet deposition from 2007 to 2013 at northern monitors was due to the impact of free tropospheric air on these sites. They found that other sites to the south and east were more influenced by local and regional emissions sources and had decreases in wet deposition. We observed these same increases in wet deposition but with our longer record, also observed apparent increases in precipitation at these sites, linked to climate change. We believe that these precipitation increases are the primary drivers of the observed increases in wet deposition of mercury in the northern states in this region, rather than contributions from the free troposphere. Combined with the results of other studies, it appears likely that the increased precipitation at these northern sites is in part scavenging mercury from the atmosphere that was emitted by local and regional emission sources. This suggests that mercury deposition in this region would respond to decreases in local and regional emissions sources, although this response may be muted by future increases in precipitation, if they continue.

Risch and Kenski (2018) provide a different line of support for the importance of local and regional sources to mercury cycling. They used the HYSPLIT model to calculate back-trajectories for air masses during episodes with both high precipitation and high mercury concentrations at the IN21 monitor. They found that during these high mercury deposition episodes, the air masses reaching the monitor consistently came from the south and southwest (Figure 15), suggesting that sources in these areas contributed to the highest levels of mercury reaching this site. They concluded that local and regional sources contributed to the mercury deposition, not just continental or global emissions.

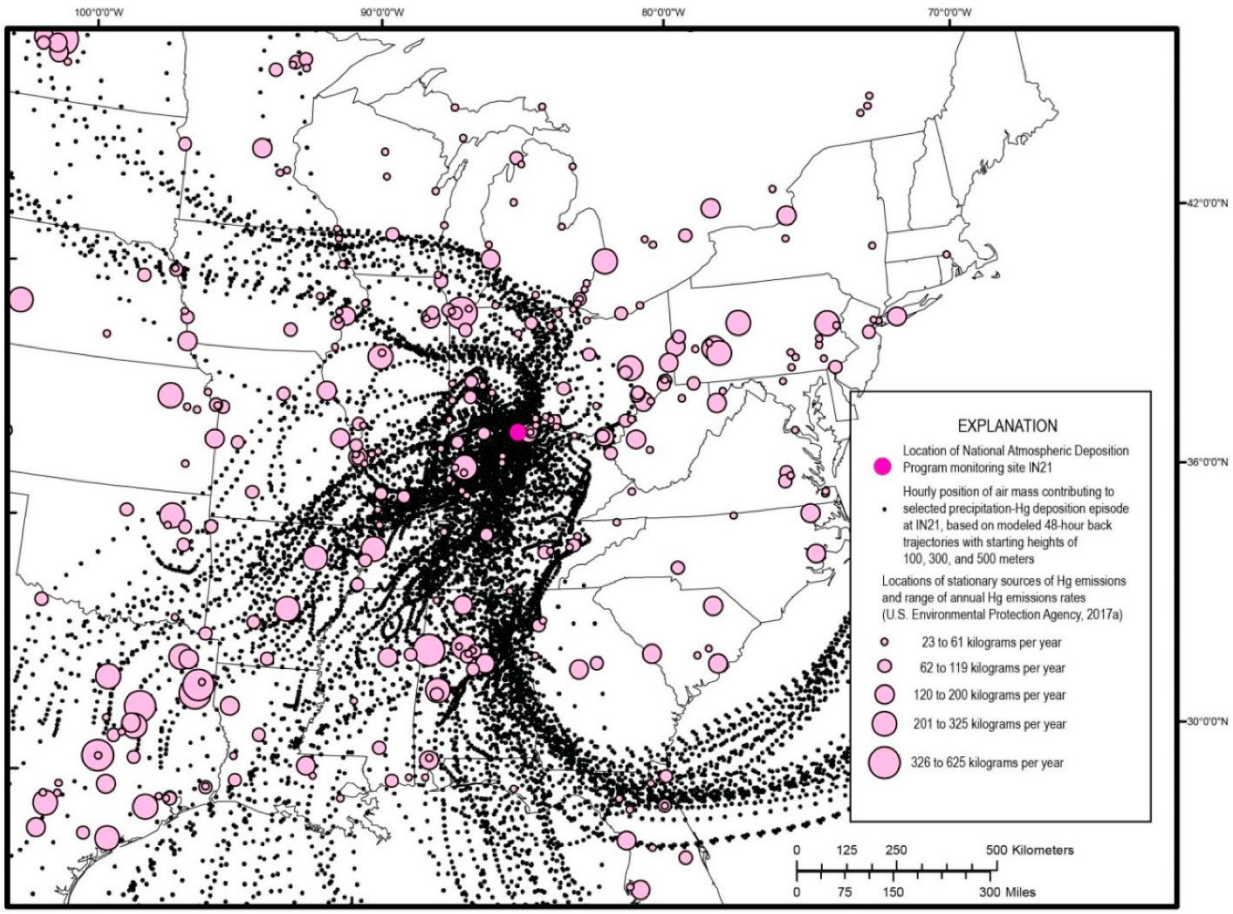

Figure 15. Modeled 48-hour back trajectories from the IN21 monitor during five high mercury deposition episodes from 2009-2015. Stationary source emissions are also shown for 2014. From Risch and Kenski (2018).

