PENNSTATE

1855

\

Atmospheric Mercury Deposition in Pennsylvania in 2008

Elizabeth W. Boyer
Jeffrey W. Grimm
Kevin S. Horner
James A. Lynch
Matthew A. Borden

About the Study Team

- **Elizabeth W. Boyer**, Ph.D. (principal investigator) is an Associate Professor of Water Resources, School of Forest Resources, and is Assistant Director (for water), Penn State Institutes of Energy & the Environment.
- **Jeffrey W. Grimm** (lead statistician) is a senior Research Assistant, Penn State Institutes of Energy and the Environment.
- **Kevin S. Horner** (lead field technician) is a senior Research Technologist, Penn State Institutes of Energy and the Environment.
- **James A. Lynch**, Ph.D. (lead consultant, former principal investigator 1981-2009) is a Professor Emeritus of Forest Hydrology, School of Forest Resources.
- **Matthew A. Borden** (field technician) is a Research Assistant, Penn State Institutes of Energy & the Environment.

About the Report

- This report was prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, within Penn State Institutes of Energy & the Environment.
- The work presented here, detailing monitoring of wet atmospheric mercury deposition at a network of sites across Pennsylvania, was sponsored by the Pennsylvania Department of Environmental Protection.
- The findings are those of the authors and are not necessarily those of The Pennsylvania State University.
- This publication is available in alternative media on request.
- For more information, contact E.W. Boyer, Penn State Institutes of Energy & the Environment, 108 Land & Water Building, University Park, PA 16802. Phone 814-865-8830. E-mail ewb100@psu.edu.

TABLE OF CONTENTS

LIST OF FIGURES

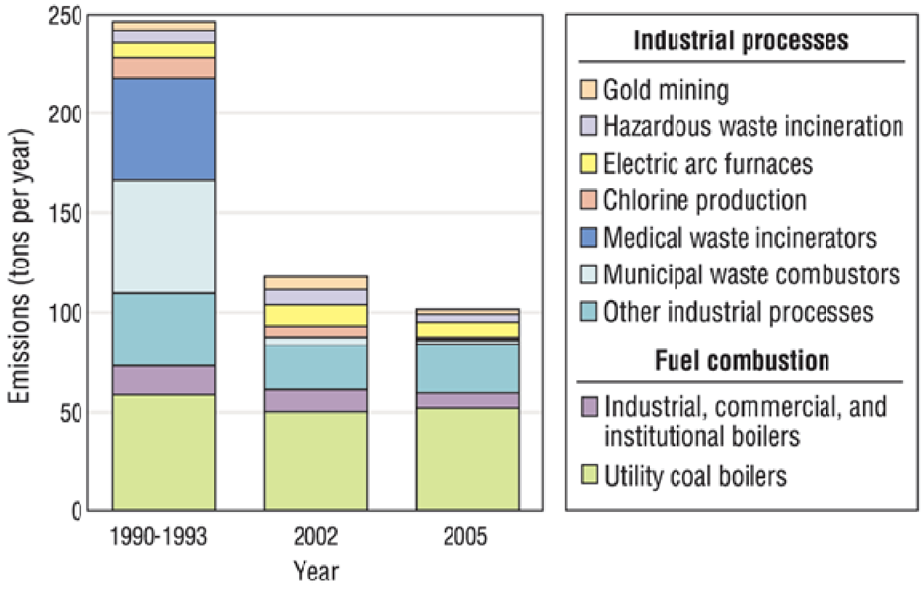
LIST OF TABLES

INTRODUCTION

Mercury Deposition and Emissions

Atmospheric deposition occurs when airborne constituents are transferred to the earth's surface. There are many sources of emissions to the atmosphere, and many pathways where constituents in the atmosphere are transported and deposited to the landscape. Atmospheric deposition can occur as *wet deposition* (via precipitation - in rain, snow, clouds, and fog) and as *dry deposition* (via dry fallout -including particles, aerosols, and gases). *Total* deposition is taken to be the sum of wet plus dry contributions. Airborne emissions can be transported for short or long distances before being deposited to the landscape. Thus individual emissions sources can affect broad regions, and even relatively undisturbed areas can be blanketed with inputs of pollutants via atmospheric deposition. This report focuses specifically on *wet atmospheric deposition of mercury* in Pennsylvania in 2008.

Mercury occurs naturally in the environment in air, soil, and water. Mercury (Hg) pollution is widespread. A primary mechanism of dispersal of mercury in the environment is by *emissions* to the atmosphere followed by *deposition* (both wet and dry) to the earth's surface. Mercury is emitted to the atmosphere from natural activities, such as volcanic eruptions, and from anthropogenic activities, such as the combustion of fossil fuels and industrial processes. The U.S. Environmental Protection Agency has conducted a National Emissions Inventory (NEI) regularly, every 3 years, since 1990. The NEI includes information about the sources and magnitudes of domestic mercury emissions, from both point and nonpoint sources. *Note: there is a lag in the availability of emissions data; NEI 2005 was released in 2007, and the subsequent NEI 2008 will be released in 2011.*



[a] 1990-1993 is considered the baseline period for mercury emissions. The baseline period spans multiple years due to the availability of emissions data for various source categories. The data presented for the baseline period are annual emissions (tons per year) and are therefore comparable to the 2002 and 2005 data.

[b] Mercury emissions from mobile sources are not depicted because they have been estimated only for inventory years 2002 (0.8 tons) and 2005 (1.1 tons), not for the baseline period.

Figure 1. *Mercury emissions in the U.S. by anthropogenic source sector in 2005. Emissions have declined about 58% since 1990. This figure is taken from U.S. EPA's report on the environment (US EPA 2009).*

NEI data show that anthropogenic mercury emissions to the atmosphere from the U.S. have declined in recent decades, largely due to decreased emissions from municipal and medical waste incinerators (USEPA 2009, Figure 1). The electric utility industry is a major (and currently the primary) anthropogenic source of mercury emissions to the atmosphere in the U.S.; while the manufacturing, mining, and waste management sectors are additional sources (USEPA 2009, Figure 1). Within the U.S. electric sector, total emissions of mercury from coal are currently much higher than from other fossil fuels used to produce electric power. There are several reasons for this – a disproportionately large amount of coal is combusted, and mercury emission rates (e.g., pounds Hg emitted per megawatt hour) are higher-on-average for coal than for other fossil fuels such as oil or natural gas (USEPA 2010c). Coal burning power plants have been the largest single anthropogenic source of total mercury emissions to the air in the U.S. in recent years, and emissions from coal-fired power plants in the U.S. have varied relatively little over the past two decades compared to changes in other sectors (USEPA 2009, Figure 1).

Though information on mercury emissions from the NEI is publicly available only through 2005 at present, more contemporary information on mercury emissions from many industrial point sources is available from another U.S. EPA database, the annual Toxics Release Inventory (TRI). Facilities in certain industries which manufacture or use mercury above specific amounts are legally required to report annually on their emissions. Since 2000, the threshold is 10 pounds (0.005 tons) for reporting releases of elemental mercury, and 100 pounds (0.05 tons) for reporting releases of mercury compounds, chemical substances that contain mercury. According to TRI data, all industries in the U.S. released 4.6 tons of mercury and 58.1 tons of mercury compounds in 2008 (USEPA 2010c, Figure 2). Of the mercury compounds emitted to the air in 2008, 75% was released from the electrical power industry (USEPA 2010c, Figure 2).

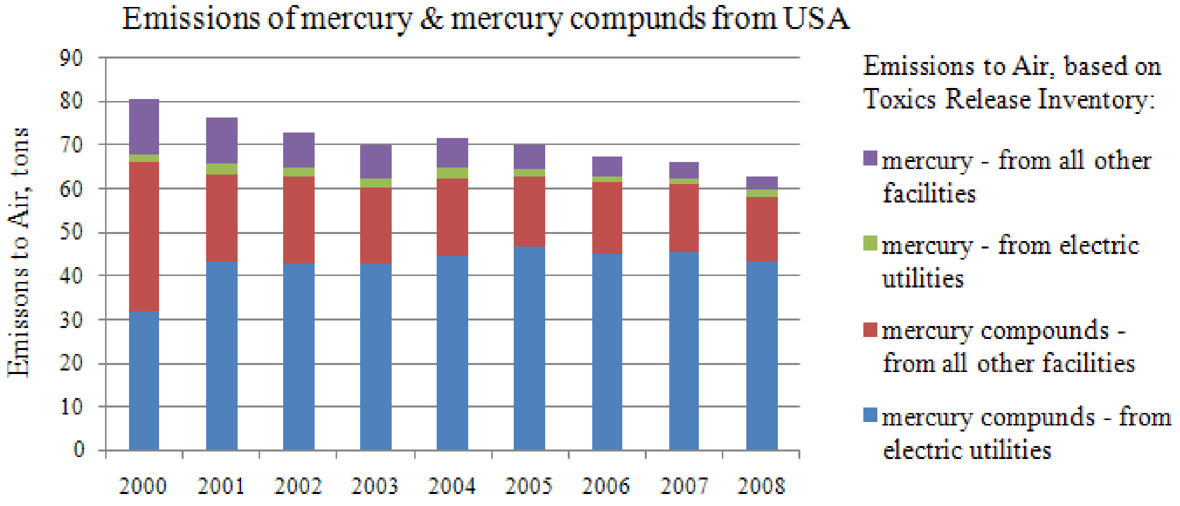


Figure 2. *Releases to air in the United States from mercury (gaseous elemental) and mercury compounds (containing mercury), based on data from the Toxics Release Inventory. Emissions of mercury compounds arise largely from electric utilities (US EPA 2010).*

The distribution of electric utilities is not uniform across the nation, and Pennsylvania (PA) is located downwind of clusters of coal-fired utilities that are located in the mid-West and the Ohio River Valley (Figure 3, M.J. Bradley & Associates 2010).

