Mercury Deposition Monitoring in Kansas: Network Report for 2014

Our Vision – Healthier Kansans living in safe and sustainable environments.

Prepared December 2015

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Introduction

Elemental mercury volatilizes and evaporates into the atmosphere where is circulates freely and constitutes the "global pool" of mercury. Human sources of mercury include by-products of coal-fire combustion, municipal and medical incineration, and mining of metals for industry. Natural sources of atmospheric mercury include outgassing from volcanoes and geothermal vents and evaporation from naturally enriched soils, wetlands and oceans. Some elemental mercury is converted to reactive gaseous mercury in the atmosphere and is deposited back on to the surface of the Earth. This deposition of mercury is monitored by the Mercury Deposition Network which is coordinated through the National Atmospheric Deposition Program.

The Kansas Mercury Wet Deposition Network (KMDN) was established in 2009 per K.S.A. 75-5673. The statute required that the Kansas Department of Health and Environment (KDHE) design a statewide mercury deposition network consisting of at least six monitoring sites. Monitoring activities were to take place for a period of time long enough to determine trends (five or more years) is also specified in that statute. In 2014 K.S.A. 75-5673 was amended eliminating the site quantity requirement. This amendment allowed for KDHE to review the appropriateness of the site locations based on five years of data.

The network was designed to assure compatibility with the Mercury Deposition Network (MDN). The MDN, coordinated through the National Atmospheric Deposition Program (NADP), is designed to study and quantify the atmospheric fate and deposition of mercury. The single largest source of mercury pollution in the U.S. is atmospheric emissions and subsequent deposition associated with combustion from coal-fired power plants, waste incinerators, and chlorine production plants. Atmospheric deposition to surface waters and wetlands has been linked to movement of mercury through the food web, resulting in high concentrations in fish and mammal populations. Mercury affects humans through fish consumption, resulting in health risks especially to fetuses and young children. Fish consumption advisories commonly define populations sensitive to mercury as women who are pregnant, may become pregnant, or are nursing and children age 17 or younger.

This report contains a description of the KMDN, information on Mercury deposition and a discussion on the 2014 data.

Description of the Kansas Mercury Wet Deposition Network

The complete Kansas Mercury Wet Deposition Monitoring Network (KMDN) consists of six sites distributed across the state. The locations of sites in the states of Nebraska and Oklahoma were also taken into consideration to optimize regional mercury network coverage. A map of the network appears below in Figure 1. Each site was chosen to meet particular criteria. Specific regional and local siting criteria must be met before any site is accepted into the national MDN. Sampling at all sites is performed on a weekly basis, with sample retrieval every Tuesday. Clean sample glassware is installed for collection of the next week's sample at

the time of the operator's site visit. All samples are sent to a national laboratory used by the MDN.

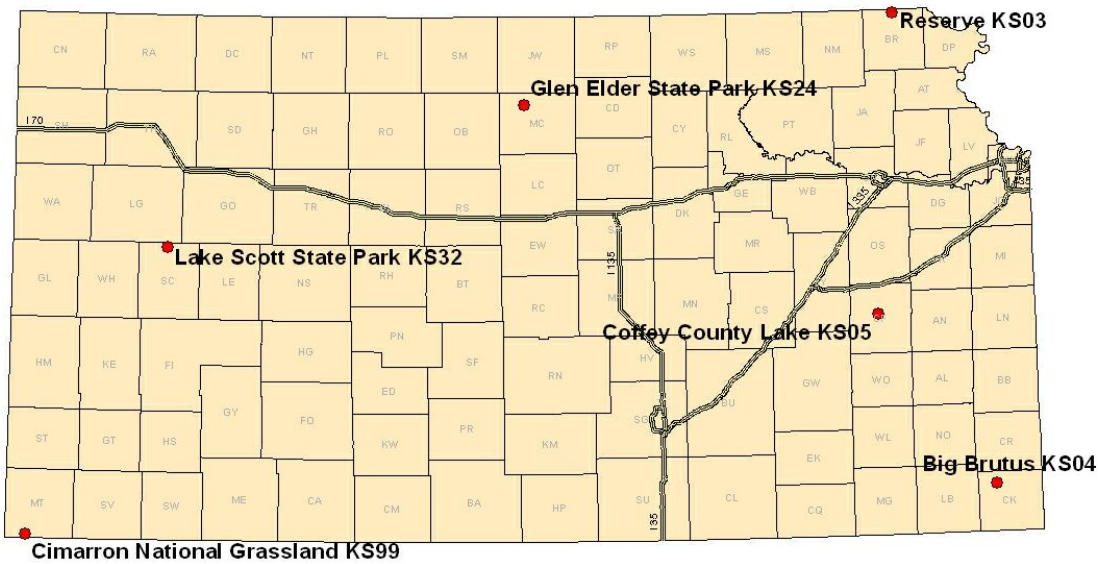


Figure 1. Map of the Kansas Mercury Wet Deposition Network 2009-2014

Sample analysis and coordination through this national cooperative research program are performed under contract.

Discussion of Factors Affecting Mercury Deposition

Most mercury in the atmosphere is present as elemental mercury (Hg^0). Some of this mercury is converted to reactive gaseous mercury (Hg^{2+}), which is the predominant form flushed from the atmosphere by precipitation. It is generally believed that most atmospheric Hg^{2+} is in the form of mercuric chloride ($HgCl_2$). In general, concentration and deposition amounts are higher during the warmer months.

Seasonal variation occurs for several reasons:

1) Higher temperatures and faster reaction rates cause more rapid chemical conversion.

2) More oxidants, such as ozone (O_3) and hydroxyl ions (OH^-), which can convert Hg^0 to Hg^{2+} are present.

3) Higher concentrations of Hg^0 are present in the atmosphere due to higher emissions from increased power generation, etc.

4) Seasonal increases in precipitation flush more mercury out of the air more efficiently.

There are three factors which affect deposition of atmospheric mercury at any given location. These are:

1) **Concentration,** which is affected by local, regional and global sources.

   The total amount of mercury from non-local sources circulating freely in the Earth's atmosphere at any given time constitutes the "global pool" of mercury. It is estimated that 95 percent of the global pool is Hg^0; this mercury circulates for a period of time estimated to be between 6 months to 2 years. Local contributions to mercury concentrations vary considerably across the planet and within the United States, depending on the distance from the point of measurement to local and regional sources. Local mercury contribution can impact local and/or regional deposition, especially if it is emitted in a reactive form (e.g., Hg^{2+}).

2) **Precipitation,** which removes mercury from the atmosphere.

