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Spatial Patterns and Temporal Changes in Atmospheric-Mercury Deposition for the Midwestern USA, 2001–2016

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Abstract: Spatial patterns and temporal changes in atmospheric-mercury (Hg) deposition were examined in a five-state study area in the Midwestern USA where 32% of the stationary sources of anthropogenic Hg emissions in the continental USA were located. An extensive monitoring record for wet and dry Hg deposition was compiled for 2001–2016, including 4666 weekly precipitation samples at 13 sites and 27 annual litterfall-Hg samples at 7 sites. This study is the first to examine these Hg data for the Midwestern USA. The median annual precipitation-Hg deposition at the study sites was 10.4 micrograms per square meter per year (μg/m^2/year) and ranged from 5.8 μg/m^2/year to 15.0 μg/m^2/year. The median annual Hg concentration was 9.4 ng/L. Annual litterfall-Hg deposition had a median of 16.1 μg/m^2/year and ranged from 9.7 to 23.4 μg/m^2/year. Isopleth maps of annual precipitation-Hg deposition indicated a recurring spatial pattern similar to one revealed by statistical analysis of weekly precipitation-Hg deposition. In that pattern, high Hg deposition in southeastern Indiana was present each year, frequently extending to southern Illinois. Most of central Indiana and central Illinois had similar Hg deposition. Areas with comparatively lower annual Hg deposition were observed in Michigan and Ohio for many years and frequently included part of northern Indiana. The area in southern Indiana where high Hg deposition predominated had the highest number of extreme episodes of weekly Hg deposition delivering up to 15% of the annual Hg load from precipitation in a single week. Modeled 48-h back trajectories indicated air masses for these episodes often arrived from the south and southwest, crossing numerous stationary sources of Hg emissions releasing from 23 to more than 300 kg Hg per year. This analysis suggests that local and regional, rather than exclusively continental or global Hg emissions were likely contributing to the extreme episodes and at least in part, to the spatial patterns of precipitation-Hg deposition in the study area. Statistically significant temporal decreases in weekly precipitation-Hg concentrations in the study area between the periods 2001–2013 and 2014–2016 were observed, coinciding with reported reductions in Hg emissions in the USA required by implementation of national Hg emissions-control rules. These decreases in atmospheric-Hg concentrations are believed to have resulted in the reduced atmospheric-Hg deposition recorded because precipitation depths between the two periods were not significantly different. The Hg-monitoring data for the study area identified an atmospheric deposition response to decreased local and regional Hg emissions.

Keywords: mercury; atmospheric deposition; precipitation; litterfall; Midwestern USA

1. Introduction

1.1. Mercury in the Environment

Mercury (Hg) is a persistent environmental contaminant and can accumulate and concentrate in food webs as methylmercury (MeHg), presenting a health risk to humans and wildlife [1]. MeHg

exposure can result in adverse neurological, cardiovascular and reproductive effects in humans [2]. Developing infants and children are most susceptible to the harmful effects of MeHg but adults have been affected by MeHg poisoning too [3]. Neurological development and reproduction in wildlife can be damaged by MeHg exposure [4]. Because MeHg concentrations are highest at top levels in the aquatic food web, humans, wild mammals and birds who consume fish risk exposure to harmful concentrations of MeHg. Public health agencies have issued advisories that warn about consumption of freshwater and marine fish because of risks from Hg [5].

Most of the Hg in aquatic and terrestrial ecosystems comes from atmospheric deposition and atmospheric Hg predominantly originates from human activities [3,6,7]. The three operationally-defined species of atmospheric Hg are gaseous elemental Hg (GEM), gaseous oxidized Hg (GOM) and particulate-bound Hg (PBM), as summarized in previous research [6–8]. Transfers of GOM and PBM from the atmosphere to the biosphere occur episodically in precipitation (rain, snow, sleet, hail and fog), which is sometimes called wet deposition and is called precipitation-Hg deposition hereafter. Other transfers of GEM, GOM and PBM from the atmosphere to vegetation, soil, impervious surfaces and water, called dry-Hg deposition hereafter, can be more continuous. The vertical dry-deposition velocity to a forest landscape can be 2 to 5 times larger than the velocity to other landscapes for all three Hg species because the greater leaf surface area and canopy roughness in a forest intercepts air flow and amplifies dry-Hg deposition to vegetation [8].

Previous studies of atmospheric-Hg deposition in the USA have not focused on the Midwestern region. Rather, studies have had a national scope [9–12], or targeted a large region including part of the Midwest [13–18]. Some earlier studies focused on a single Midwestern state [19–25]. Therefore, the study described here fills a geographic gap in atmospheric-Hg research by investigating a multi-state area in the Midwestern USA with an extensive Hg-monitoring record and considerably high amounts of long-term anthropogenic Hg emissions.

1.2. Purpose and Scope

The purpose of this study was to describe spatial patterns and temporal changes in atmospheric-Hg concentrations and Hg deposition and to relate the observations to potential contributing factors such as weather and Hg sources in a study area centered on Indiana and four surrounding Midwestern states in the USA (Illinois, Michigan Lower Peninsula, Ohio and Kentucky). Precipitation-Hg and dry-Hg deposition data for this study were compiled and summarized for 2001–2016. Interpretations from this study explain the long-term status of atmospheric-Hg deposition in an intensively monitored study area with substantial anthropogenic Hg emissions.

1.3. Hg Emissions Sources

The Midwestern USA region has a history of numerous anthropogenic Hg emission sources, including those with high annual emission rates. As of 2014, 7861 kg/year of Hg were emitted from 3940 stationary sources in the five states of the study area [26]. These 5 states include 32% of the 12,377 sources and 20% of the 39,395 kg of Hg emissions in the 48 states in the continental USA. The Hg sources in the study area were broadly distributed geographically (Figure 1) and varied by 5 orders of magnitude in annual Hg emission rates (Table 1). A large percentage of the sum of annual Hg emissions in the study area came from a small number of sources. Most sources contributed a relatively small percentage of the total for the study area. Considering Indiana as an example, the sum of the top 10% of ranked annual Hg emissions (from 36 of 358 sources) amounted to 1807 kg, which was 97.5% of the state's total. The two dominant categories for these 36 Hg emissions sources were electric power generation and primary metal manufacturing, accounting for 77.5% of the 1807 kg. Comparable results were tabulated for the other four states, indicating the stationary sources with the highest Hg emissions were consistently important throughout the study area (Figure 1). Annual Hg emissions varied for each state from emissions inventories as of 2008, 2011 and 2014 [26–28], but comparative ranks among states were the same, from highest to lowest totals—Ohio, Indiana, Michigan, Illinois

and Kentucky (Figure 2). In addition, the relative contributions of Hg emissions from the six categories were comparable from year to year and state to state, where electric power generation and primary metals manufacturing contributed approximately three-fourths of the totals. For the top 1% of ranked Hg emissions in the continental USA, 21 of the 124 sources (17%) are in the study area, accounting for 3274 of the 22,286 kg (15%) of the total Hg emissions. Those top 124 sources contribute 57% of total Hg emissions in the continental USA. A comparison of the distribution of stationary Hg emissions sources in the USA with those in this study area can be made by consulting maps from the National Oceanic and Atmospheric Administration [29], Castro and Sherwell [30] and Risch et al. [31].

Table 1. Annual mercury emissions from stationary sources in states from Midwestern USA study area.