9 Conclusions

While trends in atmospheric concentrations of mercury are difficult to discern based on the limited data available, there are clear patterns in the spatial distribution and trends in both wet and litterfall dry deposition of mercury in the Great Lakes region. Both wet and litterfall deposition are highest in the

southern areas near the Ohio River Valley and lowest in the far northern parts of the region. However, these regional differences have decreased over time. Wet deposition of mercury is slightly increasing in the northern part of the region, likely due to increased precipitation, but strongly decreasing in the south, likely in response to decreased mercury emissions. Trends in litterfall deposition are unclear in the north but decreasing in the southern part of the region, and additional work is needed to better characterize dry deposition within the Great Lakes regions. This work supports the findings of other studies that local and regional emissions sources contribute to mercury deposition in this region, likely in combination with global sources.

10 Methods

NADP data were downloaded from the NADP website (https://nadp.slh.wisc.edu/). AMNet data were converted from hourly averages into annual mean concentrations, with data completeness determined as the percentage of days with valid data available for each year. MDN and litterfall data were downloaded as annual averages using NADP's default data completeness criteria and were converted to 5-year mean values. A 5-year mean is shown if there was valid data for any year in that time period; accordingly, some means will include data for only one or two years whereas others will include data for all five years.

11 Acknowledgements

We thank Dr. Sarah Janssen and Dr. David Krabbenhoft of the U.S. Geological Survey and Dr. David Gay of the National Atmospheric Deposition Program for very helpful discussions about mercury cycling and for providing relevant research papers. Drs. Janssen and Gay also reviewed this report and provided comments that greatly improved the report. We also acknowledge discussions with state environmental program staff from the states of Minnesota and Michigan, which helped shape this work.

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13 Appendix: Supplemental Figures

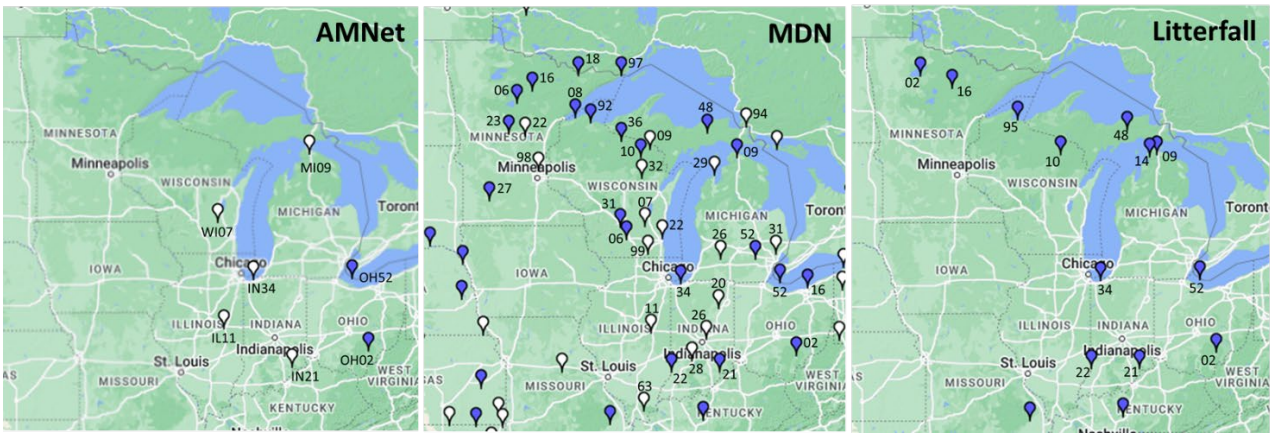

Figure 16. Distribution of NADP sampling sites in the Great Lakes region with site names, including inactive sites (white pins) and active sites (blue pins).