   Precipitation essentially "flushes" mercury from the atmosphere. It is this mercury that is measured to determine the deposition data values. In general, mercury concentrations appear to be higher when it begins to rain or snow, and lower at the end of a precipitation event. This is most evident during periods of prolonged precipitation (i.e., over a period of several hours to several days).

3) **Location** with regard to proximity of local sources.

   As stated above (Factor 1), local mercury concentrations vary considerably across the planet and within the United States, depending upon the distance from the point of measurement to local and regional sources. This factor also varies with wind direction, i.e., whether the sampling point is upwind or downwind of such sources at the time of sampling. In general, the closer a monitor is to a source, provided that it is downwind of that source, the higher the mercury concentration.

   Across Kansas, there can be dramatic shifts in sources of the air coming into the state. For example, southeast Kansas is much more likely to receive tropical air from the south. Out west, this region is dominated by atmospheric flows from farther west (i.e., Pacific air, continental air, etc). This can exert a significant influence on what the atmosphere contains and what gets flushed out. Kansas sources include electrical generating units, cement kilns and mining operations.

Mercury Wet Deposition Network Data

The purpose of the MDN is to collect mercury wet deposition data over a long period of time to monitor trends in the levels of mercury deposited over the earth's surface. Short term data analysis is difficult because of seasonal and year to year variability in precipitation amounts and mercury concentrations.

Quality assurance of MDN data occurs at two levels. All data are first reviewed by the national contract laboratory for completeness and accuracy, and assigned codes for samples that were mishandled, contaminated, or affected by equipment malfunction. The final laboratory data set is

then forwarded to the MDN Program Office for final quality assurance before generation of annual average concentration and wet deposition maps and posting to the website. http://nadp.sws.uiuc.edu/MDN/annualmdnmaps.aspx

Data generated by the Kansas Mercury Deposition Network will be posted to the KDHE website as available and annually to a national database.

Results for 2014

The Kansas trend charts on pages 4, 5, and 6 show mercury concentration, mercury wet deposition, and total precipitation respectively from 2009-2014 for each site. Please note that the 2014 report does not include the site designated KS05, Coffey County Lake. This is due to a large number of invalid samples. Samples were invalidated by the contract laboratory in large part because of equipment malfunctions. The nature of the malfunctions was an aging and weathered sensor that operates the top hatch of the collector during precipitation events. The sensor was reportedly opening during non-precipitation events such as the presence of large concentrations of dust and plant matter affecting the sensor. Figures 2 and 3 show a spatial variability in the precipitation-weighted mean concentration and wet deposition of total mercury in the five remaining Kansas sites. All data collected and tabulated from 2009 to 2014 is also listed in the table in Appendix A.

1. Concentration, expressed in nanograms of mercury per liter (ng/L) of precipitation collected.

This is the amount of mercury present in the precipitation collected by the sampler. Concentration measurements provide a long-term record of mercury levels in precipitation across the United States.

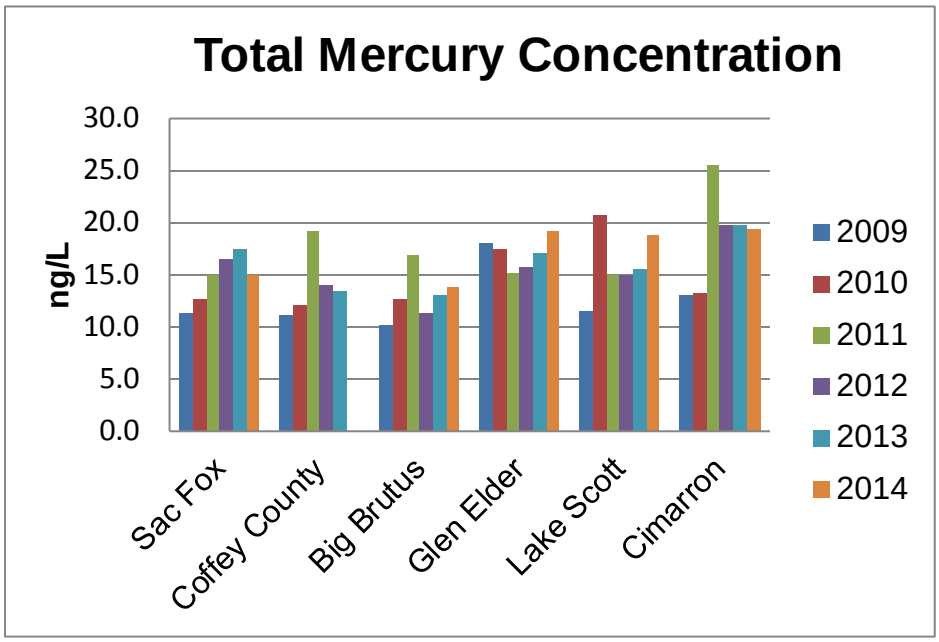


Figure 2.
Total mercury concentrations for the Kansas sites 2009-2014, Coffey County Lake 2009-2013

2. Deposition, expressed in micrograms of mercury per square meter (µg/m^2).

This is the amount of mercury deposited by precipitation on each square meter of ground at the sampling site. Deposition values, expressed in micrograms of Hg per square meter per unit of time **(µg/m^2/year)**, provide annual estimates of the amount of mercury loaded onto the surface of the earth in the vicinity of each sampling site. It is a portion of this mercury which enters bodies of water and ultimately enters the food chain through aquatic systems.