State	Annual Hg Emissions [a] (kg/year)	Number of Sources [a]	Median Annual Hg Emission per Source (kg/year)	Range of Top 10% of Ranked Hg Emissions per Source (kg/year)	Percentage of Total State Emissions from Top 10% of Sources
Indiana	1852	358	0.018	5.67 to 361	97.5
Illinois	1323	2234	0.005	0.11 to 207	98.2
Kentucky	929	255	0.005	2.45 to 152	98.4
Michigan	1513	569	0.014	2.04 to 290	97.5
Ohio	2244	524	0.023	2.36 to 230	97.6
Study area	7861	3940	0.009	0.39 to 361	98.9

Note: Hg: mercury; kg/year: kilogram per year; [a]: 2014 National Emissions Inventory [26].

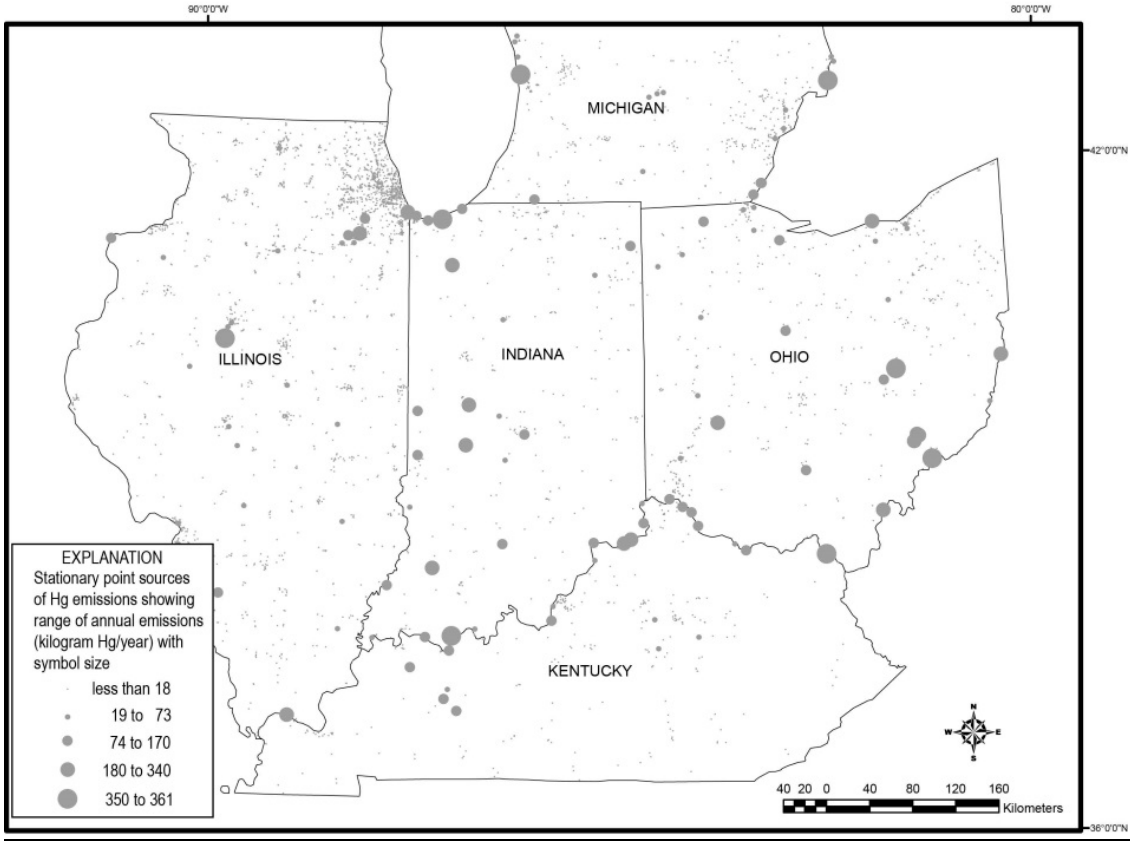

Figure 1. Stationary sources of Hg emissions in Midwestern USA study area (2014 National Emissions Inventory [26]).

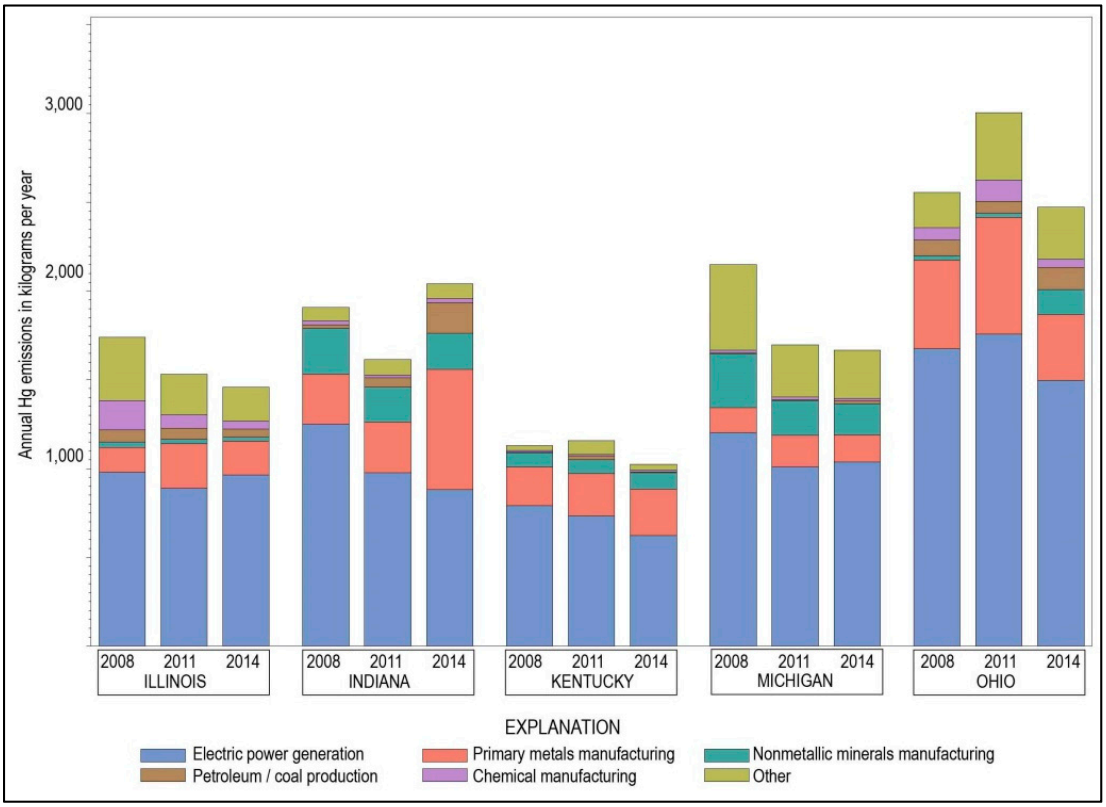

Figure 2. Annual Hg emissions from categories of stationary sources in states of Midwestern USA study area (2008, 2011 and 2014 National Emissions Inventories [26–28]).