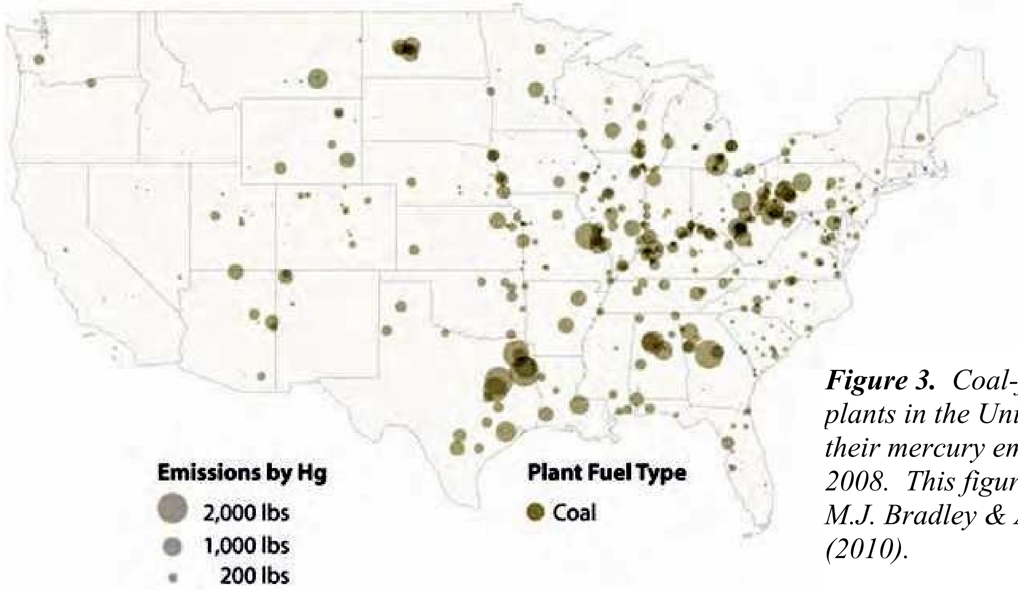


***Figure 3.** Coal-fired power plants in the United States, and their mercury emissions in 2008. This figure is taken from M.J. Bradley & Associates (2010).*

Some emissions from the U.S. are deposited locally and regionally, while others combine with a large pool that circulates globally. In addition to domestic emissions, it is well known that the U.S. receives substantial inputs of Hg that are transported into the nation from other countries (USEPA 2010b, NRC 2009, Seigneur et al 2004, Pacyna et al. 2006). Anthropogenic emissions of mercury from the U.S. and North America are small relative to the global budget (Pacyna et al. 2006, Figure 4; note that 1 tonne (or metric ton) = 1 ton (or U.S. short ton).

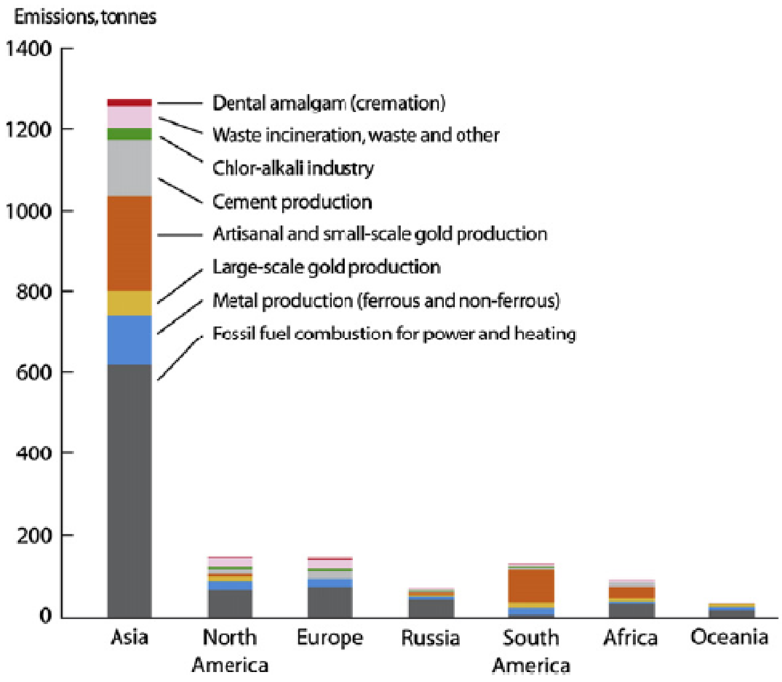


***Figure 4.** Global emissions of mercury to the atmosphere in 2005, by anthropogenic source sector. This figure is taken from Pacyna et al. 2010.*

Using global simulation models, Siegneur et al. (2004) quantified the contributions of mercury emissions that contributed to total (wet+dry) mercury deposition in the United States in the late 1990's. They found that, on average, local and regional anthropogenic emissions contributed about 30%, natural emissions contributed about 33%, and global anthropogenic emissions contributed about 37% (Siegneur et al. 2004). Local and regional anthropogenic emissions of Hg contributed about 24% to wet deposition, 43% to dry deposition, and 30% to total (wet+dry) deposition.

A recent synthesis effort of the Hubbard Brook Research Foundation articulates concepts of mercury emissions, deposition, and effects in the U.S. Northeast (Driscoll et al. 2007a, 2007b). Those and other studies articulate that emissions of mercury to the atmosphere can travel from short to very long distances before being deposited onto the landscape, and transport in the atmosphere is greatly affected by the chemical *form* of the emissions (Figure 5). The vast majority of the mercury that is transported long-range or globally was emitted in *gaseous elemental forms*, which is relatively inert, is not easily dissolved in water, and can be transported up to thousands of miles (Driscoll et al. 2007a, NRC 2009). In contrast, divalent (oxidized) mercury is emitted in *reactive gaseous or particulate forms,* is highly reactive, is easily dissolved in water, and is typically deposited locally to regionally (Driscoll et al. 2007a, NRC 2009). Mercury emitted in gaseous elemental forms can be transformed into more reactive forms in the atmosphere, often occurring when ground level ozone is elevated or when sea salt is entrained the air, and enhancing local or regional deposition of mercury (Driscoll et al. 2007a).

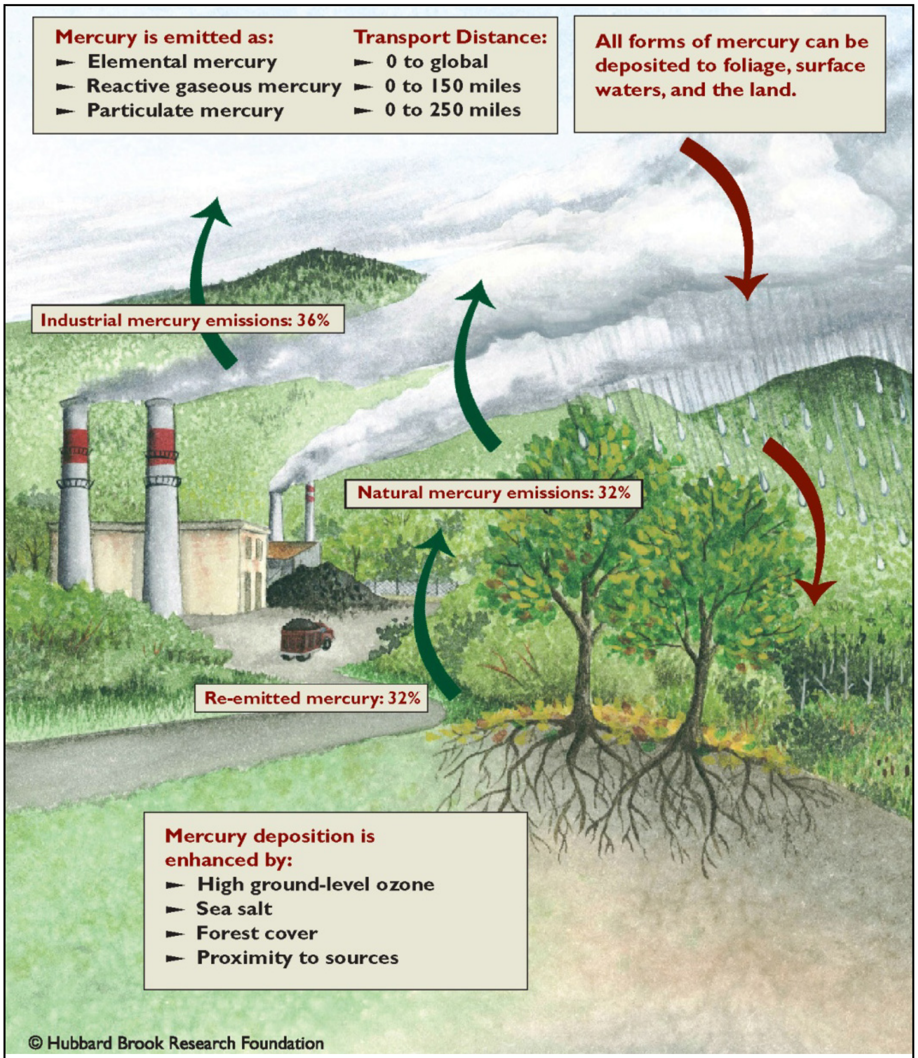


Figure 5. *Mercury emissions and deposition. The distance that mercury can travel in the air before being deposited varies, and is related to the form of mercury emitted. This figure is taken from Driscoll et al. 2007a.*

These differences in reactivity and transport highlight the fact local mercury emissions, in addition to global sources, can be important to understanding local effects, despite the fact that global emissions are high relative to local emissions.