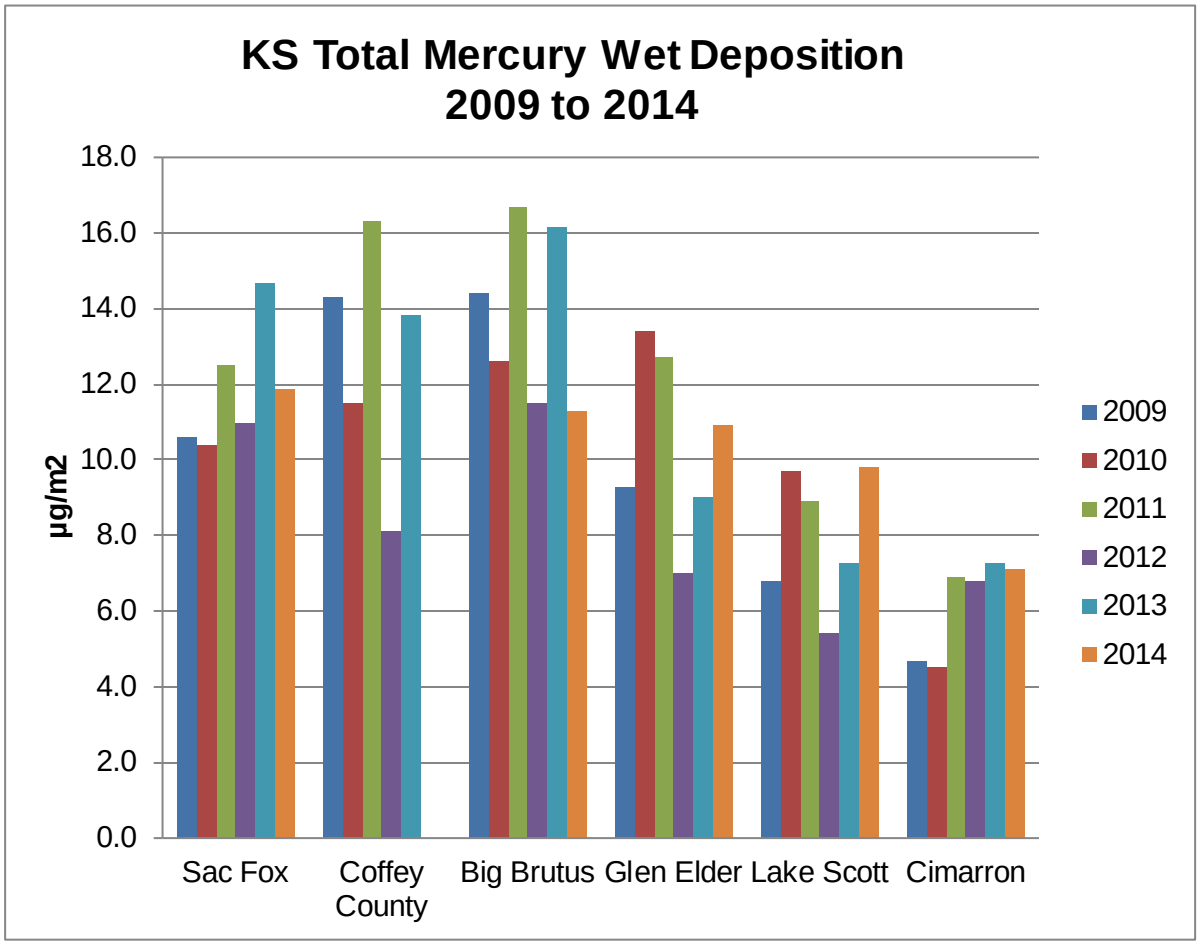


Figure 3. Total mercury wet deposition for Kansas sites 2009-2014, Coffey County Lake 2009-2013

3. Total precipitation depth collected, expressed in centimeters (cm).

This is the depth of precipitation, snow and rain, collected which when multiplied by the concentration, gives total wet deposition of mercury on the surface.

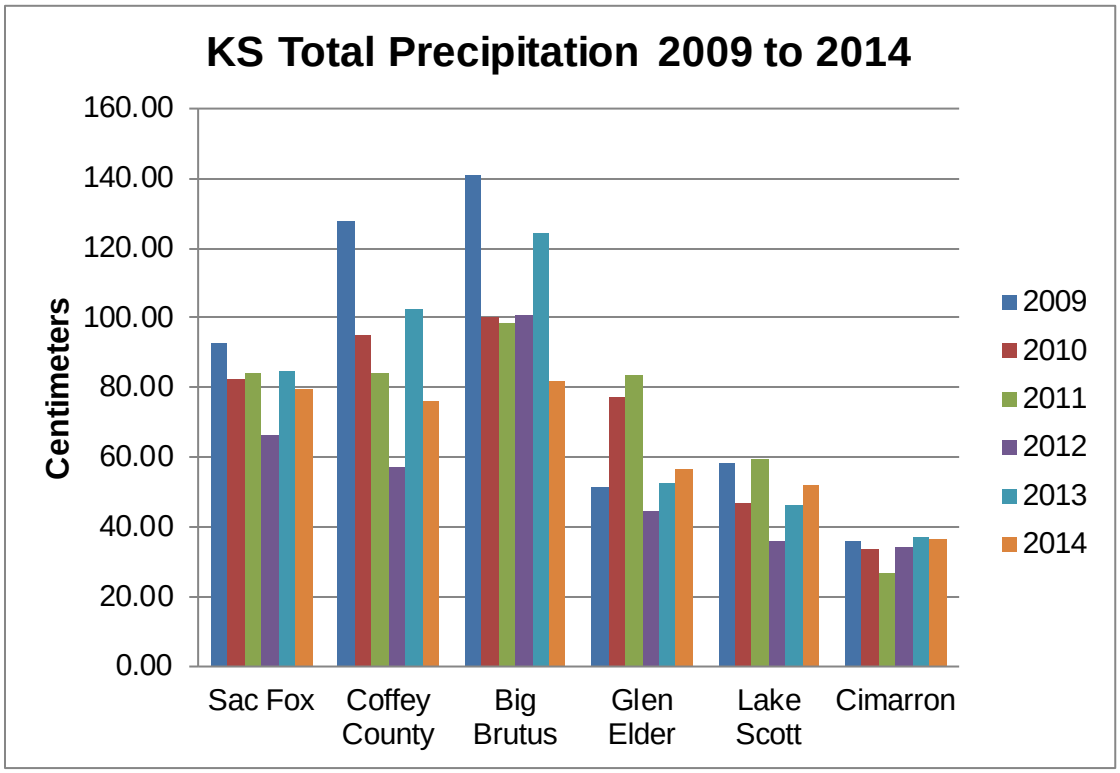


Figure 4. Total Precipitation for Kansas sites 2009 to 2014.

Discussion of 2014 Results

Sites with higher average mercury concentrations in precipitation are not necessarily the sites with the highest wet deposition of mercury. For example, the Cimarron site, which is located in the southwest corner of the state, had the highest average concentration of total mercury (19.4 ng/L); but with 36.7 cm of precipitation, this site had one of the lowest wet deposition values of mercury for 2014. In another example, Big Brutus showed a modest increase in concentration from 13.0 ng/L in 2013 to 13.8 ng/L in 2014. Wet deposition for those years was 16.1 ug/m^2 and 11.3 ug/m^2 respectively. The difference in wet deposition with a modest increase in concentration at Big Brutus is likely due to a decrease in precipitation from 124.1 cm in 2013 and 81.6 cm in 2014. Also noteworthy are the results from the Sac and Fox site. KS03 showed a decrease in concentration from 17.4 ng/L in 2013 to 15.0 ng/L in 2014. Deposition also decreased from 14.7 ug/m^2 in 2013 to 11.9 ug/m^2. A decrease in precipitation was also noted with 84.5 cm collected in 2013 and 79.6 cm collected in 2014. Decreases in concentration normally have a corresponding increase in precipitation therefore even though there was less precipitation collected, precipitation events could have increased in duration and sources of mercury emissions decreased. Sites KS24 and KS32 at Glen Elder and Lake Scott saw increases in concentration, deposition and precipitation. Again, what is normally anticipated when there is an increase in precipitation is a decrease in concentration of mercury, therefore even though there was more precipitation collected precipitation events could have decreased in duration and sources of mercury emissions increased.