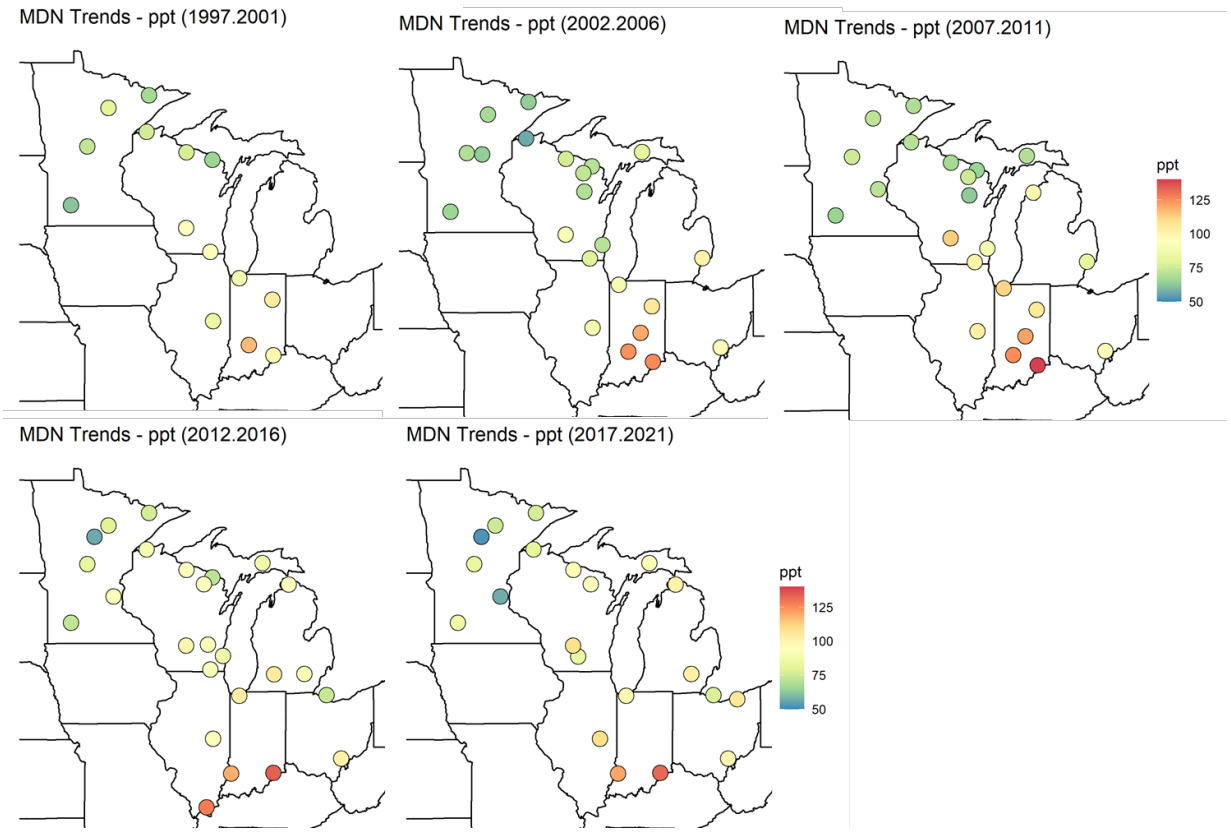

Figure 17. Maps of precipitation (cm/year) at MDN sites, averaged into 5-year bins.