The Electric Power Research Institute (EPRI 2006a) estimates that 40% of mercury releases to the atmosphere from U.S. power plants is emitted as water-soluble oxidized (reactive) mercury, while about 60% is emitted as elemental (non-reactive) mercury.

Environmental Concerns

Because it does not degrade in the environment, much of the mercury emitted to the atmosphere eventually deposits onto land or water bodies. Biological transformations can produce methylmercury, which is the primary form of mercury implicated with regard to negative effects. Mercury is of serious concern as a pollutant, because it is a persistent, bio-accumulative, and toxic contaminant, with effects depending on the chemical form, rate, and path of exposure (USGS 2000). Mercury accumulation in the environment can pose substantial health risks -- for humans (especially pregnant women, developing fetuses, and young children), for wildlife (especially fish, birds, and mammals), and for ecosystems (terrestrial and aquatic). A recent synthesis effort, aiming to link science to policy, considers mercury contamination in forest and freshwater ecosystems in the northeastern United States (Driscoll et al. 2007a, Driscoll et al. 2007b, Evers et al. 2007). Human exposure to mercury occurs largely through fish consumption (USGS 2000, NRC 2009). Due to mercury contamination, most states have advisories against consuming fish for specific water bodies. Pennsylvania currently has a *statewide* advisory for fish consumption of mercury for all rivers and lakes that was first initiated in 2001 (USEPA 2008).

There has been concern over mercury in the environment for many decades. The U.S. EPA conducted a detailed assessment of the magnitude of mercury emissions by source, the health and environmental implications of these emissions and depositions, and the availability and cost of control technologies, in the *Mercury Study Report to Congress* (USEPA, 1997). Though the state of the science for mercury have rapidly evolved, from assessments and regulations to impacts and mitigation technologies, this report remains a resource for information about concepts of mercury pollution and the status at that time. The National Research Council recently reviewed the health effects of methylmercury, considered mercury exposure and toxicity, and discusses some scientific aspects and policy decisions involved in the regulation of mercury (NRC 2000). Current primary portals for information about exposure, effects, and control technologies in the United States are available from the U.S. Environmental Protection Agency (USEPA, 2010), from the U.S. Geological Survey (USGS, 2010a), and from the U.S. Department of Health & Human Services (USHHS, 2010).

Atmospheric Deposition

Deposition of mercury from the atmosphere occurs as both wet and dry deposition. Wet deposition occurs when reactive gaseous mercury dissolved in precipitation is deposited on the surface of the Earth. Particulate-bound mercury is also deposited by this mechanism, but it is a relatively minor component (in most areas) when compared to dissolved reactive gaseous mercury. Dry deposition occurs when both gaseous and particulate forms of mercury are deposition on the Earth’s surface.

Modeling

Computer modeling is one method that is used to quantify atmospheric deposition of mercury at regional and global scales, and to consider sources and fate of mercury. The U.S. EPA and the Electric Power Research Institute (EPRI) both use different modeling approaches that include a global mercury chemistry and atmospheric transport modeling, and yield similar patterns of mercury deposition across the U.S (EPRI 2006). Such models rely on data from the U.S. National Emissions Inventory (and inventories of other countries), and are computationally intensive, and thus simulations for base years (using actual emissions observations rather than scenarios) are lagged substantially in time (EPRI 2006b, Vijayaraghavan et al. 2008). A recent plume-in-grid model simulation of atmospheric mercury deposition the U.S. in 2004 (based on emissions data from 1999-2000) is shown in Figure 6a (from EPRI 2006). This simulation depicts total (wet + dry) atmospheric mercury deposition, and highlights the significance of deposition in Pennsylvania. Recognizing the importance of long-range transport of mercury, this modeling approach was also used to estimate the percent contribution to mercury deposition that originates *outside* of the United States. These results suggest that a larger fraction of atmospheric deposition in Pennsylvania's deposition originates from emissions *within* the U.S. compared to most other areas of the nation (Figure 6b).

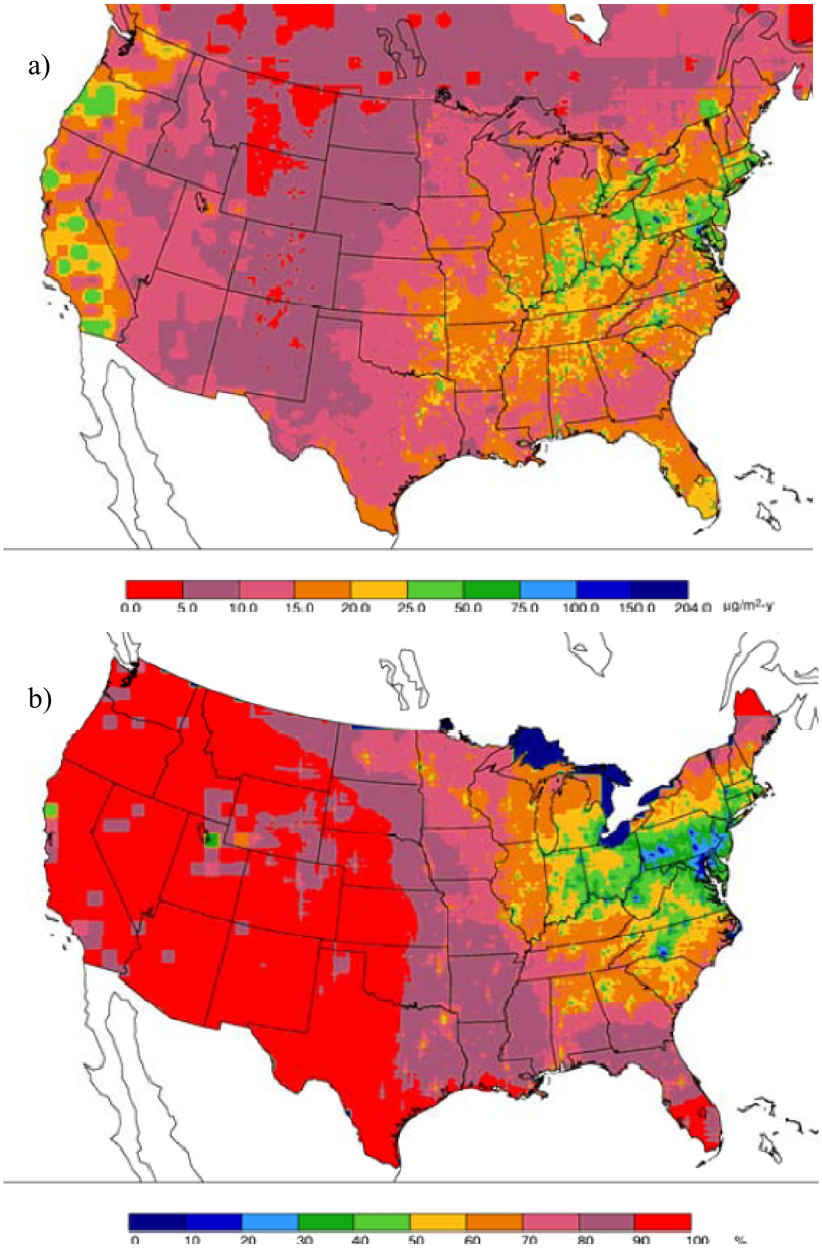


Figure 6. *a) Total (wet+dry) atmospheric mercury deposition in the United States in 2004, based on a global atmospheric transport model. b) Percent contribution to mercury deposition in the U.S from non-U.S. sources. These figures are based on an atmospheric transport model, and were taken from EPRI (2006b).*

Modeled results (Figure 6a) also indicate relatively high levels of mercury deposition in eastern and western Pennsylvania with less deposition occurring across the center region (Figure 1), especially across the north central counties. This spatial pattern is similar to the distribution of wet mercury deposition results based on data from Mercury Deposition Network sites located in Pennsylvania and discussed in the results section of this report.

Monitoring

Routine monitoring for mercury deposition via precipitation was initiated in the United States In 1996 when the National Atmospheric Deposition Program (NADP) began the Mercury Deposition Network (MDN) (NADP 2008). The MDN now has a national, cooperative network of over 100 sites where wet mercury deposition is monitored (Figure 7). There are currently nine active MDN mercury monitoring sites in Pennsylvania (Figure 8, Table 1), which are supported by the Pennsylvania Department of Environmental Protection (PA DEP) and are the subject of the data presented in this report.