The end of 2013 completed 5 years of collecting precipitation to analyze the concentration and wet deposition of mercury across six sampling sites in Kansas. A full review of the Kansas Mercury Deposition Network occurred in late 2014. After five years of completed data, the total mercury wet deposition has been relatively consistent at each site, with no clear signs of an increasing or decreasing trend. Two sites were identified for further investigation. KS99 at Cimarron is the site consistently receiving the least amount of precipitation and therefore less deposition of mercury. KS99 was selected for closure at the end of 2014. KS04 at Big Brutus is the site consistently receiving the highest amount of precipitation and a corresponding higher amount of deposition. However KS04 is located where other monitors are operating. Similarities between these sites were identified and KS04 was selected for closure.

Network Cost Analysis

Costs associated with the KMDN are presented in the table below. All costs are covered by Air Fee Fund revenues.

Kansas Mercury Deposition Network Operating Costs: Jan. 1, 2014 – Dec. 31, 2014		
Cost Category	**Item Description**	**Category Totals**
Salaries and Fringes		$38,909
Supplies	Low toxicity antifreeze	$60
Operator and Site Use Fees		$22,500
Travel	Travel ($0.505/mile)	$684
Shipping	Samples to Laboratory	$15,000
Laboratory Analysis	Mercury Analysis	$60,084
Total Operating Cost		$137,237

Appendix A

Annual Date 2014

January through December

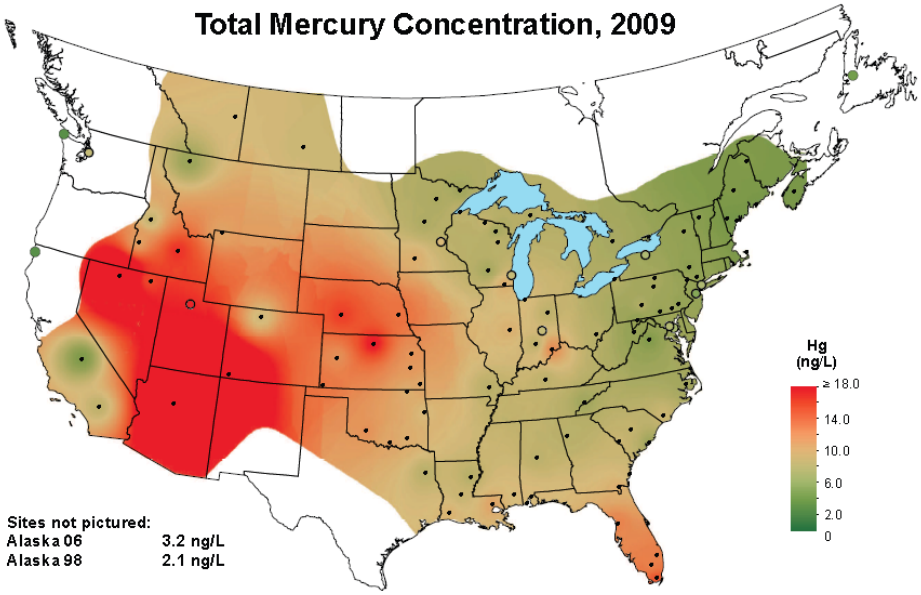
Concentration ng/L	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Sac Fox	11.4	12.6	14.9	16.5	17.4	15.0
Coffey County	11.2	12.1	19.3	14.1	13.5	NA*
Big Brutus	10.2	12.6	17.0	11.4	13.0	13.8
Glen Elder	18.0	17.4	15.2	15.7	17.1	19.2
Lake Scott	11.6	20.8	14.9	15	15.6	18.8
Cimarron	13.1	13.3	25.6	19.8	19.7	19.4
Deposition ug/m^2	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Sac Fox	10.6	10.4	12.5	11.0	14.7	11.9
Coffey County	14.3	11.5	16.3	8.1	13.8	NA*
Big Brutus	14.4	12.6	16.7	11.5	16.1	11.3
Glen Elder	9.3	13.4	12.7	7.0	9.0	10.9
Lake Scott	6.8	9.7	8.9	5.4	7.3	9.8
Cimarron	4.7	4.5	6.9	6.8	7.3	7.1
Precipitation cm	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Sac Fox	92.9	82.5	83.8	66.6	84.5	79.6
Coffey County	127.6	95.0	84.4	57.4	102.4	76.1
Big Brutus	141.1	100.0	98.2	100.8	124.1	81.6
Glen Elder	51.6	77.0	83.5	44.5	52.6	56.8
Lake Scott	58.6	46.6	59.7	36.0	46.6	51.9
Cimarron	35.8	33.8	26.9	34.3	37.0	36.7

*Coffey County Lake was not analyzed due to large number of invalid samples, please see results section of this report for more information.

Appendix B

National Mercury Concentration/Wet Deposition Maps 2009-2014

National mercury data are summarized for each year by calculating the annual average values from each site and plotting the information on a national map. The most recent national average concentration and total deposition maps for calendar year 2014 appear in on page 14. A set of these MDN maps, dating back to 1998, can be found at http://nadp.sws.uiuc.edu/MDN/annualmdnmaps.aspx.