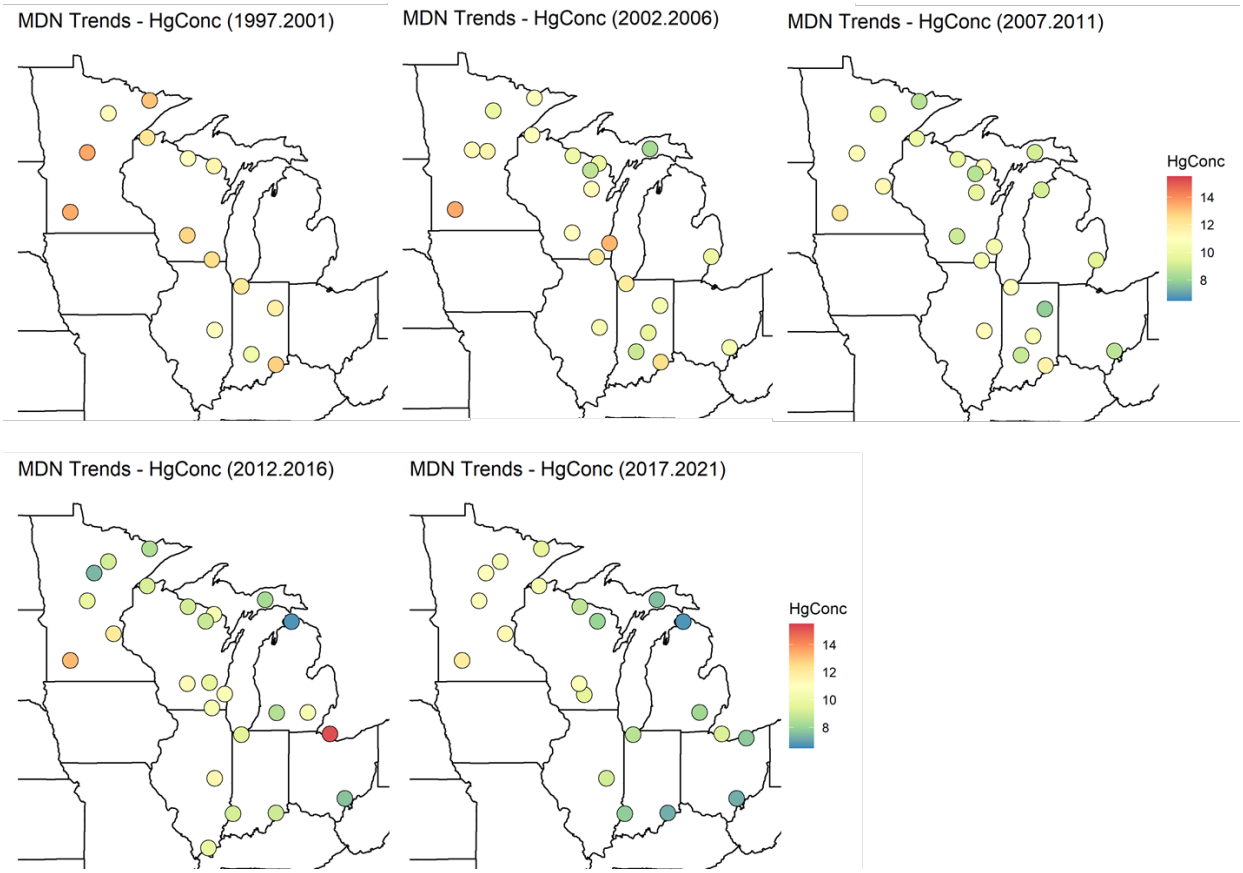

Figure 18. Maps of mercury concentrations in rainwater (ng/L) at MDN sites, averaged into five-year bins.