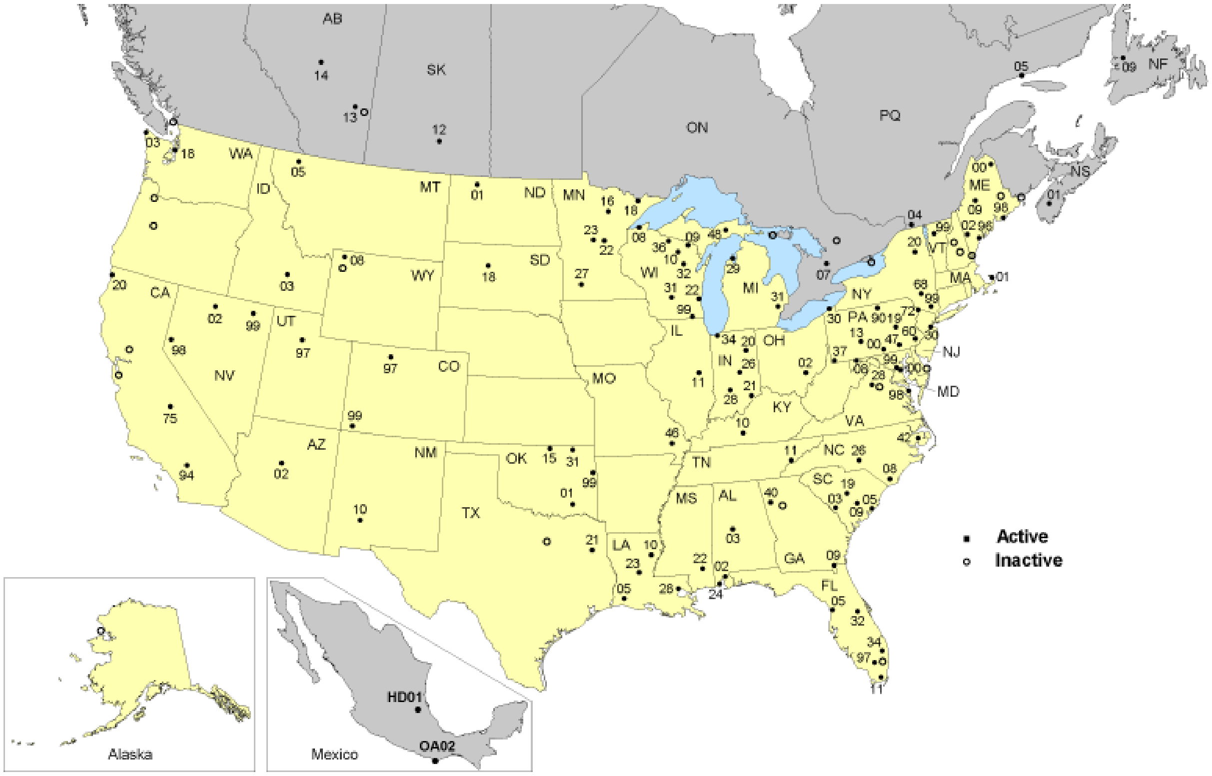


Figure 7. *Location of National Atmospheric Deposition Program / Mercury Deposition Network sites in the United States and Canada in 2007. Most of the monitoring sites in Pennsylvania are supported by the PA Department of Environmental Protection.*

NETWORK DESIGN AND OPERATION

Monitoring Site Locations

In 2008, there were eight MDN mercury monitoring sites in Pennsylvania (Figure 8, Table 1). Eight of these sites are supported by the Pennsylvania Department of Environmental Protection (PA DEP), Bureau of Air Quality Control in cooperation with The Pennsylvania Bureau of State Parks (PA30, PA90, and PA52), The National Park Service (PA13 and PA60), The U.S. Forest Service, Northeast Forest Experiment Station (PA72), The Pennsylvania State University, Fruit Research and Extension Center at Arendtsville (PA00), and Millersville University (PA47). Further information about each site is available online at the NADP MDN web site.

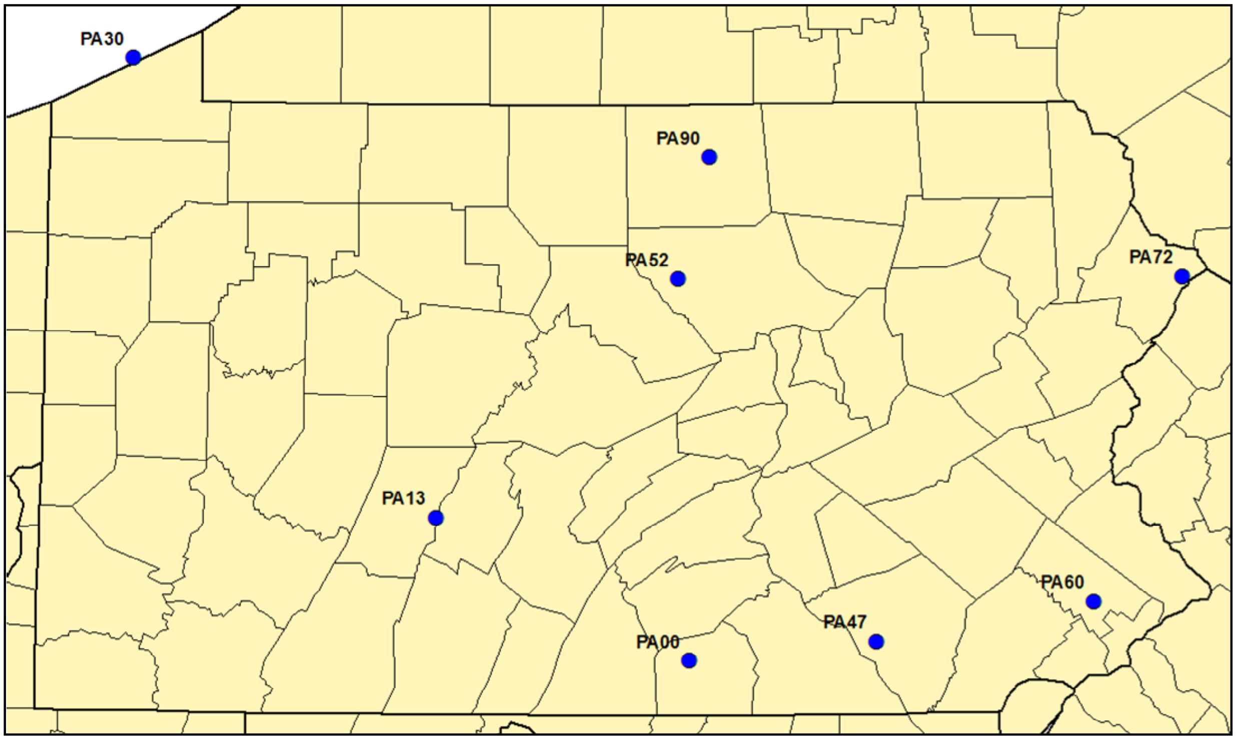


Figure 8. *Location of National Atmospheric Deposition Program / Mercury Deposition Network sites in Pennsylvania in 2008.*

Monitoring for wet mercury deposition was initiated at the various sites in PA over the years since 1997 (Table 1). Today, work continues to determine the magnitude and distribution of wet atmospheric mercury deposition in PA, establishing a long term record that will enable explorations of changes in rates and patterns over space and time. Participation of the PA sites in the national MDN program provides a nationally-consistent survey of wet-deposition concentrations and fluxes, and facilitates consideration of regional and international deposition patterns. High-quality monitoring data are key to developing and evaluating models (e.g., predictions of mercury at unmonitored sites, or scenarios of mercury in response to changes), and for guiding policy efforts. This report represents a summary of precipitation chemistry and wet deposition data collected at the mercury monitoring sites in Pennsylvania in 2008. Precipitation and precipitation chemistry (mercury concentrations) were measured at each site weekly, from which rates of wet atmospheric mercury deposition were calculated.

Table 1. *Location of National Atmospheric Deposition Program - Mercury Deposition Network monitoring sites in Pennsylvania in 2008*

Site No.	Latitude	Longitude	County	Elevation Meters	Sampling Started
PA00	39.9231	-77.3078	Adams	269	11/16/2000
PA13	40.457	-78.56	Cambria	739	01/07/1997
PA30	42.1558	-80.1134	Erie	177	06/20/2000
PA47	39.99	-76.3862	Lancaster	85	11/26/2002
PA52	41.3639	-77.3561	Lycoming	228	07/31/2007
PA60	40.1166	-75.8833	Montgomery	46	11/23/1999
PA72	41.3275	-74.8203	Pike	212	09/15/2000
PA90	41.8043	-77.1903	Tioga	476	01/07/1997

Sampling Protocols

In establishing the MDN, The National Atmospheric Deposition Program (NADP) sought to ensure uniformity in commitment, in sampling protocols, and in analytical techniques and sampling procedures. These are the ingredients essential to a successful network design and operation. To this end the NADP/MDN monitoring program designated specific precipitation collection equipment to be used throughout the network which allows precipitation to be recorded, collected and verified. A strict weekly sampling protocol and a clear definition of sample type further makes comparisons between sites possible.