1.4. Atmospheric-Hg Monitoring

Monitoring atmospheric-Hg deposition is a necessary complement to regulations of Hg emissions to the air. The National Atmospheric Deposition Program (NADP) has the primary atmospheric-Hg monitoring networks in the USA. The NADP is an affiliation of federal, state, local, tribal, academic and private entities that sponsor the operation of individual monitoring sites or groups of sites. The Mercury Deposition Network (MDN) measures precipitation-Hg deposition [32]. In the MDN, uniform protocols are used to collect composite weekly precipitation samples and to measure precipitation depths. Standardized equipment includes an automated precipitation collector plus a continuous-recording rain gage. The Hg concentration in the sample and the precipitation depth are used to compute weekly precipitation-Hg deposition. Data are quality assured by internal and external programs [33]. Annual precipitation-Hg deposition for Midwestern states has been included in previous large-scale assessments using data from the NADP-MDN. In these assessments, Prestbo and Gay [10] reported a range of precipitation-Hg deposition from 8 to 13 micrograms per square meter per year (μg/m^2/year) for 1996–2005, while Risch et al. [16] found 7 to 17 μg/m^2/year for 2002–2008 and the National Atmospheric Deposition Program maps [34] reported 7 to 14 μg/m^2/year for 2009–2015. Data from NADP-MDN were included in this study.

The NADP has two monitoring networks for dry-Hg deposition. First, the Litterfall Mercury Monitoring Initiative (LMMI) measures ambient litterfall-Hg deposition [35]. In this network, passive collectors near MDN sites are used to obtain autumn litterfall samples that are analyzed for Hg concentration and litterfall mass to compute annual litterfall-Hg deposition. Risch et al. [18] reported mean annual litterfall-Hg deposition in Midwestern states were the highest in the eastern USA and ranged from 12.6 to 18.8 μg/m^2/year for 2007–2014. Litterfall Hg is thought to represent 75% of dry-Hg deposition to deciduous forests in North America and Europe [36] and was reported previously to be

60 to 80% of dry-Hg deposition at sites in the eastern USA [16,37–40]. Data from NADP-LMMI were included in this study.

Second, the Atmospheric Mercury Network (AMNet) [41,42] measures semi-continuous, surface-air concentrations of GEM, GOM and PBM. Research by Zhang et al. [43] stated the range of modeled annual dry-Hg deposition in the eastern USA was 5.1 to 23.8 μg/m^2/year during 2009–2014. These annual rates were based on AMNet GEM, GOM and PBM concentrations and modeled vertical deposition velocities matched to land cover near each site, with daily data aggregated into annual values. The range of modeled annual dry-Hg deposition aligned closely with annual litterfall-Hg deposition measured at MDN sites [43]. Data from NADP-AMNet sites were not included in this study because sites were absent in Midwestern states before 2016.

2. Methods

Annual precipitation-Hg data for the study sites during 2001–2016 were derived from weekly monitoring data in the NADP-MDN data base [44]. Annual data from years with monitoring observations completed for all 52 weeks were compiled and data from incomplete years were not included. Weekly observations with precipitation depth <0.25 mm and no reported Hg concentration were not included (<12% of all observations). Data from weekly precipitation samples in complete years were examined in this study and included weeks with (a) a valid precipitation depth >0.25 mm and reported Hg concentration and Hg deposition (>97% of all samples); and (b) a valid precipitation depth >0.25 mm and estimated Hg concentrations and Hg deposition (<3% of all samples). Missing weekly Hg values were estimated with data from valid samples using the methods from previous research [10,16,23]. Weekly precipitation-Hg deposition is the product of Hg concentration (in nanogram per liter, ng/L) and precipitation depth (in mm), yielding nanogram per square meter (ng/m^2/week). Annual precipitation-Hg deposition is the sum of the weekly deposition values, in microgram per square meter per year (μg/m^2/year) and annual Hg concentration is the sum of weekly precipitation-weighted Hg concentrations (products of weekly Hg concentration and the ratio of weekly precipitation depth to annual precipitation depth).

Annual litterfall-Hg data for the study sites during 2007–2016 were derived from Risch [45,46]. Litterfall-Hg samples were collected and analyzed with standardized methods [18]. Annual litterfall dry mass in gram per square meter (g/m^2) and annual litterfall-Hg concentration in nanogram per gram (ng/g) were used to compute the annual litterfall-Hg deposition in μg/m^2/year, the same units as those for annual precipitation-Hg deposition.

Nonparametric statistics were used to compare data from sites, samples and time periods in this study. The Wilcoxon rank-sum test was applied to determine differences between two groups. The Kruskal-Wallis rank-sum test was applied to determine differences among multiple groups and the Tukey multiple comparisons of medians was applied to pairs among those groups. Relations among factors contributing to Hg deposition were examined with the Spearman rank correlation coefficient *rho* and linear regression. A *p*-value less than 0.05 was selected to indicate a statistical significance.

An inverse-distance weighting algorithm in geographic information system software was used to prepare isopleth grids of annual precipitation-Hg concentrations for MDN sites in and near the study area for selected years. These precipitation-Hg concentration grids were multiplied by an overlay of annual precipitation depths for the corresponding years, obtained from PRISM [47]), to create isopleth maps of annual precipitation-Hg deposition. These maps were used to interpret spatial patterns of annual precipitation-Hg deposition in the study area.

The air pollution transport and dispersion modeling system HYSPLIT [48] was used to calculate the paths of air masses contributing to selected precipitation-Hg deposition episodes in the study area during 2009–2015 when continuous, digital precipitation depth data were recorded at the monitoring sites. The 40-km gridded input data to HYSPLIT were from the National Oceanic and Atmospheric Administration [49]. Precipitation-Hg deposition episodes that were examined contained hourly precipitation depth totals >2.54 mm. For the selected episodes, HYSPLIT was used to calculate the

hourly position coordinates of the contributing air mass during 48 h preceding the episode. Back trajectories were plotted from starting heights of 100 m, 300 m and 500 m above ground level [50]. These trajectories were not constrained and the actual height of the air mass as it traveled could vary from ground level to the boundary layer at 1000 m to 2000 m. The most recent Hg-emission data [26] were overlain on a map that combined the back trajectories paths for the three starting heights for the selected episodes.

3. Results

3.1. Precipitation-Hg Deposition

Annual and weekly precipitation-Hg data were compiled for 13 sites in the study area (Figure 3, Table 2). Complete annual records were not available for every year at all sites in the study period (Table 3). Because the most annual records during 2001–2016 were from sites in Indiana, separate interpretive analyses for Indiana were made for comparison with the study area.

Figure 3. National Atmospheric Deposition Program Hg-data sites in Midwestern USA study area.

Table 2. Characteristics of National Atmospheric Deposition Program sites in Midwestern USA study area.

State	Site ID Number	Abbreviated Site Name	Latitude (Decimal Degrees)	Longitude (Decimal Degrees)	Elevation (Meters)	MDN	LMMI
Indiana	IN20	Roush Lake	40.8401	−85.4639	244	yes	yes
	IN21	Clifty Falls	38.7622	−85.4202	256	yes	yes
	IN22	SW Agr. Center	38.7408	−87.4855	134	yes	yes
	IN26	Fort Harrison	39.8583	−86.0208	260	yes	yes
	IN28	Bloomington	39.1464	−86.6133	256	yes	no
	IN34	Indiana Dunes	41.6318	−87.0881	208	yes	yes

Table 2. *Cont.*

State	Site ID Number	Abbreviated Site Name	Latitude (Decimal Degrees)	Longitude (Decimal Degrees)	Elevation (Meters)	MDN	LMMI
Illinois	IL11	Bondville	40.0528	−88.3719	212	yes	no
	IL63	Dixon Springs	37.4356	−88.6719	161	yes	no
Kentucky	KY10	Mammoth Cave	37.1317	−86.1480	236	yes	yes
Michigan	MI26	Kellogg	42.4103	−85.3928	288	yes	no
	MI52	Ann Arbor	42.4164	−83.9019	267	yes	no
Ohio	OH02	Athens	39.3078	−82.1182	275	yes	yes
	OH52	South Bass Island	41.6582	−82.8270	177	yes	no

ID. identification; MDN: Mercury Deposition Network; LMMI: Litterfall Mercury Monitoring Initiative.