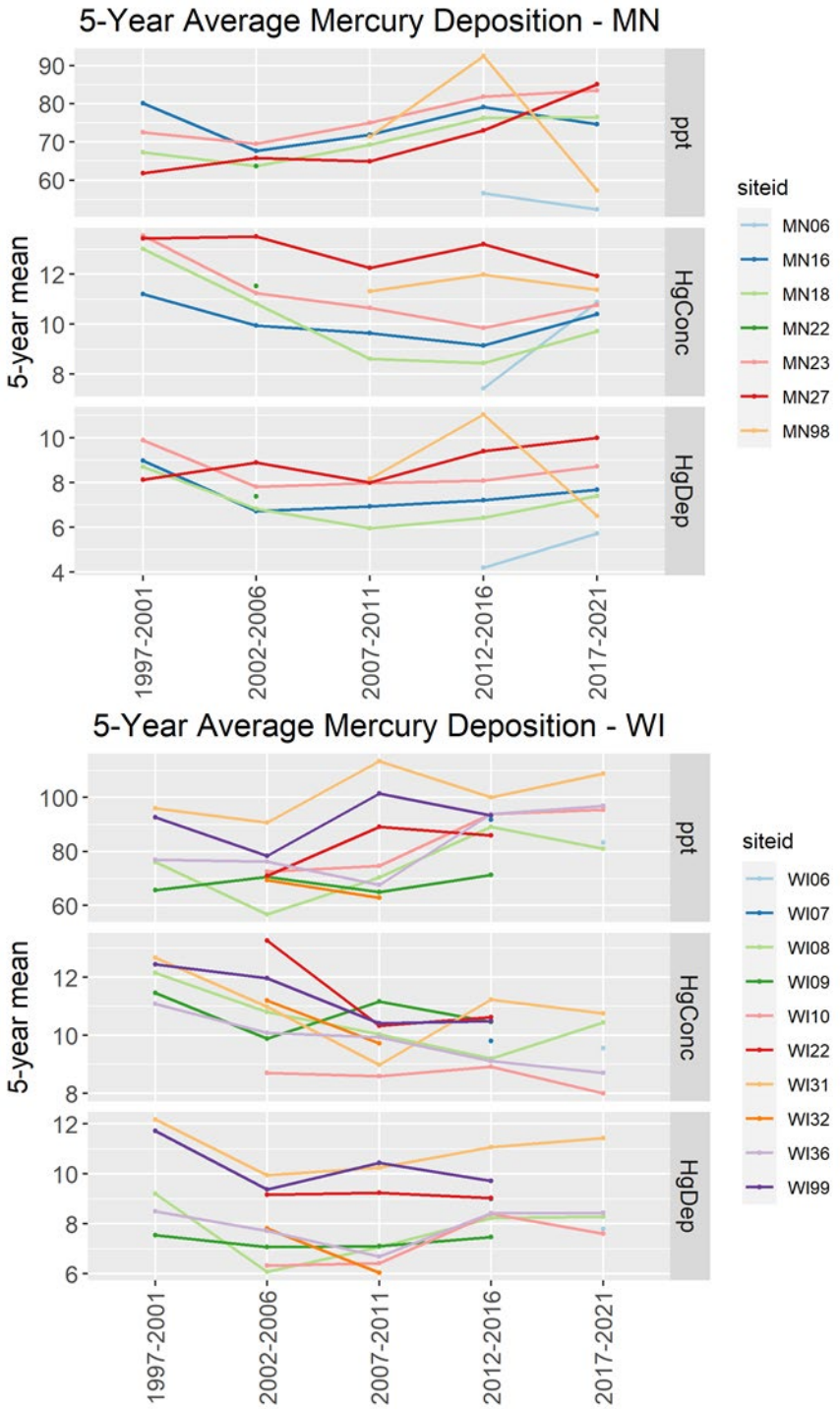

Figure 19. Trends in precipitation (ppt), mercury concentration (HgConc), and mercury deposition (HgDep) at MDN sites in (top) Minnesota and (bottom) Wisconsin, averaged into five-year bins.

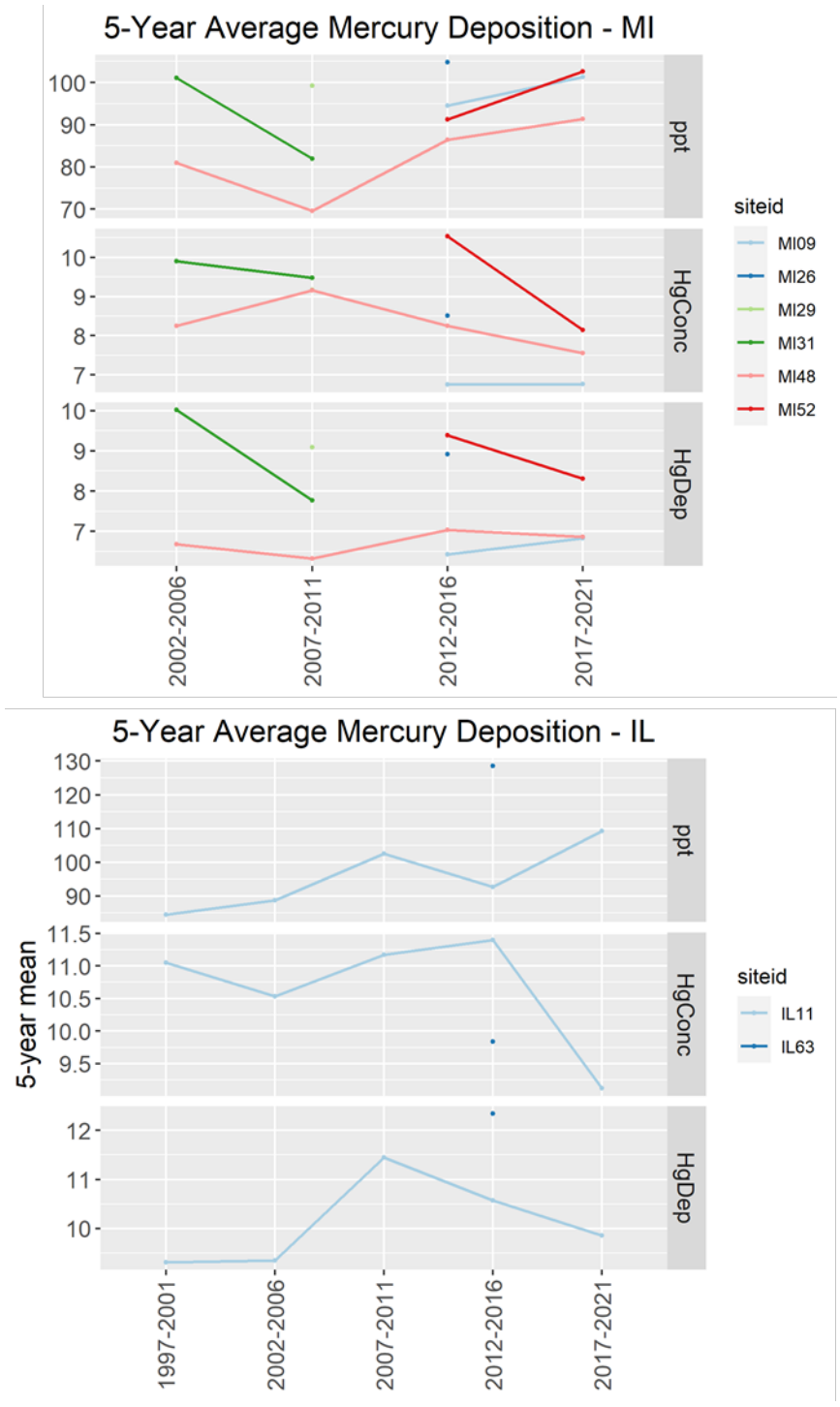

Figure 20. Trends in precipitation (ppt), mercury concentration (HgConc), and mercury deposition (HgDep) at MDN sites in (top) Michigan and (bottom) Illinois, averaged into five-year bins.