Laboratory Analyses

All of the samples from the entire MDN network are analyzed for mercury concentrations at the Mercury Analytical Laboratory (termed “HAL”) operated by Frontier Global Sciences, Inc., in Seattle, WA. This laboratory is an internationally recognized leader in the testing of mercury with ultra-clean techniques, and has been awarded the highest laboratory accreditation, ISO 17025. Once the sample arrives at the HAL (see below), the analytical methods they use to quantify mercury in freshwaters at low concentrations are modifications of those given in U.S. EPA Methods 1631 and 1669, and as detailed in the Mercury Analytical Laboratory quality assurance plan (NADP 2006). A concise overview of these methods is also provided on the

MDN web site (NADP 2010, see "laboratory methods" tab). Briefly, upon arrival at the laboratory, the bottles are unpacked in a clean air low-Hg (< 0.05 ng/mL) station where 0.2 N BrCl in HCl reagent is added to each bottle to give a final concentration of 1%. This reagent oxidizes all of the mercury present in the sample to Hg(ll). The caps are replaced, and the bottles are shaken for at least four hours to remove adsorbed mercury from the bottle walls and to fully oxidize any suspended particles. Weighed sample aliquots (50-100 mL) are poured into 125 mL Teflon bottles prior to analysis. Two-hundred mL of 20% hydroxylamine-hydrochloride is added to each aliquot to eliminate free halogens; the aliquot is then poured into a purge vessel. To reduce the conversion of Hg(ll) back to Hg0, 300 μL of 25% $SnCl_2$ are added to the sample, and the sample is purged with ultra-pure nitrogen onto a gold-coated, silica trap. The traps are then analyzed for total mercury by thermal desorption, dual gold trap amalgamation, and cold vapor atomic fluorescence. Peaks are quantified by peak height. The method detection limit for *mercury concentration* in a 100 mL sample is about 0.1 ng/L. Wet atmospheric *mercury deposition* is computed as the product of mercury concentration in precipitation multiplied by the precipitation amount from the rain gage (with appropriate unit conversions).

Field Instrumentation and Methods

A modified Aerochem Metrics Model 301 Automatic Sensing Wet/Dry Precipitation Collector used in the NADP/MDN was designed to sample precipitation and allow for analysis of mercury. The sampling train is designed so that the sample will contact only glass surfaces to minimize contamination. Precipitation is caught in a glass funnel and stored in a two-liter glass bottle, previously charged with 20 mL of dilute hydrochloric acid (0.12 M) used as a preservative. This is sufficient acid to maintain a pH of less than 2 in the sample collection bottle to prevent microbial activity. The two-liter bottle holds a maximum volume equivalent to 12.7 cm (five inches) of precipitation. The sampling train consists of a 124 mm (inner diameter) borosilicate glass funnel, a thin (3 mm inner diameter) capillary tube, and a 2-liter borosilicate glass bottle. Even though connections between the funnel and capillary tube and between the capillary tube and sample collection bottle are not air tight, the sampling train effectively inhibits evaporation during the weekly sampling period. Additional modifications include: Teflon-coated lid supports and Teflon-wrapped lid seal foam pads; flexible sleeves at the base of the lid arms; an insulated enclosure around the collector base; and a thermostatically controlled heater and fan to maintain a given temperature range within the enclosure and to melt snow collected in the funnels.

Field operators receive a pre-cleaned sampling train each week from the HAL (this glassware preparation is described below). The standard *sampling period* is the interval between sampling train installation and sampling train removal. Typically, samples accumulate for one week. The sampling train is removed from the collector and replaced on Tuesday mornings. If it is raining or snowing at collection time the sampling train is changed after the precipitation stops, but in no case later than 5:00 PM on Tuesday. The wet-side sampling train is replaced weekly and sent to the HAL, even if no precipitation was collected during the sampling period. This standard sampling protocol results in 52 samples (some years 53 samples) submitted for analysis per year.

Once the exposed sampling train is removed each week, it is returned to the Mercury Analytical Lab at Frontier Geosciences, Inc., Seattle, WA, along with the sample bottle containing any collected precipitation. All operators wear plastic gloves when handling the sampling train and follow special procedures to avoid contaminating the sample. Any overflow from the bottle is collected and measured but it is not included with the sample sent to the lab. Each site is also equipped with a Belfort weighing bucket rain gauge (Belfort Instruments, Baltimore, MD) that provides a weekly chart with rainfall amounts and distribution. MDN sites in Pennsylvania that are supported by the Bureau of Air Quality Control are also equipped with a standard non-recording funnel-type rain gauge. Rainfall volumes, as small as one mm, can be measured. The recording rain gauge has an "event recorder" that marks the chart each time the lid on the Aerochem Metrics sampler opens and closes. This indicates whether the sampler was open during wet periods and closed during dry periods. The precipitation amount measured by the recording rain gauge is used in the calculation of wet deposition. If no rain gauge chart is available, the volume from the non-recording gauge is used as a back-up. In the unlikely event that volume measurements from both rain gauges are not available, the "bottle catch" is used to calculate the amount of precipitation. All sample bottles are capped with a teflon-lined cap and are sent to the HAL in a cooler on Tuesdays via overnight mail, even if no precipitation was collected during the sampling period.

Glassware preparation

Both the sampling train and the precipitation sample bottle are glass and are prepared by the HAL. Precipitation samples are collected and stored in 1-liter borosilicate glass bottles with Teflon lined, phenolic resin caps. Initial cleaning is by heating to 70 °C for 48 hours in 4 M HCl, followed by a thorough rinsing in low-Hg (< 1 ng/L) distilled deionized water (DDW). The caps are cleaned by soaking for 48 hours in 0.1 M HCL at room temperature. Before use, bottles are filled with DDW containing 5 mL of BrCl in concentrated HCL, capped, and placed in a low-Hg (< 15 ng/m2), Class-100 clean air station for 24 hours. Bottles are then emptied, thoroughly rinsed with DDW, and allowed to dry for several hours in the clean air station. Each bottle receives 20 ± 0.5 mL of 0.12 M HCl (Hg < 0.5 ng/L), and the lids are tightly fastened. While still at the clean air station, the bottles are enclosed in new polyethylene bags and packed into polyethylene foam-lined shipping containers. The funnels and capillary tubes are cleaned by rinsing in nitric acid (HNO_3) followed by rinsing in DDW. The openings to the funnel and tube are wrapped in aluminum foil and the glassware placed in a muffle furnace at 500°C for 4 hours. After cooling, the aluminum foil is removed and the funnel and capillary tube are placed in separate new polyethylene bags and packed in a shipping container.

Sample Types

Between precipitation events the mercury wet deposition sampling train is covered by a motor-activated lid. When precipitation occurs, a sensor activates the motor which moves the lid from the wet deposition side to a dry-side plastic bucket. In the discussion that follows, samples will be referred to as Wet-Side for the mercury deposition samples or Dry-Side for the dry-side bucket. Material collected in the dry-side bucket is not analyzed by the MDN. Definitions of sample types are as follows:

- *Wet-Deposition-Only Sample:* A Wet-Side sample exposed only to precipitation and that has been protected from dry-fall during rain-free periods. Dry deposition exposures of less than 6 hours in any sampling period and less than 30 minutes at the end of any single event are considered insignificant. This is the type of sample normally collected in MDN.
- *Bulk Sample:* A Wet-Side sample that has been exposed continuously to both wet and dry depositions for the entire sampling period. This can occur when the sampler motor fails and the lid remains in the open position for the whole sampling period.

- *Undefined Sample:* Any Wet-Side sample that does not meet one of the above definitions (i.e.,part-week or unknown duration of exposure to dry deposition).

Quality Assurance Samples

Quality assurance samples include: *travel blanks, field blanks, and system blanks*. The *travel blanks* are bottles that are shipped with the regular sampling train and stored unopened in the enclosure during the sample period. They are returned to HAL unopened after the specified period. *Field blanks* are samples from dry weeks where all equipment has operated perfectly and there is no indication of precipitation. In other words, the sampler is operating properly on inspection, the enclosure temperature is in the proper range, and the rain gauge and event recorder worked properly and showed no indication of any precipitation. Even a single trace event disqualifies a sample from being a *field blank.* About once a year, site operators receive a 500 mL bottle labeled *system blank* containing pre-analyzed deionized water. This bottle is stored in the enclosure until a dry week occurs. At the end of the next sampling period with no precipitation, the operator opens the lid by wetting the sensor. The operator then pours half of the deionized water from the 500 mL bottle into the funnel in circular motions, wetting the sides of the funnel. The rinse water goes into the sample bottle. The sampling train and sample bottle are then collected according to the procedures for weekly sampling. The 500 mL bottle with the unused portion of the rinse water is capped and returned to HAL in the sample cooler with the sample bottle and sampling train.

Data Completeness Criteria

NADP/MDN criteria for data completeness include the following: 1) at least 75% of the year (or other summary period) is represented by valid samples; 2) there must be information on precipitation amounts for at least 90% of the year; 3) there must be valid samples representing at least 75% of the precipitation measured for the year; and, 4) total precipitation measured from the sample volume (bottle catch) must be at least 75% of the amount measured by the rain gage for the year. Data completeness criteria are used to assure uniformity in the comparison of data collected at all MDN sites.

Summary Periods

Total mercury concentrations and depositions are summarized into annual and seasonal periods. Annual summaries are presented for each calendar year (January-December) as well as each climatic year (December-November). Seasonal periods are defined quarterly as winter (December-February), spring (March-May), summer (June-August) and fall (September-November). These seasons were selected because they closely match seasonal climatic patterns observed in Pennsylvania. Eight MDN sites were in operation in Pennsylvania for all 2008 (Figure 8, Table 1). Weekly concentrations and wet deposition estimates for each site in 2008 are included in the Appendix of this report.