Table 3. Annual precipitation-Hg records for Midwestern USA study area, 2001–2016.

Year	National Atmospheric Deposition Program Mercury Deposition Network Site Identification Number												
	IN20	IN21	IN22	IN26	IN28	IN34	IL11	IL63	KY10	MI26	MI52	OH02	OH52
2001	yes	yes			yes	yes	yes						
2002	yes	yes			yes	yes	yes						
2003	yes	yes			yes	yes	yes		yes				
2004	yes	yes		yes	yes	yes	yes		yes				
2005	yes	yes		yes	yes	yes	yes		yes			yes	
2006	yes	yes		yes	yes	yes	yes		yes			yes	
2007	yes	yes		yes	yes	yes	yes		yes			yes	
2008	yes	yes		yes	yes	yes	yes		yes			yes	
2009	yes	yes		yes	yes	yes	yes		yes			yes	
2010						yes	yes		yes				
2011		yes				yes	yes		yes				
2012						yes	yes		yes				
2013							yes		yes				
2014		yes	yes			yes	yes	yes	yes	yes	yes	yes	yes
2015		yes	yes			yes	yes	yes	yes	yes	yes	yes	yes
2016		yes	yes			yes	yes		yes		yes	yes	

Note: yes indicates complete annual record (52 weeks of monitoring observations); shaded indicates incomplete annual record.

Data from the 5-state study area included 4666 samples out of 5304 observations from 2 to 16 complete annual records per site (Table S1 in Supplementary Materials). Data for sites in Indiana were from 2492 samples out of 2860 observations from 3 to 15 annual records per site, which comprise 61% of samples in the study area. Overall, the median annual Hg deposition was 10.4 $\mu g/m^2$/year, with a median annual Hg concentration of 9.4 ng/L and median annual precipitation depth of 1098 mm/year. Sites in Indiana had higher values in that the median annual Hg deposition was 11.4 $\mu g/m^2$/year with a median annual Hg concentration of 9.6 ng/L and median annual precipitation depth of 1154 mm/year. For individual sites in the study (Table 4), median annual Hg deposition ranged from 5.8 $\mu g/m^2$/year at OH52 with 2 years of data (2015–2016) to 15.0 $\mu g/m^2$/year at IN21 with 13 years of data (2001–2016).

Table 4. Summary of annual precipitation-Hg data by site for Midwestern USA study area, 2001–2016.

Site ID Number	Number of Years	Number of Weekly Observations [a]	Number of Weekly Precipitation Samples [b]	Median Annual Precipitation-Hg Deposition (mg/m^2)	Median Annual Precipitation-Weighted Hg Concentration (ng/L)	Median Annual Precipitation Depth (mm)
IN20	9	468	400	9.4	9.2	1049
IN21	13	676	602	15.0	11.6	1289
IN22	3	156	134	10.1	8.1	1152
IN26	6	312	279	10.6	9.4	1184
IN28	9	468	395	10.5	8.6	1244
IN34	15	780	682	10.4	10.7	1071
IL11	16	832	718	9.9	10.9	882
IL63	2	104	89	12.3	9.8	1285
KY10	14	728	661	10.7	8.1	1315
MI26	2	104	100	8.6	8.3	1048
MI52	3	156	143	8.8	9.8	900
OH02	8	416	376	8.8	8.4	930
OH52	2	104	87	5.8	8.4	704

Note: ID: identification; Hg: mercury; mg/m^2: microgram per square meter; ng/L: nanogram per liter; mm: millimeter; [a] "Observation" is rain gage and precipitation collector in operation, regardless of measured weekly precipitation depth. [b] "Sample" is measured weekly precipitation depth >0.25 mm.

The median weekly Hg deposition in all samples from the study area, 2001–2016 was 144 ng/m^2/week, with a median weekly Hg concentration of 9.5 ng/L and a median weekly precipitation depth of 17.0 mm. Samples from sites in Indiana had higher values in that median weekly Hg deposition was 157 ng/m^2/week, with a median weekly Hg concentration of 9.9 ng/L and a median weekly precipitation depth of 17.8 mm.

3.2. Litterfall-Hg and Atmospheric-Hg Deposition

Annual litterfall-Hg deposition was measured at 5 sites in Indiana, one site in Ohio and one site in Kentucky, for 3 to 8 years 2007–2016 (Tables 5 and 6). Annual litterfall-Hg deposition in the study area ranged from 9.7 to 23.4 $\mu g/m^2$/year, with a median of 16.1 $\mu g/m^2$/year, based on annual litterfall Hg-concentrations that ranged from 33.4 to 58.8 ng/g, with a median of 45.1 ng/g and annual litterfall mass that ranged from 236 to 588 g/m^2, with a median of 377 g/m^2 (Table 7). Summary data for Indiana were similar. The sum of precipitation-Hg and litterfall-Hg deposition is a reasonable estimate of the annual atmospheric-Hg deposition, assuming that most of the annual dry-Hg deposition to a forest landscape comes from litterfall [18]. Based on this assumption, estimated annual atmospheric-Hg deposition in the study area ranged from 17.5 to 39.2 $\mu g/m^2$/year, with a median of 26.4 $\mu g/m^2$/year. Summary data for Indiana were similar.

Table 5. Characteristics of Litterfall Mercury Monitoring Initiative sites in Midwestern USA study area.

Site ID Number	Abbreviated Site Name	Deciduous Forest-Cover Type	Tree Species
IN20	Roush Lake	maple-beech-birch	maple, poplar, ash, cherry, elm
IN21	Clifty Falls	oak-hickory	poplar, maple, elm, sassafras, red cedar
IN22	SW Agr. Center	oak-hickory	sycamore, hackberry, elm, honey locust, paw paw
IN26	Fort Harrison	oak-hickory	poplar, maple, oak, cherry
IN34	Indiana Dunes	oak-hickory	black oak, white oak, shagbark hickory, sugar maple, red maple, black walnut, black cherry
KY10	Mammoth Cave	oak-hickory	oak, maple, hickory, ash
OH02	Athens	oak-hickory	oak, maple, hickory, cherry

ID: identification.

Table 6. Annual litterfall-Hg records for Midwestern USA study area, 2007–2016.

Year	National Atmospheric Deposition Program Litterfall Mercury Monitoring Initiative Site Identification Number						
	IN20	**IN21**	**IN22**	**IN26**	**IN34**	**KY10**	**OH02**
2007	yes	yes		yes	yes	yes	yes
2008	yes	yes		yes	yes	yes	yes
2009	yes	yes		yes	yes	yes	yes
2010							
2011							
2012					yes		
2013					yes		
2014					yes		
2015		yes	yes		yes		
2016		yes	yes		yes		

Note: yes indicates Litterfall Mercury Monitoring Initiative site operation per year; shaded years indicate no data collection.

Table 7. Atmospheric-Hg deposition data for Litterfall Mercury Monitoring Initiative sites in Midwestern USA study area, 2007–2016.