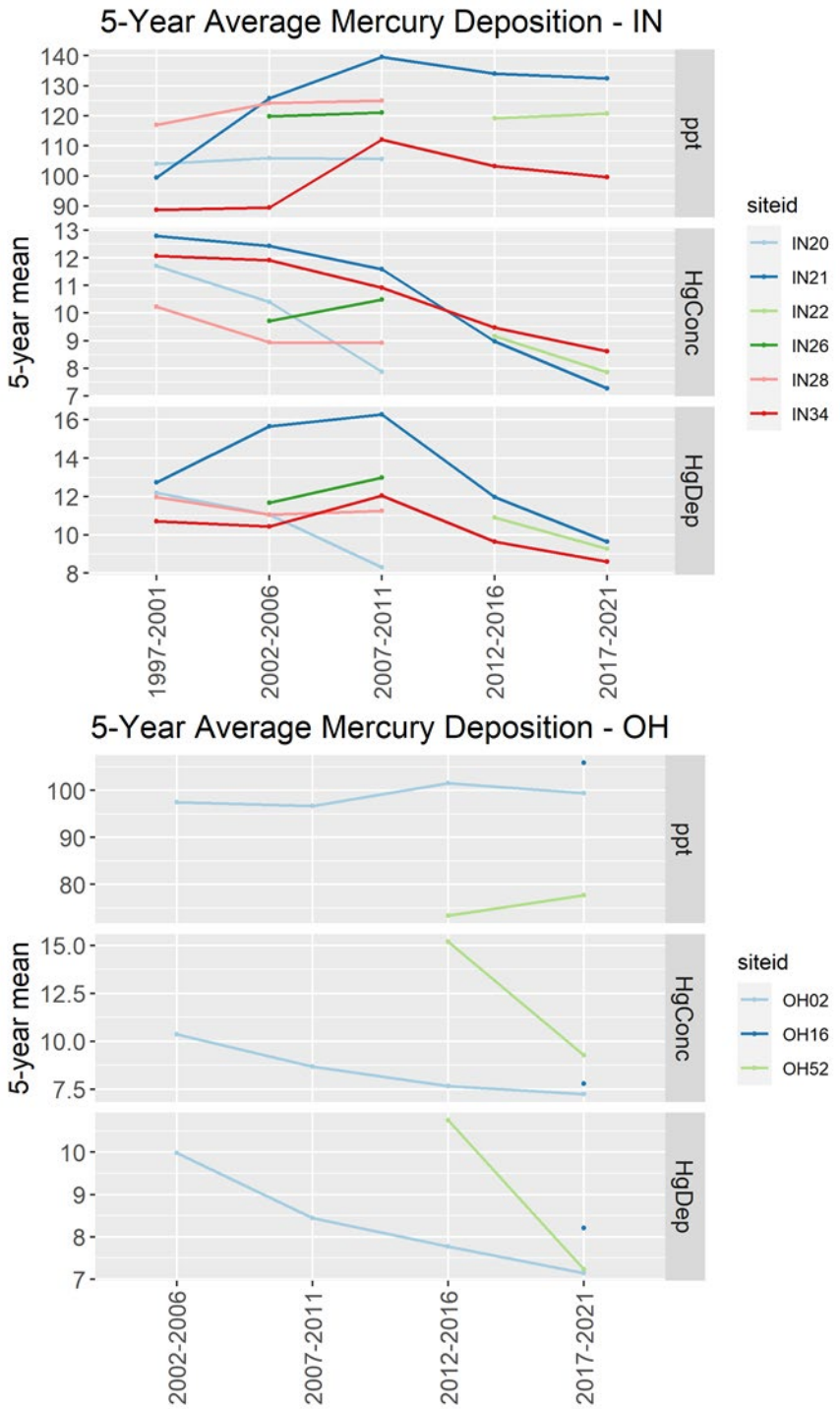

Figure 21. Trends in precipitation (ppt), mercury concentration (HgConc), and mercury deposition (HgDep) at MDN sites in (top) Indiana and (bottom) Ohio, averaged into five-year bins.