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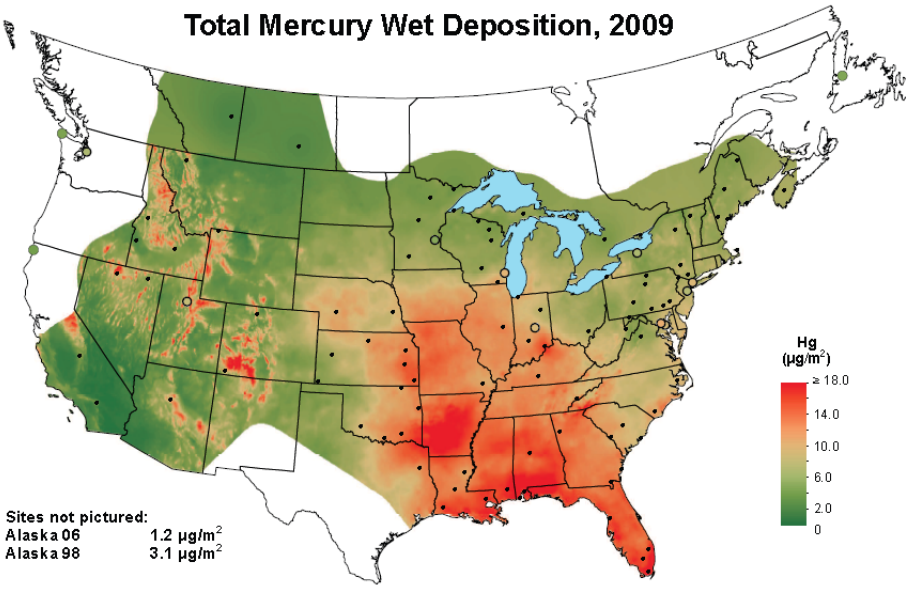
http://nadp.isws.illinois.edu



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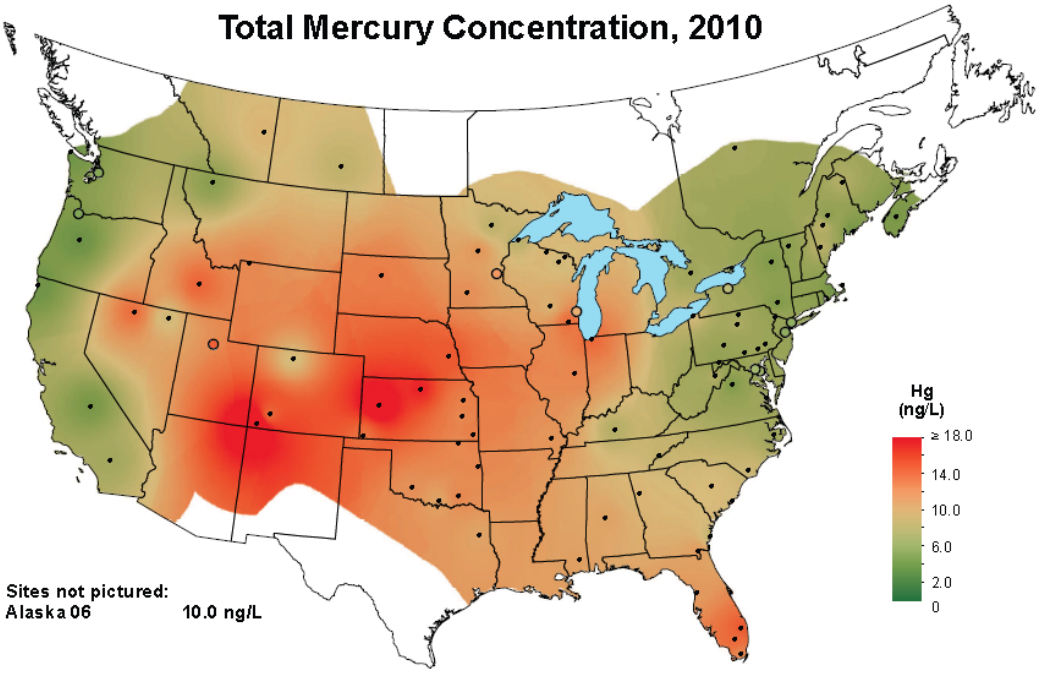

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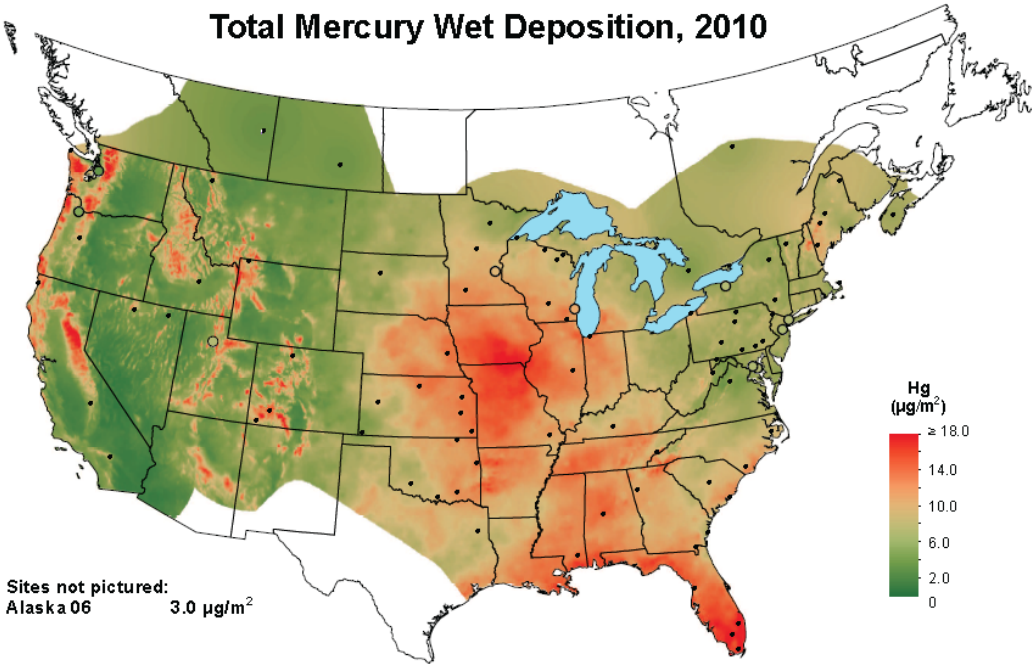