RESULTS AND DISCUSSION

Network Performance

A maximum of 52 samples (some years 53) can be collected at each MDN site during the course of a complete year of operation. An annual summary of weekly sampling periods indicating the number of samples collected at each site and a distinction between sampling periods without precipitation, trace precipitation samples, and a valid versus invalid sample designation at each MDN site in Pennsylvania from 1997 through 2008 is shown in Table 2. In 2008 the maximum number of possible weekly samples was 416. Thirty of the sampling periods in 2008 contained no precipitation, while 34 sampling periods in 2008 were identified as invalid samples because of low sample volume relative to precipitation volume measurements or due to contamination, primarily to sample exposure to atmospheric inputs during rain-free periods. The vast majority of low volume samples occurred during the winter months when precipitation occurs as snow, which is much more difficult to capture than liquid precipitation. The latter category of invalid samples represents samples that were exposed to dry deposition and thus potentially not representative solely of wet deposition inputs. This group of samples would also include those contaminated with bird droppings, leaves, insects, etc. The number of valid sampling periods, which includes sampling periods without precipitation, in 2008 was 382. These samples provided mercury concentration estimates for 98.3% of the total precipitation collected at the eight MDN sites in 2008 (Table 2). Since network operations began in 1997, approximately 91.8% of all sampling periods provided valid samples for mercury analysis and that these samples on averages captured more than 98.2% of the total precipitation across the network. These results indicate that the network is well run and that the vast majority of samples are collected correctly with minimal loss of results from missed precipitation or possible contamination of samples.

Results of all weekly analyses (valid and invalid samples) from all MDN sites in Pennsylvania for 2008 are summarized in the Appendix. The 2008 annual volume-weighted total mercury concentrations and annual wet deposition estimates for all MDN sites located in the United States and southern Canada are presented in the text of the report. These summary maps and statistics are based on only valid samples and include only those MDN sites that met data completeness criteria. The following discussion of total mercury concentrations and wet deposition estimates in Pennsylvania will, for the most part, be limited to data collected in 2008. Seasonal variations at these sites will also be discussed. Discussion of long-term temporal patterns will be limited to the Hills Creek (PA90) and Allegheny-Portage NHS (PA13) sites both of which have been in operation since 1997 and the Valley Forge (PA60) site that has been in operation since 1999. A multi-quadric equation spatial interpolation algorithm (Hardy, 1976) of 2008 annual and seasonal total mercury concentrations and wet depositions are also presented. Where available, these interpolations include MDN sites located around the periphery to Pennsylvania. The resulting concentration and wet deposition spatial interpolations for 2008 are discussed relative to past observations of concentration and deposition.

Table 2. Annual summary of weekly sampling periods indicating the number and distribution of sample types and quality at each Mercury Deposition Network site in Pennsylvania from 1997 through 2008.

Site	Year	# Samples Collected	# Samples Without Precipitation	# Trace Samples		# Invalid Samples	# Samples Missing	# Valid Samples	Total Amount of Precipitation	
				Analyzed	Not Analyzed				Collected	With Analysis
									---------- Inches	-----------
PA00	2000*	5	2	0	0	2	0	3	3.62	3.62
	2001	51	7	0	1	7	0	44	23.56	23.45
	2002	52	3	0	1	7	0	45	40.13	39.38
	2003	52	4	0	1	5	2	47	46.46	45.94
	2004	52	6	0	0	7	0	45	50.30	49.40
	2005	53	6	0	1	4	0	49	41.40	41.35
	2006	52	8	0	0	2	0	50	42.58	42.05
	2007	52	6	0	1	3	0	49	37.42	37.32
	2008	52	5	0	2	5	0	47	49.34	44.39
PA13	1997	51	4	0	0	1	0	50	46.56	46.56
	1998	52	1	0	0	0	0	52	37.79	37.79
	1999	52	5	0	0	2	0	50	38.23	38.06
	2000	53	3	0	0	9	0	44	36.40	34.37
	2001	52	3	0	0	8	0	44	31.71	30.36
	2002	52	1	0	0	4	0	48	40.83	40.79
	2003	52	0	0	2	5	0	47	53.78	52.58
	2004	53	2	0	1	4	0	49	55.00	54.50
	2005	53	4	0	0	1	0	52	39.72	39.72
	2006	52	3	0	0	3	0	49	44.34	44.33
	2007	52	2	0	0	4	0	48	44.20	43.97
	2008	52	1	0	0	7	0	45	43.59	43.57
PA30	2000*	28	2	0	0	2	0	26	22.71	22.04
	2001	52	5	0	0	10	0	42	32.93	30.55
	2002	52	7	0	0	2	0	50	38.96	38.96
	2003	52	3	0	1	1	0	51	40.32	39.87
	2004	52	3	0	0	5	0	47	48.39	47.47
	2005	52	6	0	0	2	0	50	39.46	37.73
	2006	52	2	0	0	4	0	48	43.47	42.42
	2007	52	4	0	0	4	0	48	40.68	39.77
	2008	52	3	0	0	4	0	48	46.63	46.63

Table 2 (continued).

Site	Year	# Samples Collected	# Samples Without Precipitation	# Trace Samples		# Invalid Samples	# Samples Missing	# Valid Samples	Total Amount of Precipitation	
				Analyzed	Not Analyzed				Collected	With Analysis
									---------- Inches -----------	
PA37	1999*	31	5	0	0	0	0	31	19.48	19.48
	2000	53	4	0	0	4	0	49	33.37	32.97
	2001	51	0	0	0	3	0	48	37.50	37.33
	2002	52	3	0	0	3	0	49	43.38	43.27
	2003	53	2	0	2	2	0	51	49.19	49.16
	2004	52	4	0	0	2	0	50	52.66	52.63
	2005	53	10	0	0	5	0	48	39.83	39.30
	2006	52	6	0	0	3	0	49	40.00	39.34
	2007	52	4	0	0	4	0	48	44.10	43.84
PA47	2002*	5	0	0	0	1	0	4	4.95	2.65
	2003	53	3	0	0	3	0	50	53.94	53.91
	2004	52	8	0	0	5	0	47	46.92	45.79
	2005	53	4	0	2	3	0	50	44.39	44.38
	2006	52	5	0	2	5	0	47	48.71	48.62
	2007	52	4	0	0	4	0	48	37.04	36.98
	2008	52	3	0	0	2	0	50	42.27	42.26
PA52	2007*	22	2	0	0	0	0	22	17.91	17.91
	2008	52	2	0	0	5	0	47	40.65	39.84
PA60	1999*	5	1	0	0	0	0	5	4.36	4.36
	2000	53	8	0	0	1	0	52	47.10	47.10
	2001	51	10	0	0	6	0	45	29.56	28.75
	2002	52	7	0	0	2	2	50	47.15	46.74
	2003	52	6	0	2	2	0	50	54.69	54.68
	2004	50	7	0	1	4	0	46	54.18	53.70
	2005	53	9	0	0	4	0	49	45.12	42.89
	2006	52	4	0	0	12	0	40	52.86	52.84
	2007	52	7	0	0	12	0	40	44.74	44.74
	2008	52	10	0	0	6	0	46	47.73	47.46
PA72	2000*	16	1	0	0	3	0	13	11.15	11.13
	2001	52	4	0	0	2	0	50	35.20	35.17
	2002	52	3	0	0	4	0	48	46.72	45.10
	2003	52	4	0	0	5	0	47	60.30	60.11
	2004	52	5	0	0	1	0	51	51.73	51.31
	2005	53	5	0	0	1	0	52	59.98	59.98
	2006	52	4	0	0	4	0	48	53.09	48.33
	2007	52	3	0	0	12	0	40	50.92	41.70
	2008	52	5	0	0	2	0	50	55.00	54.86

Table 2 (continued).

Site	Year	# Samples Collected	# Samples Without Precipitation	# Trace Samples		# Invalid Samples	# Samples Missing	# Valid Samples	Total Amount of Precipitation	
				Analyzed	Not Analyzed				Collected	With Analysis
									---------- Inches -----------	
PA90	1997	51	2	0	0	3	0	48	29.91	29.08
	1998	52	1	0	0	1	0	51	32.91	32.91
	1999	52	6	0	0	4	0	48	31.52	31.08
	2000	53	3	0	0	14	0	39	30.35	26.42
	2001	52	1	0	0	17	0	35	29.47	26.96
	2002	52	4	0	0	1	0	51	33.24	33.19
	2003	52	2	0	0	4	0	48	43.28	43.22
	2004	52	2	0	2	0	0	52	48.34	48.33
	2005	53	2	0	0	2	0	51	41.69	41.62
	2006	52	3	0	0	5	0	47	40.16	40.11
	2007	52	2	0	0	1	0	51	35.20	35.20
	2008	52	1	0	0	3	0	49	36.38	36.32
Total	1997	102	6	0	0	4	0	98	76.48	75.65
	1998	104	2	0	0	1	0	103	70.71	70.71
	1999	140	17	0	0	6	0	134	93.58	92.97
	2000	261	23	0	0	35	0	226	184.70	177.66
	2001	361	30	0	1	53	0	308	219.93	212.56
	2002	369	28	0	1	24	2	345	295.35	290.07
	2003	418	24	0	8	27	2	391	401.95	399.45
	2004	415	37	0	4	28	0	387	407.51	403.13
	2005	423	46	0	3	22	0	401	351.59	346.97
	2006	416	35	0	2	38	0	378	365.21	358.04
	2007	416	32	0	1	44	0	372	334.29	323.52
	2008	416	30	0	2	34	0	382	361.59	355.33

* Sampling conducted at this site for less than one year.

Mercury Concentrations and Deposition

Weekly Ranges

Ranges of mercury concentrations observed in precipitation and the associated rates of atmospheric deposition are highly variable both annually and seasonally across Pennsylvania (Table 3).