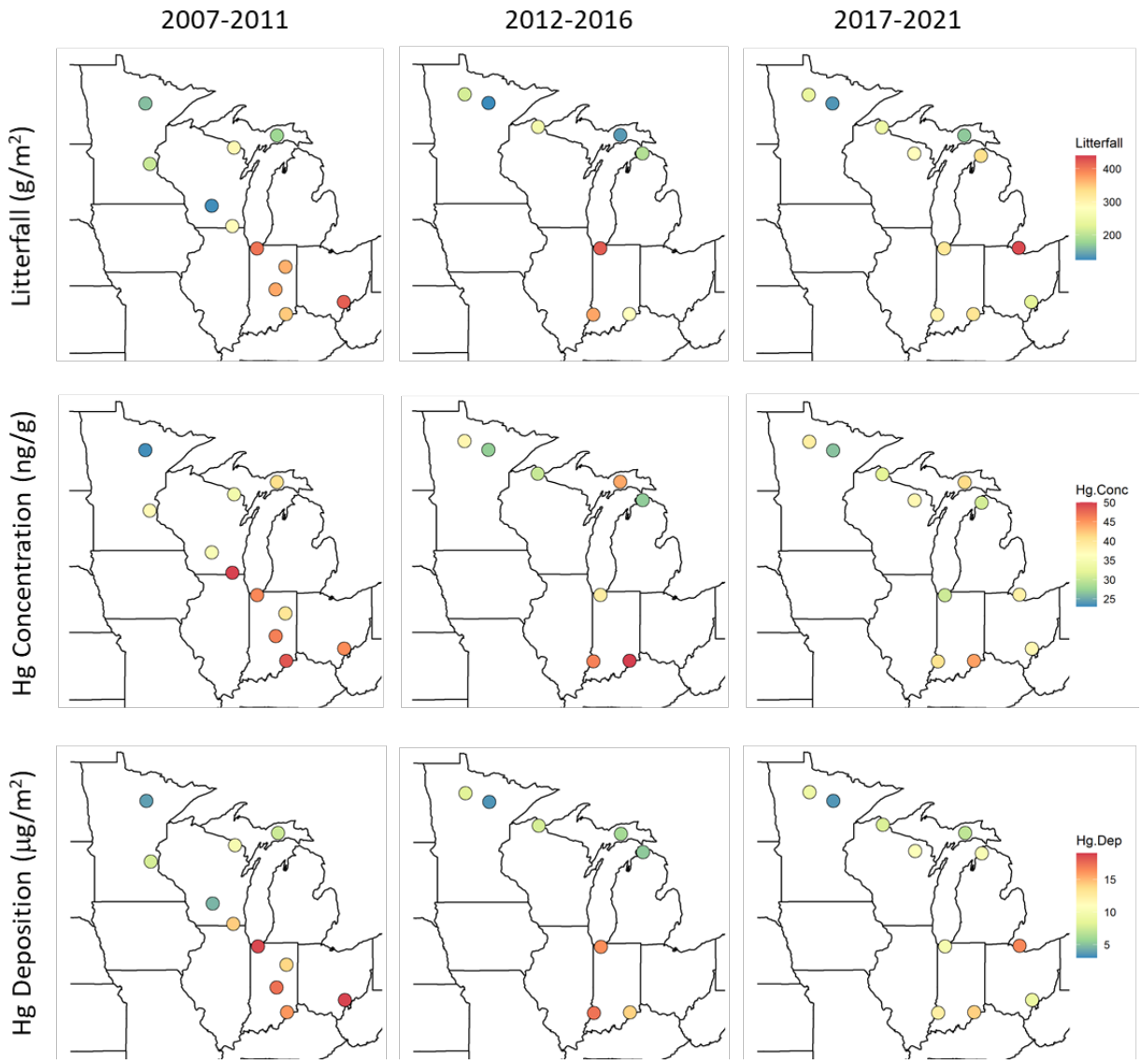

Figure 22. Maps of (top) litterfall mass, (middle) mercury concentration in litterfall, and (bottom) mercury deposition in litterfall for three five-year periods.