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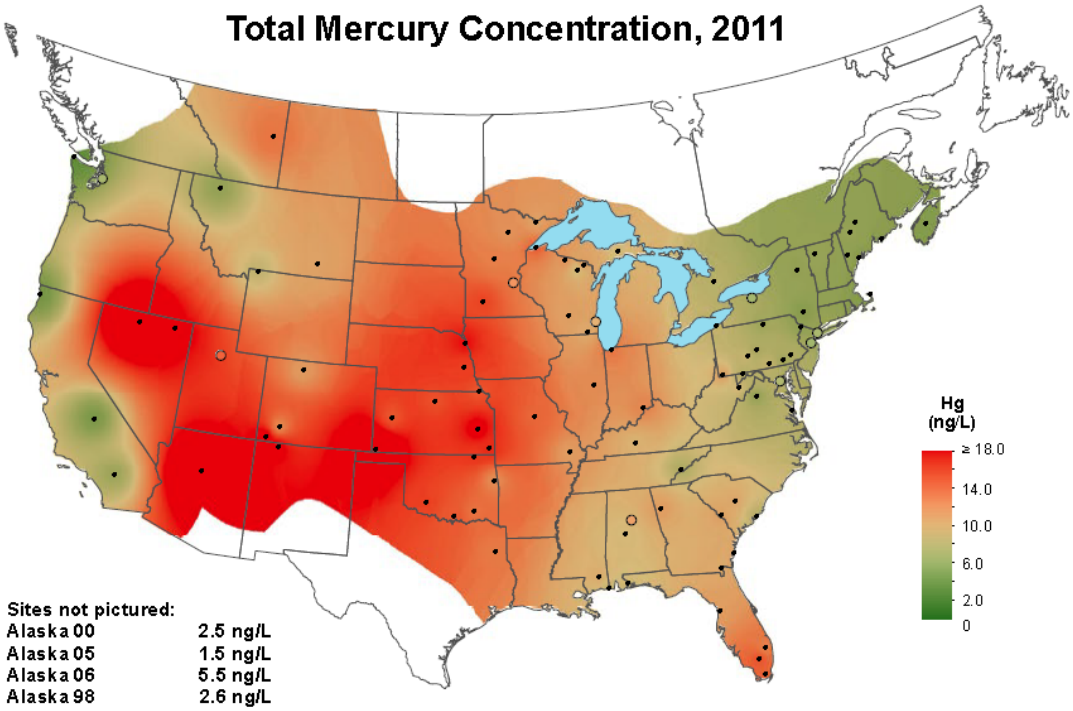

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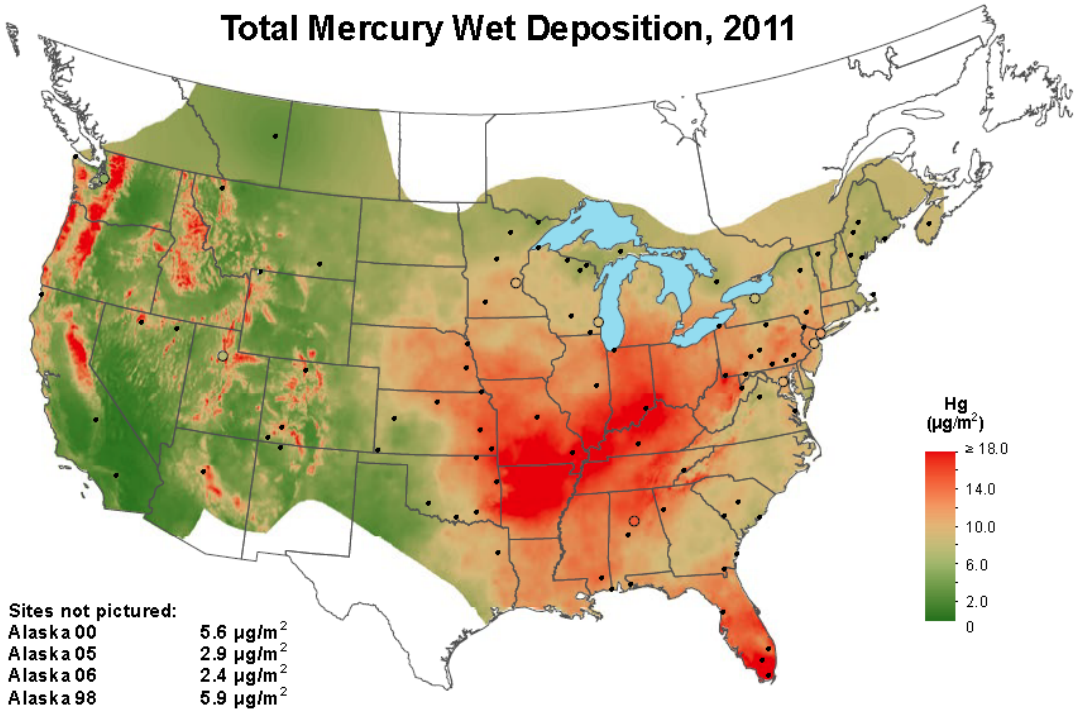

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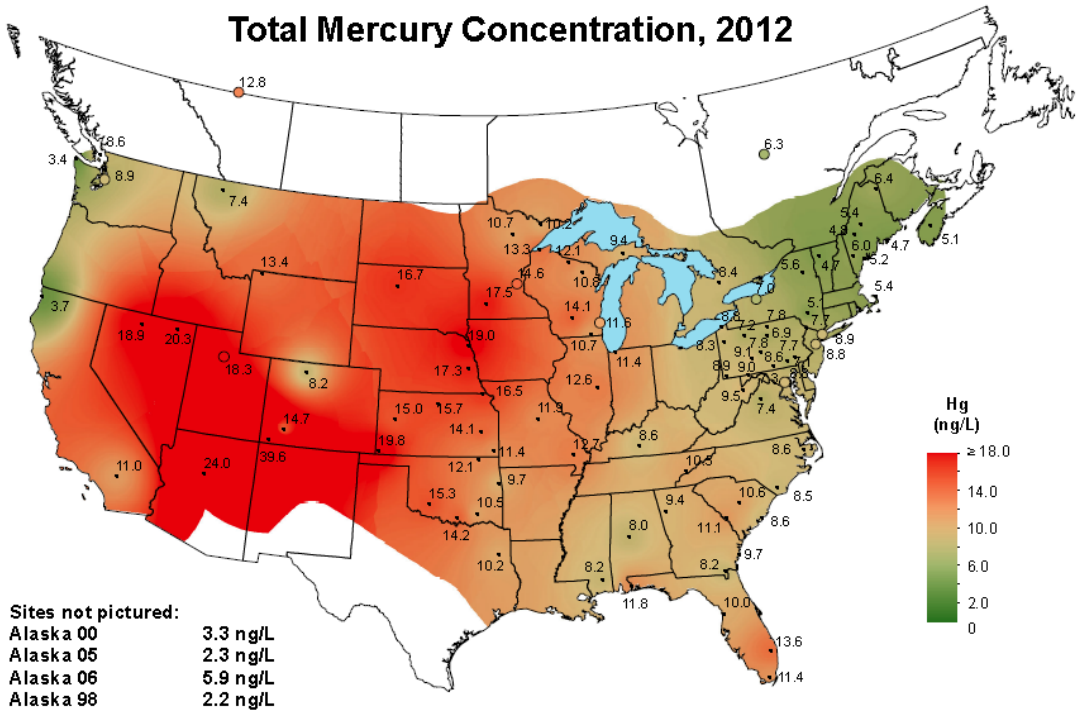