Site ID Number	Year	Annual Litterfall-Hg Concentration (ng/g) [a]	Annual Litterfall Mass (g/m^2) [b]	Annual Litterfall-Hg Deposition (mg/m^2/year) [c]	Annual Precipitation-Hg Deposition (mg/m^2/year) [d]	Estimated Annual Atmospheric-Hg Deposition (mg/m^2/year) [e]
IN20	2007	33.4 ± 19.6	588	19.7	7.6	27.3
	2008	45.1 ± 3.6	274	12.3	9.5	21.8
	2009	41.3 ± 1.5	236	9.7	7.8	17.5
IN21	2007	34.0 ± 22.3	475	16.1	12.0	28.1
	2008	53.4 ± 2.8	322	17.2	16.3	33.5
	2009	58.8 ± 1.0	252	14.8	16.5	31.3
	2015	49.3 ± 2.5	283	14.0	12.4	26.4
	2016	50.6 ± 3.5	281	14.2	10.0	24.2
IN22	2015	47.1 ± 3.8	418	19.7	10.1	29.8
	2016	45.4 ± 3.8	328	14.9	9.5	24.4
IN26	2007	48.2 ± 12.1	445	21.5	9.8	31.3
	2008	47.8 ± 0.6	409	19.5	19.7	39.2
	2009	42.8 ± 1.9	260	11.1	9.6	20.7
IN34	2007	58.3 ± 11.0	402	23.4	10.6	34.0
	2008	45.4 ± 2.2	446	20.3	12.1	32.4
	2009	33.7 ± 3.3	368	12.4	10.0	22.4
	2012	40.7 ± 2.2	423	17.2	8.8	26.1
	2013	40.6 ± 1.7	377	15.3	13.8	29.1
	2014	35.2 ± 0.9	507	17.8	12.0	29.8
	2015	38.7 ± 3.9	417	16.1	8.3	24.4
	2016	39.4 ± 1.8	383	15.1	7.6	22.7
KY10	2007	36.1 ± 8.9	349	12.6	10.2	22.8
	2008	39.9 ± 1.9	318	12.7	10.2	22.9
	2009	45.2 ± 4.1	277	12.5	12.1	24.6
OH02	2007	50.1 ± 9.8	431	21.6	8.7	30.3
	2008	37.6 ± 3.8	499	18.8	9.8	28.6
	2009	49.0 ± 1.2	329	16.1	6.8	22.9

Note: ID, identification; Hg: mercury; ng/g: nanogram per gram; g/m^2: gram per square meter; mg/m^2/year: microgram per square meter per year; [a]: Annual mean Hg concentration in litterfall samples ± standard deviation of mean; [b]: Annual sum of the litterfall mass in gram dry weight per square meter; [c]: Annual litterfall-Hg deposition computed as the product of annual mean Hg concentration and annual litterfall mass, using non-rounded values; [d]: Annual precipitation-Hg deposition from National Atmospheric Deposition Program [44]; [e]: Sum of annual litterfall-Hg deposition and annual precipitation-Hg deposition.

4. Discussion

4.1. Spatial Patterns in Hg Deposition

Spatial patterns of precipitation-Hg deposition in the study area were examined with statistical analysis of the weekly data and with isopleth maps of annual data. Statistical analysis revealed a spatial pattern of differences in weekly precipitation-Hg deposition. During 2001–2016, Hg deposition at IN21 (median 196.2 ng/m^2/week, 13-year record) was significantly higher ($p < 0.001$) than that at IL11, IN20, IN34, MI26, MI52, OH02 and OH52 (Figure 3, Table 8). The sites in Indiana differed according to the same spatial pattern of the study area in that the southeastern site IN21 was significantly higher ($p = 0.001$) than the northeastern site IN20 and the northwestern site IN34. In contrast, Hg deposition at 7 sites located in the central and southern part of the study area was not significantly different—IN21, IN22, IN26, IN28, IL63 and KY10. The site with the highest median weekly precipitation-Hg deposition was IL63 with 198.3 ng/m^2/week, which was significantly different from 4 sites during 2014–2016—MI26, MI52, OH52 and OH02. Some of the statistical differences among sites in the study can be attributed to the temporal changes discussed in the next section and comparisons limited to the years with complete annual records for each site (Table 3). Annual litterfall-Hg deposition (Table 7) and estimated atmospheric-Hg deposition (sum of litterfall-Hg and precipitation-Hg deposition) for 2007–2016 were not significantly different among 7 sites in the study area or among 5 Indiana sites ($p = 0.25$ and $p = 0.54$, respectively).

Table 8. Summary of weekly precipitation-Hg data by site for Midwestern USA study area, 2001–2016.

Site ID Number	Number of Years	Number of Weekly Precipitation Samples [a]	Median Weekly Precipitation-Hg Deposition (ng/m^2)	Median Weekly Precipitation-Hg Concentration (ng/L)	Median Weekly Precipitation Depth (mm)
IN20	9	400	136.6	9.4	17.3
IN21	13	602	196.2	10.8	21.0
IN22	3	134	141.9	8.4	18.0
IN26	6	279	158.3	8.8	17.8
IN28	9	395	159.8	9.4	19.8
IN34	15	682	137.3	10.2	15.2
IL11	16	718	137.2	10.8	14.2
IL63	2	89	198.2	10.4	21.3
KY10	14	661	158.1	8.3	20.1
MI26	2	100	95.0	7.6	14.3
MI52	3	143	89.3	8.0	11.4
OH02	8	376	116.7	8.3	16.5
OH52	2	87	63.6	8.1	9.6

Note: ID: identification; Hg: mercury; ng/m^2: nanogram per square meter; ng/L: nanogram per liter; mm: millimeter; [a]: Sample is measured weekly precipitation depth >0.25 mm.

Isopleth maps of annual precipitation-Hg deposition were prepared for 2005–2009 and 2014–2016 (Figure 4). These 12 years had a sufficient number of sites with complete annual records to support spatial grids of Hg-concentrations to map the study area. Color coding of annual Hg deposition on the maps indicates a recurring spatial pattern similar to the one revealed by the statistical analysis. High deposition in southeastern Indiana near IN21 was present each year, frequently extending to southern Illinois. Areas with low annual Hg deposition were mapped in Michigan and Ohio for many years and frequently included part of northern Indiana.