Concentration. Since monitoring for mercury at the sites began in 1997, weekly *minimum concentrations* ranged from 0.08 to 4.87 ng/L, while weekly *maximum concentrations* ranged from 9.32 to 671.49 ng/L. In 2008, weekly *minimum concentrations* ranged from 1.86 to 3.22 ng/L, while weekly *maximum concentrations* ranged from 23.99 to 97.57 ng/L. Minimum weekly concentrations of mercury in precipitation are generally in the 1 ng/L to 3 ng/L range at all sites for most years of observations. Maximum weekly concentrations of mercury in precipitation are generally in the 20 ng/L to 50 ng/L range, with some samples exceeding 100 ng/L (Table 3).

Deposition. Since monitoring began at the sites in 1997, weekly *minimum depositions* ranged from 0.22 ng/m^2 to 78.28 ng/m^2, while weekly *maximum depositions* ranged from 132.04 ng/m^2 to 3183.38 ng/m^2 (Table 3). In 2008, weekly *minimum depositions* ranged from 3.29 ng/m^2 to 26.85 ng/m^2, while weekly *maximum depositions* ranged from 589.54 ng/m^2 to 1061.31 ng/m^2 (Table 3).

Annual Patterns

Concentration. Mean annual and seasonal volume-weighted mercury concentrations based on weekly precipitation samples collected at MDN sites in Pennsylvania from 1997 through 2008 are shown in Table 4. Annual means are presented for each calendar year (January through December) as well as for the climatic year (December through November). In calendar year 2008, mean annual concentrations of mercury in precipitation at sites in Pennsylvania ranged from 7.66 ng/L at Hills Creek State Park in Tioga County (PA90) to 9.4 ng/L at Valley Forge in Montgomery County (PA60) (Table 4).

Deposition. Mean annual and seasonal wet mercury depositions observed at MDN sites in Pennsylvania from 1997 through 2008 are shown in Table 5. Annual means are presented for each calendar year (January through December) as well as for the climatic year (December through November). In calendar year 2008, wet atmospheric mercury deposition at sites in Pennsylvania ranged from 7.08 µg/m^2 at Hills Creek State Park in Tioga County (PA90) to 11.39 µg/m^2 at Valley Forge National Historic Site in Montgomery County (PA60) (Table 5). The Tioga County site (PA90) has consistently received the smallest annual amounts of wet mercury deposition of any site in Pennsylvania, while the Valley Forge Site (PA90) typically receives the highest amount of wet mercury deposition among the monitoring stations in Pennsylvania.

Seasonal Patterns

Mercury concentrations in precipitation show definite seasonal patterns at most MDN sites in the nation. Average summer (June-August) total mercury concentrations for the entire network are generally higher than any other seasonal period and about 1.5 to 2.0 times the concentrations observed during the fall (September-November) and winter (December-February) periods.

Although patterns of seasonal mean concentrations in Pennsylvania are similar to the national network, they are highly variable between sites as well as within sites and between years (Table 4). Seasonal variability is largely controlled by climatic parameters, such as the form and amount of precipitation, air temperature, atmospheric stability, storm direction, among others and likely seasonal variations in mercury emissions.

Given the number of complete years of observations and the variable number of sites in operation from year to year, there are a total of 72 maximum seasonal mean observations across the state since mercury monitoring began in Pennsylvania through 2008. Of the 72 possible *maximum* seasonal means in mercury *concentration,* 51 (71%) of them occurred during the summer while 19 (26%) occurred during the spring (Table 4). The remaining two maximum seasonal means occurred during the winter. In contrast, of the 72 possible *minimum* seasonal means in mercury concentration, 43 (60%) of them occurred during the winter while 29 (40%) occurred in the fall (Table 4). Clearly, seasonality influences total mercury concentrations in precipitation. Similarly, of the 72 possible *maximum* seasonal means in mercury *deposition*, 48 (67%) of them occurred during the summer while 20 (28%) occurred during the spring (Table 5). In contrast, of the 72 possible *minimum* seasonal means in mercury deposition, 56 (78%) of them occurred during the winter while 11 (15%) occurred in the fall (Table 5). Clearly, seasonality influences total mercury concentrations in precipitation and rates of atmospheric mercury deposition in Pennsylvania.

Spatial Patterns

Spatial patterns of mercury concentrations and deposition on an annual timescale are illustrated nationally (Figure 9), statewide annually (Figure 10), and statewide seasonally (Figures 11 & 12). These maps are based on interpolation of data from all sites that met MDN completeness criteria for 2008. There are challenges with the interpretation of these figures, given a sparse distribution of monitoring sites (see Figure 8) and a limited period of record (see Table 1). Nonetheless, these figures allow some degree of comparison of levels of mercury in Pennsylvania to the surrounding region (e.g., modest levels), and reveal patterns across the state (e.g., relatively high mercury concentrations and deposition in the southeastern portion of the state).

Patterns of mercury concentrations in precipitation and atmospheric mercury deposition in Pennsylvania are variable from year-to-year (Figures 12 and 13). The monitoring data alone are not sufficient to determine the sources of mercury to each site. Mercury concentrations and depositions represent a composite of *all* emission sources that contribute to a site, possibly a mixture of natural and anthropogenic sources that arise from local to global source areas. The general distribution of mercury emissions in Pennsylvania and adjacent states are likely to account for some of the spatial pattern across the state. Patterns of wet deposition of emitted materials are strongly determined by the interactions of lower- and upper-level winds, atmospheric lifting, storm path, and the timing of precipitation events. These meteorological determinants of deposition can exhibit dramatic year-to-year, season-to-season, and even event-to-event variability. One satisfactory way to identify and assess source-receptor relationships is to utilize a dynamic atmospheric transport model that incorporates meteorological parameters to define the pathways between emission sources and deposition sites on a per-event basis.

Table 3. *Maximum and minimum weekly mercury concentrations (ng/L) and wet deposition (ng/m^2) at ten Mercury Deposition Network monitoring sites in Pennsylvania.*

		Weekly Mercury Concentrations (ng/L)		Weekly Mercury Deposition (ng/m^2)	
Site	Year	Maximum	Minimum	Maximum	Minimum
PA00	2001	63.77	2.67	503.62	25.97
	2002	29.85	2.06	566.93	17.60
	2003	19.99	1.36	946.88	42.84
	2004	29.23	2.18	966.81	22.27
	2005	42.11	2.12	715.06	10.06
	2006	50.23	1.47	1018.37	18.27
	2007	65.78	1.77	1664.21	10.28
	2008	62.77	2.63	662.90	26.85
PA13	1997	48.47	2.15	879.54	8.37
	1998	50.57	2.80	722.88	5.82
	1999	55.41	2.19	762.76	20.80
	2000	23.92	3.07	547.97	24.20
	2001	124.10	3.32	3183.38	17.38
	2002	108.93	1.69	727.85	9.54
	2003	35.20	2.43	851.76	12.38
	2004	45.60	1.65	955.81	13.62
	2005	28.88	1.55	635.81	7.10
	2006	32.75	1.93	1194.94	8.32
	2007	26.58	1.37	819.37	23.26
	2008	48.47	2.68	770.25	24.30
PA19	2006*	23.33	2.12	891.29	9.50
	2007*	50.37	4.87	331.97	63.97
PA30	2000*	30.78	0.83	1251.90	2.07
	2001	158.97	1.38	759.84	7.54
	2002	29.18	1.39	1302.96	14.94
	2003	218.66	2.84	779.27	15.40
	2004	35.04	1.55	929.75	3.00
	2005	54.96	1.40	992.12	11.22
	2006	39.28	2.61	894.28	17.19
	2007	63.07	3.15	585.06	36.19
	2008	37.46	2.27	900.62	25.95
PA37	1999*	46.20	2.15	830.10	8.40
	2000	62.58	2.13	715.29	9.32
	2001	35.56	1.86	633.42	4.72
	2002	25.67	0.08	1040.37	0.22
	2003	36.45	1.61	1398.73	8.05
	2004	26.74	1.15	1031.98	6.03
	2005	35.82	1.32	761.82	3.19
	2006	39.34	0.16	1087.73	1.54
	2007	22.62	2.10	929.37	20.91

Table 3 (continued).

		Weekly Mercury Concentrations (ng/L)		Weekly Mercury Deposition (ng/m^2)	
Site	Year	Maximum	Minimum	Maximum	Minimum
PA47	2002*	12.14	1.21	132.04	17.21
	2003	30.39	2.14	913.53	23.48
	2004	44.23	2.77	676.66	9.15
	2005	29.56	1.11	853.25	5.98
	2006	56.42	2.06	1165.71	22.40
	2007	49.81	2.90	740.66	11.14
	2008	97.57	2.32	663.45	4.36
PA52	2007*	21.16	2.01	533.73	23.14
	2008	31.31	2.29	589.54	7.22
PA60	1999*	9.32	3.82	420.19	37.84
	2000	154.73	2.84	1234.26	16.42
	2001	44.24	2.08	875.20	10.59
	2002	54.32	1.97	919.70	20.65
	2003	71.87	1.48	922.52	22.72
	2004	34.56	1.96	1258.62	17.56
	2005	58.60	3.23	1001.15	5.32
	2006	562.37	2.01	1070.98	42.37
	2007	40.52	4.56	727.66	78.28
	2008	37.95	3.22	1061.31	3.29
PA72	2000*	25.92	2.60	759.00	14.53
	2001	36.55	2.58	663.37	16.69
	2002	53.04	1.94	2393.82	4.28
	2003	27.93	1.10	1217.17	6.25
	2004	84.93	1.29	1520.26	4.22
	2005	77.60	0.86	586.70	7.16
	2006	36.64	1.57	1181.93	17.84
	2007	36.70	2.66	726.90	18.57
	2008	61.98	1.86	1038.76	10.21
PA90	1997	68.60	1.65	629.53	14.69
	1998	40.36	0.78	654.59	1.88
	1999	671.49	1.70	1193.91	7.12
	2000	38.91	1.82	481.93	7.57
	2001	56.42	1.42	474.35	21.40
	2002	38.88	0.59	858.09	3.35
	2003	27.27	1.46	1131.66	11.16
	2004	22.37	1.75	723.03	14.17
	2005	39.04	0.60	866.57	14.58
	2006	25.74	2.06	2002.64	7.89
	2007	33.06	1.64	596.92	7.57
	2008	23.99	2.37	679.09	13.04

* Sampling conducted at this site for less than one year.