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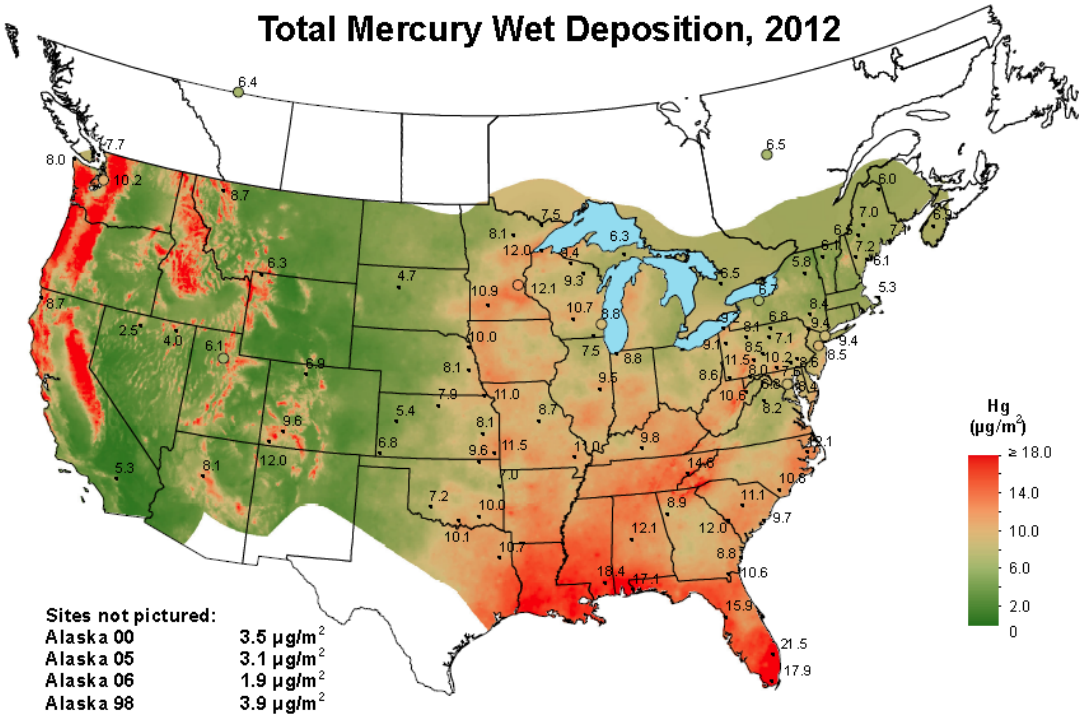

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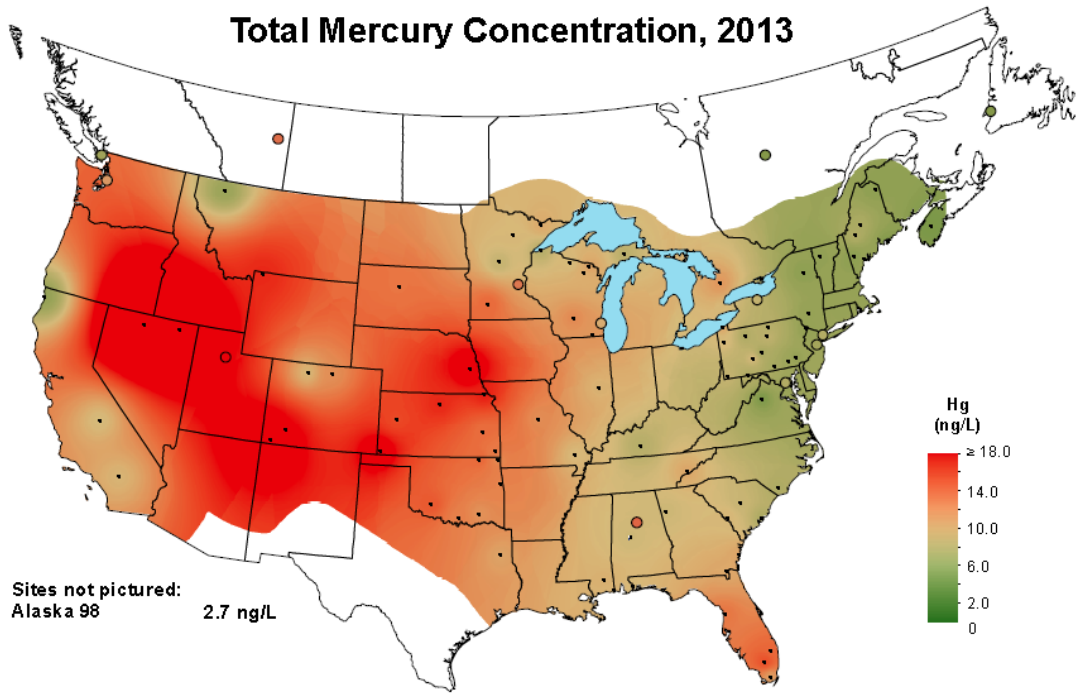

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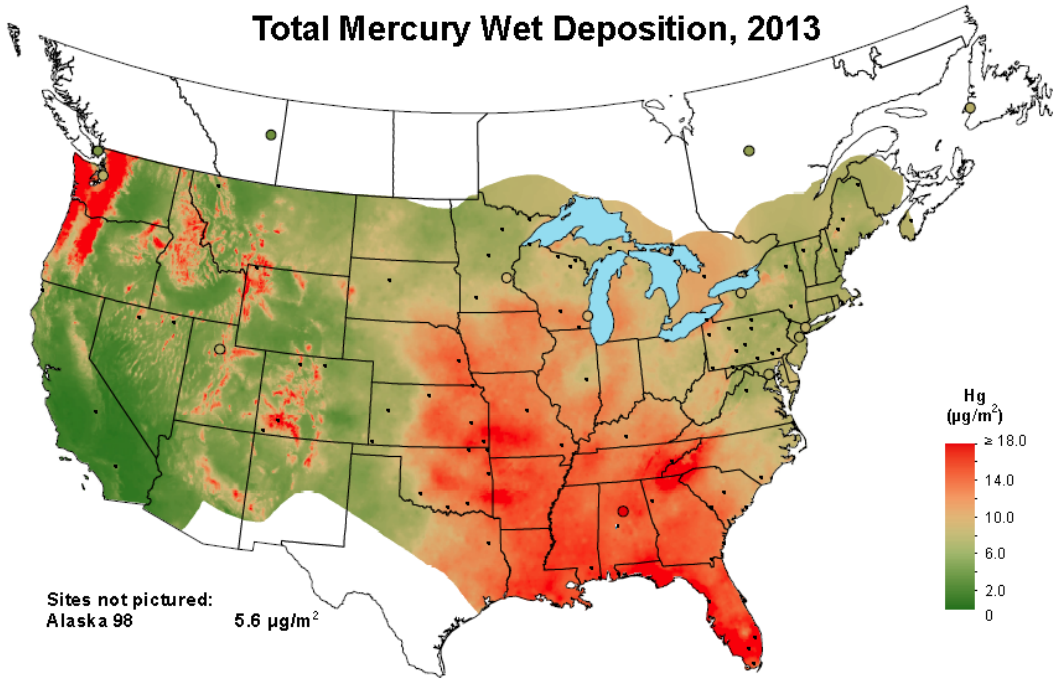