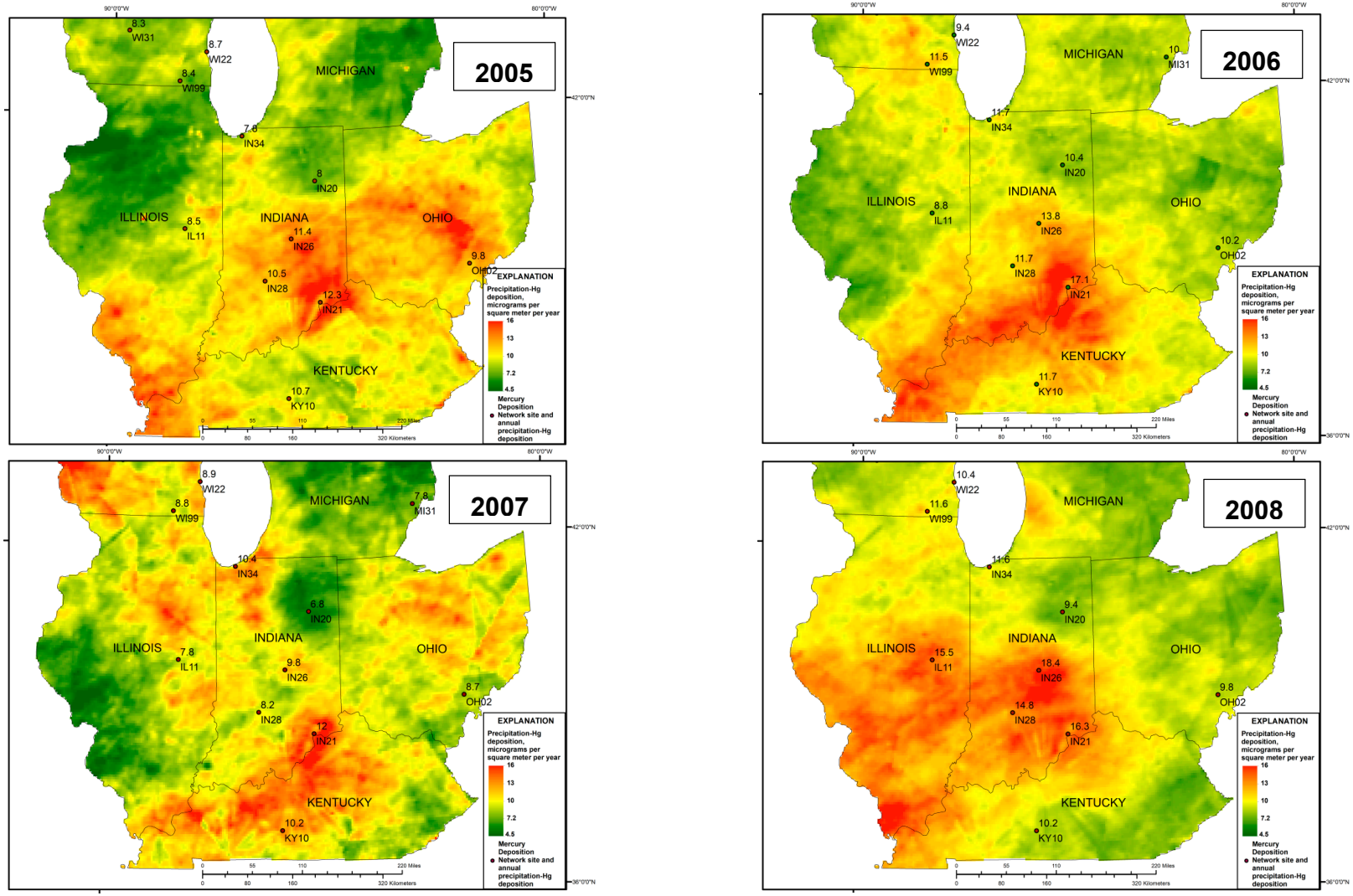

Figure 4. *Cont.*

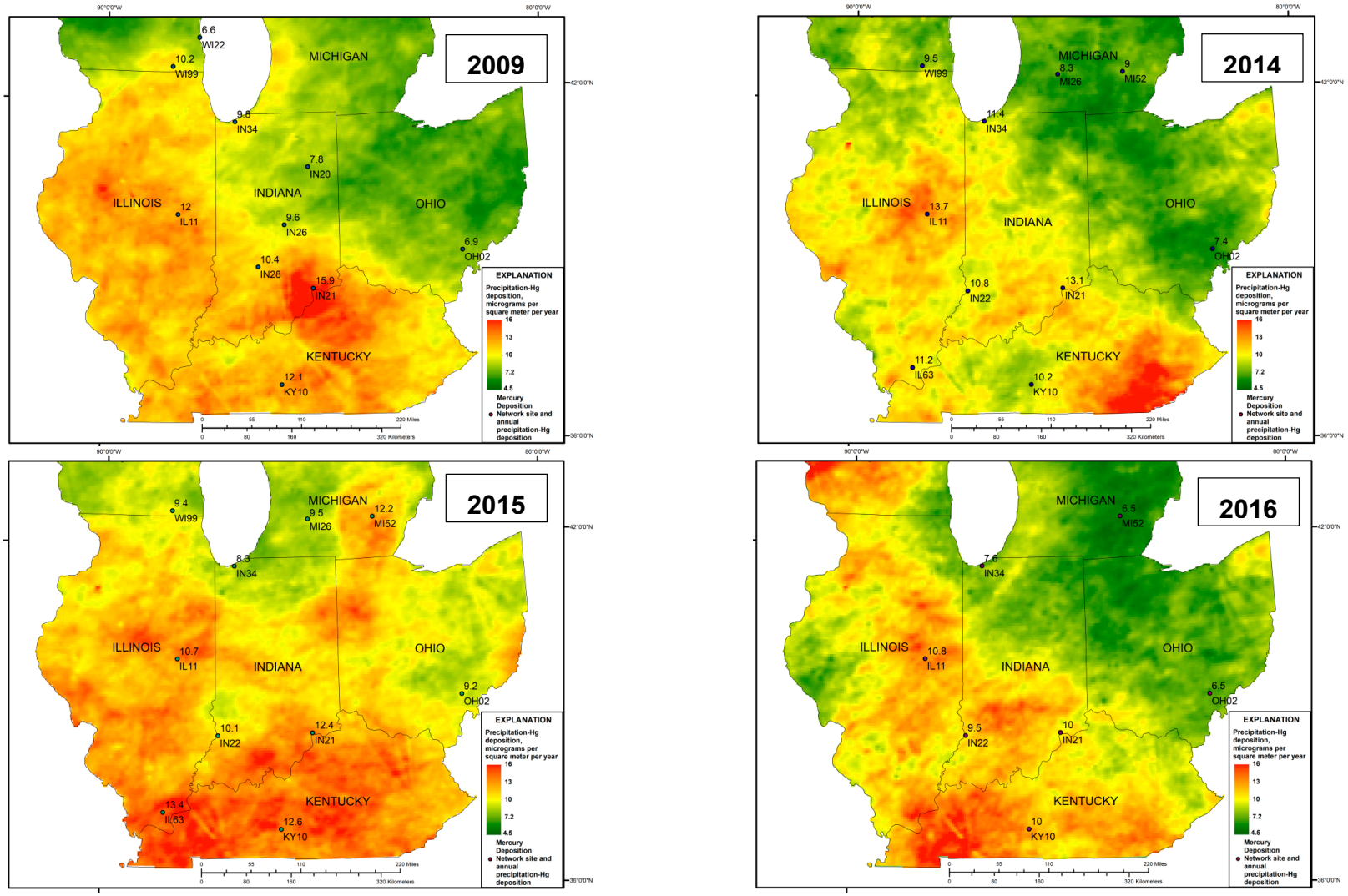

Figure 4. Isopleth maps of annual precipitation-Hg deposition in Midwestern USA study area, 2005–2009 and 2014–2016.

The isopleth maps show apparent spatial detail in precipitation-Hg deposition corresponding to the detail from the PRISM precipitation depth data, rather than the Hg concentration data but this is not an anomaly from the method. Although Hg deposition is a product of Hg concentration and precipitation depth, the data from this study area indicates that weekly Hg deposition is more highly correlated with precipitation depth (*rho* 0.833, $p < 0.001$) than Hg concentration (*rho* 0.249, $p < 0.001$). Similarly, linear regressions indicate more of the variability in weekly Hg deposition is explained by precipitation depth (coefficient of determination r^2 0.58, $p < 0.001$) than by Hg concentration (r^2 0.04, $p < 0.001$). A supporting observation is that sites in the southern part of the study area (IN21, IN22, IN28, IL63 and KY10) had significantly higher weekly precipitation depths ($p < 0.001$) than sites in the northern part of the study area (IN34, MI52 and OH52). The substantial influence of precipitation depth on precipitation-Hg deposition has been reported by other research [10,16,51–53].