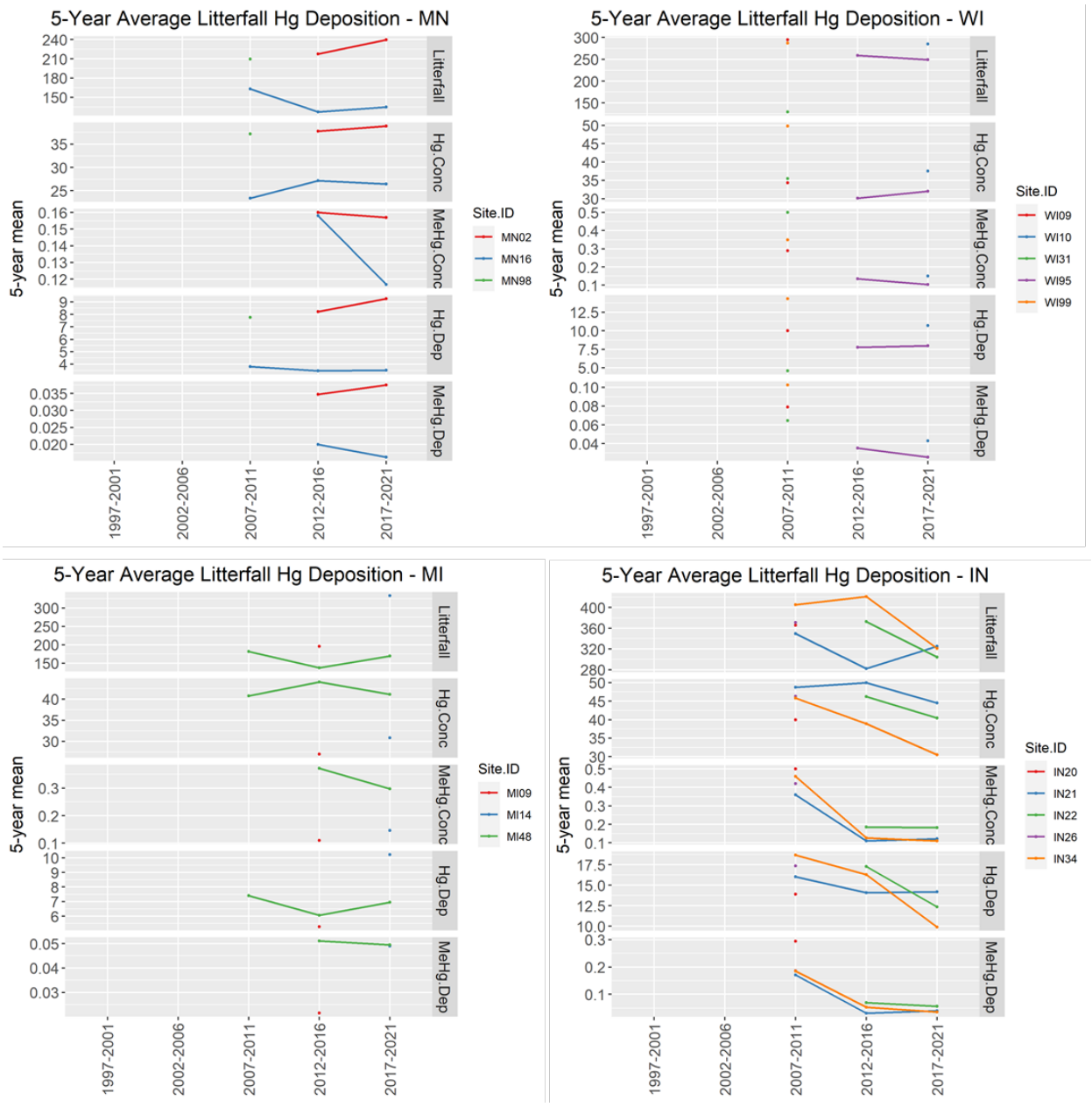

Figure 23. Trends in litterfall mass (g/m^2), mercury concentration (ng/g litter), methylmercury concentration (ng/g litter), mercury deposition in litterfall (μg/m^2), and methylmercury deposition in litterfall (μg/m^2) for MLN monitors in Minnesota, Wisconsin, Michigan, and Indiana, averaged over five-year periods.

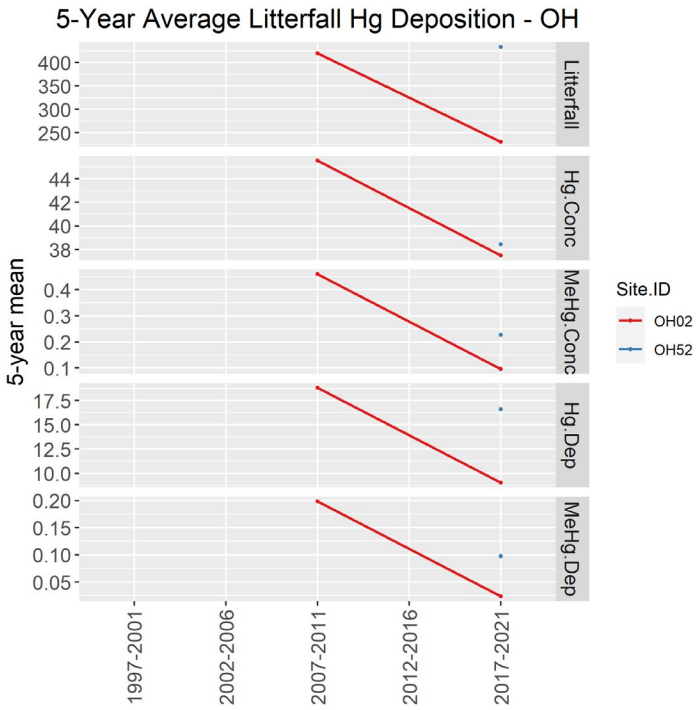

Figure 24. Trends in litterfall mass (g/m^2), mercury concentration (ng/g litter), methylmercury concentration (ng/g litter), mercury deposition in litterfall (μg/m^2), and methylmercury deposition in litterfall (μg/m^2) for MLN monitors in Ohio, averaged over five-year periods.