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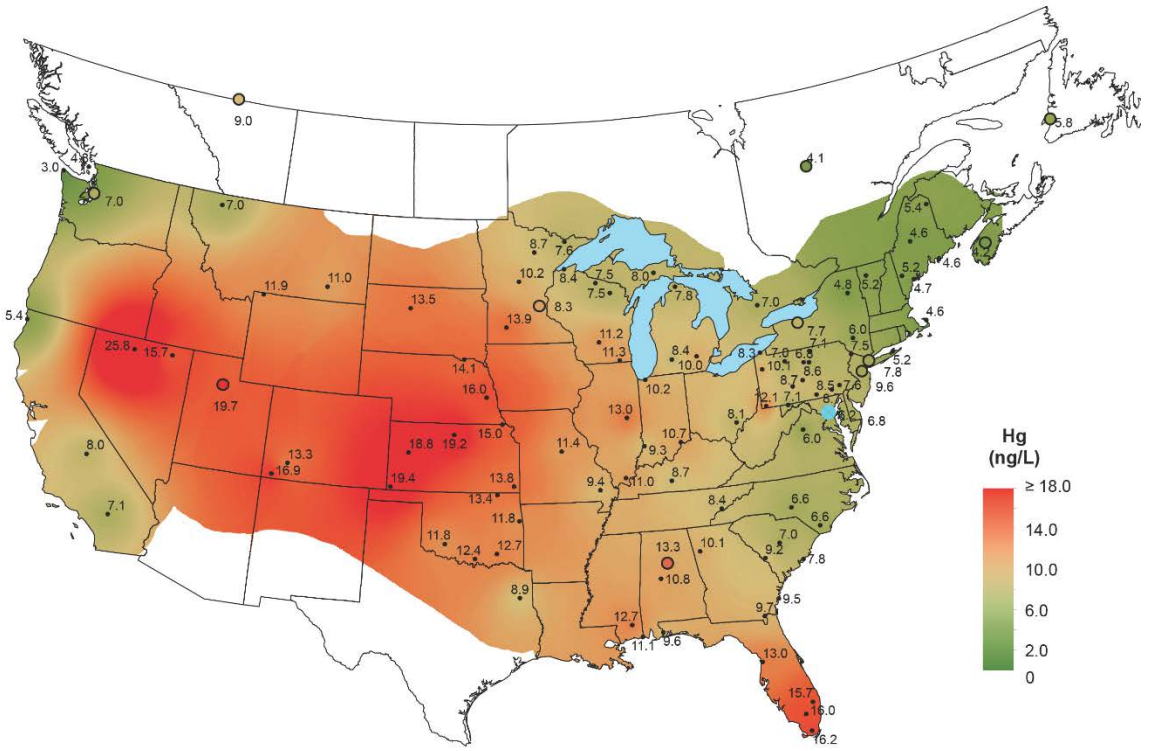
Hg
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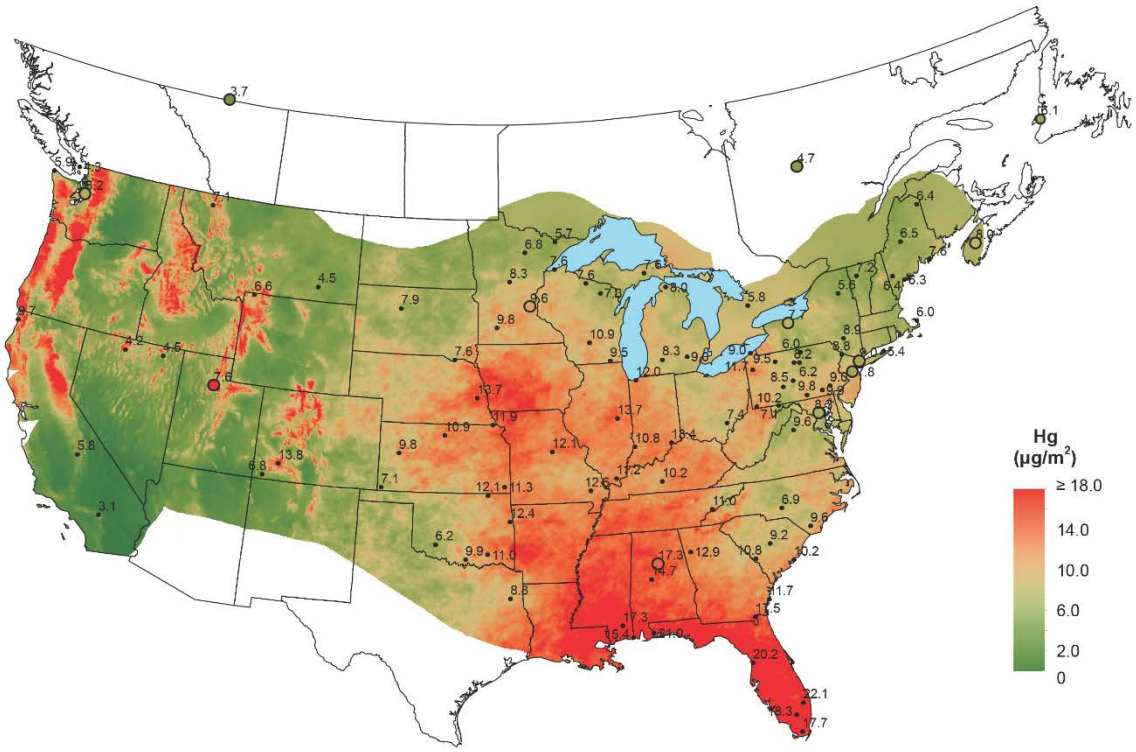
≥ 18.0
14.0
10.0
6.0
2.0
0


Hg
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14.0
10.0
6.0
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