The distribution of Hg emissions sites (Figure 1), particularly those releasing 180 to 361 kg/year of Hg, is not uniformly related to the spatial pattern of annual precipitation-Hg deposition, although the density of these emissions sites appears to coincide with the area of high Hg deposition mapped for southern Indiana. A simple comparison of the magnitude of annual precipitation-Hg deposition with annual Hg emissions from stationary sources in Indiana was made using data from Table 1 and Table S1. If the mean statewide precipitation-Hg deposition of 11.8 μg/m^2/year based on data from IN21, IN22 and IN34 in 2014 was uniform to the land area of Indiana (9.43×10^{10} m^2), the annual precipitation-Hg load statewide would have been 1094 kg, which is 60% of the 1852 kg annual Hg emissions in the state.

4.2. Extreme Episodes of Hg Deposition

A potential reason that southern Indiana consistently showed statistically and spatially high precipitation-Hg deposition is the frequency of extreme episodes of weekly Hg deposition in the study area, 2001–2016. Extreme episodes were defined as the top 0.5% of values (Table 9). Extreme Hg-deposition episodes occurred at 8 of the 13 sites in 12 of the 16 years with annual Hg deposition records and 13 of the 27 episodes were recorded for IN21. Extreme Hg-deposition episodes occurred in all seasons but most were between April and September. Only two pairs of extreme episodes occurred in the same weeks, 26 April to 3 May 2011 at IN21 and KY10 and 1 to 8 April 2014 at IN21 and IN22. Notably, the Hg deposition, Hg concentration and precipitation depths were similar among each pair, indicating the potential spatial extent of some extreme episodes.

Weekly Hg-deposition in the extreme episodes was 5 to 10 times higher than in most weekly samples. The episodes ranged from 1640 to 2602 ng/m^2/week, compared with a median of 145 ng/m^2/week and a 75th percentile of 308 ng/m^2/week for all sites for all years. The extreme episodes supplied 10 to 17% of the annual precipitation-Hg deposition in a single week but the episodes did not occur more than twice in one year at any site. Hg concentrations ranged from 7.1 to 45.4 ng/L with a median 14.9 ng/L. The median weekly Hg concentration for all samples from the study area was 9.5 ng/L, which is 36% lower. For these extreme Hg deposition episodes, precipitation depths ranged from 37.3 to 265 mm with a median 120 mm. The median weekly precipitation depth for all samples from the study area was 17.0 mm, which is 61% lower. Weekly precipitation-Hg deposition amounts for the extreme episodes in the study area and at IN21 alone were not correlated significantly with precipitation depth or Hg concentration and variability in Hg deposition was not statistically explained by either factor. The data indicate that high precipitation depth and relatively high Hg concentration contributed to each extreme episode (Table 9).

Table 9. Extreme episodes of weekly precipitation-Hg deposition in Midwestern USA study area, 2001–2016.

Site ID Number	Dates of Weekly Sample	Weekly Precipitation-Hg Deposition (ng/m^2)	Weekly Precipitation-Hg Concentration (ng/L)	Weekly Precipitation Depth (mm)	Percentage of Annual Precipitation-Hg Deposition
IN34	28 June–5 July 2011	2602	30.7	84.8	17%
IN20	1–8 July 2003	2456	11.0	222.9	16%
KY10	**26 April–3 May 2011**	2453	14.7	166.9	16%
IN21	11–19 March 2008	2422	16.7	144.8	15%
IL11	1–8 July 2008	2326	39.8	58.4	16%
IN26	3–9 June 2008	2218	20.3	109.5	12%
IN21	**26 April–3 May 2011** [a]	2158	14.7	147.3	11%
IN21	8–15 July 2003	2043	22.4	91.2	12%
IN21	29 November–6 December 2011 [a]	1891	20.3	93.2	10%
IN34	9–16 September 2008	1876	7.1	265.2	16%
IN21	7–14 March 2006	1797	12.4	144.8	11%
IN21	17–24 June 2015 [a]	1790	14.9	120.1	14%
IN21	26 August–9 September 2003	1766	10.7	165.7	10%
IN20	6–13 May 2003	1754	12.5	140.4	12%
IN21	6–14 April 2004	1742	35.7	48.8	11%
IL11	13–20 July 2010	1729	16.6	104.4	15%
IN20	8–15 June 2004	1709	14.4	118.4	15%
IN21	11–18 December 2001	1703	22.3	76.2	14%
IN21	**1–8 April 2014** [a]	1701	12.7	133.9	13%
IN26	25 April–2 May 2006	1696	45.4	37.3	12%
IN21	4–11 January 2005	1686	20.1	83.8	14%
IN34	20–27 July 2010	1660	15.8	105.2	13%
IN21	25 May–1 June 2004	1658	13.7	121.4	11%
IN28	6–13 March 2006	1657	8.7	191.5	14%
IN20	11–18 April 2006	1654	17.4	95.0	16%
IN22	**1–8 April 2014**	1644	12.1	135.9	15%
IN21	28 July–4 August 2009 [a]	1640	10.6	154.4	10%

Note: ID: identification; Hg: mercury; ng/m^2: nanogram per square meter; ng/L: nanogram per liter; mm: millimeter; **bold** indicates identical weeks; [a]: Paths of air masses contributing to precipitation-Hg episode analyzed with modeled 48 h back trajectory (Figure 5).

Modeled 48-h back trajectories of the hourly positions of the air masses for five extreme episodes of precipitation-Hg deposition at IN21 during 2009–2015 illustrate a further explanation for the high precipitation-Hg deposition (Table 9, Figure 5). The back trajectories indicate that air masses predominantly came from the south and southwest. Locations and annual Hg emissions for stationary sources overlain on the back-trajectory map show that numerous sources emitting from 23 kg to more than 300 kg Hg per year were in the path of these air masses. This analysis suggests that local and regional sources, rather than exclusively continental or global Hg emissions likely contributed to the extreme episodes and at least in part, to the spatial patterns of precipitation-Hg deposition in the study area. Other research attributed substantial contributions from local and regional Hg emissions sources to precipitation-Hg deposition in the Midwestern USA [19,20,54,55]. According to Holmes et al. [56] and Kaulfus et al. [57], warm weather, convective thunderstorms are believed to increase Hg deposition and this may be the case for many of the extreme episodes examined in this study. Such storms can incorporate additional GOM formed in the troposphere from GEM originating at local and regional sources [55], in addition to effective below-cloud and in-cloud scavenging of GOM, as described by Lynam et al. [58].

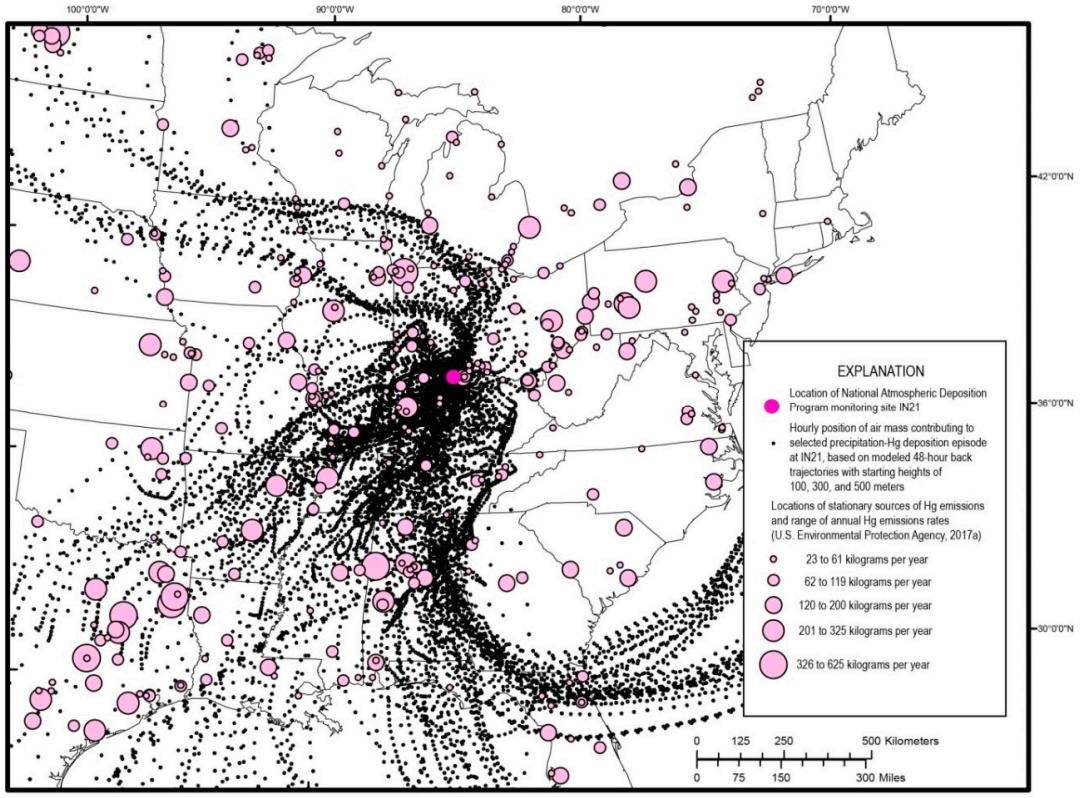

Figure 5. Modeled 48-h back trajectories for five precipitation-Hg deposition episodes at National Atmospheric Deposition Program monitoring site IN21, 2009–2015, with locations of stationary sources of Hg emissions for 2014 [26].

4.3. Temporal Changes in Hg Deposition

Temporal changes in Hg deposition can be observed in the study area during the 16-year study period. The Mercury and Air Toxics Standards (MATS) rules were finalized by U.S. Environmental Protection Agency for Hg emissions from power plants in 2011, effective in 2015 [59]. Rules for other Hg emissions sources such as cement kilns, utility boilers and medical waste incinerators were finalized in 2010, 2011 and 2013, respectively [60–62]. The expected outcome was a succession of reduced Hg emissions from these sources up to and after the effective dates.

To examine whether a temporal trend was evident in precipitation-Hg in response to these rules, the weekly data were grouped by year 2001–2012 and 2014–2016. As grouped, Hg deposition and Hg concentration were shown to be significantly lower in 2014–2016 than 2001–2013 ($p < 0.001$). The median weekly Hg deposition in 2001–2013 was 152 μg/m^2/week, compared with 123 μg/m^2/week in 2014–2016, a 19% difference and the median weekly Hg concentration was 9.9 ng/L compared with 8.3 ng/L, a 16% difference. Data for Indiana showed a similar response. Hg deposition and Hg concentration were significantly lower in 2014–2016 than 2001–2012 ($p = 0.038$ and $p < 0.001$, respectively). The median weekly Hg deposition in 2001–2012 was 161 μg/m^2/week, compared with 135 μg/m^2/week in 2014–2016, a 16% difference and the median weekly Hg concentration was 10.2 ng/L compared with 8.3 ng/L, a 19% difference. Consistent with other analysis for the study area, weekly Hg concentrations grouped 2001–2009 (median 10 ng/L) and 2010–2012 (median 9.6 ng/L) were significantly higher ($p < 0.001$) than 2014–2016 (median 8.3 ng/L). Weekly precipitation depth between these two time periods was not significantly different in the study area ($p = 0.331$) or in Indiana ($p = 0.469$), meaning the decreases in Hg deposition were related primarily to decreases in Hg concentration rather than decreases in precipitation depth. These data document a gradual decline in Hg concentrations in advance of the period when Hg emissions reductions were required.

This observation is consistent with model results by Zhang and Jaegle [63] for 2005–2010 in the Midwestern USA.

Wetherbee et al. [64] analyzed trends in annual precipitation depths at a separate group of NADP monitoring sites for 2001–2015. They reported increases in precipitation at 17 of 21 sites in the study area that were statistically significant and higher than 1 cm/year at 3 of the 17 sites. This information suggests the potential for some decreases in Hg concentrations to involve dilution by increased precipitation. Typically, increased precipitation depth would cause a corresponding increase in Hg deposition but that response was not identified in the statistical analysis. Precipitation-Hg concentrations and Hg deposition exhibited a decline during the study period.

The findings from this study in the Midwestern USA indicate that reductions in Hg emissions associated with implementation of the MATS and related rules coincided with temporal decreases in precipitation-Hg concentrations, resulting in decreased atmospheric Hg deposition. Meanwhile, precipitation depths did not significantly change. At the minimum, it can be postulated that reductions of atmospheric GOM and PBM in the study area, the species most readily scavenged from the air during precipitation, were associated with the reduced precipitation-Hg concentrations and deposition. Reductions of atmospheric GEM, the most abundant species and the one considered to dominate litterfall-Hg deposition, were inconclusive based on these Midwestern data. Annual litterfall-Hg deposition, litterfall-Hg concentrations and litterfall mass at 7 sites were not significantly different in 2007–2009 compared with 2012–2016. A study by Risch et al. [18] reported litterfall-Hg concentrations in the eastern USA were significantly lower in 2014–2016 than 2007–2009, consistent with reported declines in atmospheric GEM reported by others. The inconsistency of Midwestern litterfall-Hg data with the broader region underscores the value of the spatial focus on five states afforded by this study.

5. Conclusions

The Midwestern USA region has a history of numerous anthropogenic Hg emission sources, including those with high annual emission rates. The 5 states in this study include 32% of the sources and 20% of the Hg emissions in the 48 states of continental USA. An extensive monitoring record of weekly precipitation-Hg data and annual litterfall-Hg data from the NADP was investigated for 13 sites for a 16-year period. Although dry deposition of atmospheric Hg from litterfall was not statistically different among sites in the study, spatial patterns and temporal changes were identified with the precipitation-Hg data. Isopleth maps showed the southern part of the study area had a recurring pattern of high annual Hg deposition while the northern and eastern parts had comparatively lower annual Hg deposition. This spatial pattern was consistent with statistically significant differences determined in weekly Hg deposition among the sites. One site in the area of high Hg deposition recorded half of all extreme episodes (top 0.5%) of weekly Hg deposition in in the study area. Modeled back trajectories for extreme episodes at this site showed the storm paths crossed numerous large Hg emissions sources. A conclusion is that some of the spatial patterns are attributable to deposition of atmospheric Hg transported from local and regional emissions sources, rather than exclusively continental and global sources. Another conclusion is that statistically significant differences in weekly precipitation-Hg concentrations between periods before and after implementation of rules requiring reductions in Hg emissions were a response to these rules. The reduced Hg concentrations led to the 19% decrease in precipitation-Hg deposition in the study area in recent years.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4433/9/1/29/s1, Table S1: Summary of annual precipitation depths, Hg concentrations, and Hg deposition by year for Midwestern USA study area, 2001–2016.

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Conflicts of Interest: The authors declare no conflicts of interest.

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