Table 4. *Mean annual and seasonal volume-weighted total mercury concentrations (ng/L) in precipitation at eight Pennsylvania Mercury Deposition Network sites from 1997 through 2008. Seasonal means are based on weekly samples collected from December-February (winter) March-May (spring), June-August (summer), and September-November (fall). Annual values are presented for both climatic (December-November, Ann[1]) and calendar years (January-December, Ann[2]).*

		Volume-Weighted Mean Concentration (ng/L)											
Site	Season	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
PA00	Winter	-----	-----	-----	-----	10.47	10.19	5.24	4.88	6.12	6.60	6.25	7.40
	Spring	-----	-----	-----	-----	10.67	11.77	10.36	7.80	7.29	8.44	14.15	9.77
	Summer	-----	-----	-----	-----	16.00	9.20	10.99	10.43	12.44	9.85	11.17	11.68
	Fall	-----	-----	-----	-----	6.76	4.91	8.03	6.95	4.49	5.56	7.51	4.15
	Ann[1]	-----	-----	-----	-----	10.74	8.31	8.76	7.68	7.67	7.55	10.18	8.40
	Ann[2]	-----	-----	-----	-----	11.59	7.73	8.78	7.77	7.72	7.52	9.77	8.51
PA13	Winter	10.55	7.62	6.19	7.26	7.25	6.95	5.40	6.25	4.51	4.58	6.97	6.26
	Spring	12.64	8.65	9.85	8.76	27.95	10.65	9.62	9.05	7.63	9.77	7.76	12.56
	Summer	11.41	14.09	14.47	12.03	12.31	12.70	10.54	10.64	13.22	10.66	9.45	10.54
	Fall	4.21	13.04	6.80	9.37	7.74	5.68	6.57	5.60	5.00	6.04	7.91	8.36
	Ann[1]	9.01	10.32	9.44	9.37	15.26	9.29	8.53	8.12	7.06	7.87	8.36	9.17
	Ann[2]	9.18	10.17	9.25	9.58	14.82	9.25	8.51	8.02	6.68	8.36	8.00	9.09
PA30	Winter	-----	-----	-----	-----	12.00	8.77	6.18	7.01	6.29	7.66	5.41	5.00
	Spring	-----	-----	-----	-----	8.63	10.98	10.89	11.07	8.55	10.21	11.12	8.26
	Summer	-----	-----	-----	12.82	11.66	13.30	14.81	11.24	14.06	8.56	10.77	11.79
	Fall	-----	-----	-----	11.95	8.61	5.87	7.69	4.87	7.20	7.81	6.66	5.41
	Ann[1]	-----	-----	-----	-----	10.10	9.02	10.27	8.75	8.73	8.47	8.05	7.80
	Ann[2]	-----	-----	-----	-----	9.12	9.22	10.30	8.62	8.96	8.13	7.86	8.13
PA37	Winter	-----	-----	-----	6.04	7.50	7.34	4.85	4.79	5.25	5.69	5.75	-----
	Spring	-----	-----	46.20	13.39	9.07	9.27	12.20	9.37	7.44	9.93	8.16	-----
	Summer	-----	-----	15.51	12.63	11.29	11.26	12.18	11.59	11.16	12.98	11.04	-----
	Fall	-----	-----	7.94	10.91	9.89	5.29	7.58	6.39	6.76	6.83	6.91	-----
	Ann[1]	-----	-----	-----	10.99	9.88	8.68	10.02	8.27	7.42	8.98	8.46	-----
	Ann[2]	-----	-----	-----	11.28	9.95	8.30	10.09	8.17	7.80	8.69	8.00	-----

[1] Annual Period (December-November).

[2] Annual Period (January-December).

Table 4 *(continued).*

		Volume-Weighted Mean Concentration (ng/L)											
Site	Season	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
PA47	Winter	-----	-----	-----	-----	-----	-----	4.62	5.47	5.69	4.47	5.27	6.19
	Spring	-----	-----	-----	-----	-----	-----	8.13	11.44	8.08	8.68	7.87	9.46
	Summer	-----	-----	-----	-----	-----	-----	9.67	10.46	11.45	11.33	11.50	12.00
	Fall	-----	-----	-----	-----	-----	9.27	6.74	6.28	4.87	5.75	6.79	5.59
	Ann[1]	-----	-----	-----	-----	-----	----	7.59	8.68	7.85	7.72	8.36	8.07
	Ann[2]	-----	-----	-----	-----	-----	----	7.61	8.84	7.40	7.99	8.31	8.23
PA52	Winter	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	6.08
	Spring	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	7.79
	Summer	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	9.41	11.72
	Fall	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	7.90	6.58
	Ann[1]	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	7.97
	Ann[2]	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	7.91
PA60	Winter	-----	-----	-----	7.86	11.36	7.06	4.86	6.25	5.50	8.20	8.44	10.09
	Spring	-----	-----	-----	11.92	10.99	13.64	11.56	16.09	6.34	16.41	19.52	11.85
	Summer	-----	-----	-----	9.53	12.13	11.15	9.97	9.77	13.79	8.99	12.22	12.09
	Fall	-----	-----	8.17	10.50	8.04	4.61	7.57	5.43	10.79	8.06	8.44	5.90
	Ann[1]	-----	-----	----	10.14	11.27	9.34	8.31	8.81	8.22	9.75	11.40	9.74
	Ann[2]	-----	-----	----	10.45	10.93	8.36	8.72	8.71	8.65	10.01	10.87	9.40
PA72	Winter	-----	-----	-----	-----	7.07	8.85	4.77	3.75	4.51	3.64	4.89	5.13
	Spring	-----	-----	-----	-----	8.17	15.53	7.37	9.85	6.17	10.13	7.88	9.23
	Summer	-----	-----	-----	-----	13.92	10.46	11.13	12.90	10.92	7.85	9.90	13.78
	Fall	-----	-----	-----	8.75	7.10	3.00	6.08	8.64	3.84	7.75	4.92	5.18
	Ann[1]	-----	-----	-----	----	9.11	8.80	7.89	9.29	5.71	6.91	6.68	8.02
	Ann[2]	-----	-----	-----	----	9.39	8.34	7.63	9.64	5.36	7.50	6.48	7.89
PA90	Winter	8.71	5.34	12.45	5.14	7.04	7.73	3.67	3.36	3.77	3.55	5.99	5.40
	Spring	10.64	9.14	7.64	7.01	6.80	7.69	8.52	8.66	4.93	8.36	8.21	6.93
	Summer	13.36	14.14	10.70	14.99	7.99	10.22	9.53	8.59	12.68	12.42	11.74	12.47
	Fall	5.12	7.94	5.39	10.17	5.54	4.18	5.60	5.17	4.62	4.83	7.72	5.51
	Ann[1]	9.57	9.07	8.62	9.41	6.79	7.52	7.33	6.88	6.71	7.77	8.99	7.59
	Ann[2]	9.50	8.97	8.56	9.69	6.58	7.36	7.13	7.06	6.37	8.40	8.48	7.66

[1] Annual Period (December-November).

[2] Annual Period (January-December).

Table 5. *Annual and seasonal total mercury wet depositions (μg/m2) at eight Pennsylvania Mercury Deposition Network sites from 1997 through 2008 Seasonal depositions are based on weekly samples collected from December-February (winter) March-May (spring), June-August (summer), and September-November (fall). Annual values are presented for both climatic (December-November, Ann[1]) and calendar years (January-December, Ann[2]).*

		Wet Deposition (μg/m^2)											
Site	Season	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
PA00	Winter	-----	-----	-----	-----	1.808	1.139	1.341	1.195	1.352	1.684	1.142	2.096
	Spring	-----	-----	-----	-----	2.506	3.317	3.473	2.562	1.950	1.604	3.666	4.297
	Summer	-----	-----	-----	-----	1.842	1.881	3.432	3.918	3.293	3.306	2.817	2.339
	Fall	-----	-----	-----	-----	0.962	1.855	2.434	2.463	1.161	1.867	1.591	1.298
	Ann[1]	-----	-----	-----	-----	7.118	8.192	10.681	10.138	7.756	8.461	9.216	10.030
	Ann[2]	-----	-----	-----	-----	7.250	7.932	10.617	9.951	8.116	8.135	9.286	10.661
PA13	Winter	0.931	1.923	1.204	1.149	0.936	1.175	1.197	1.714	1.337	1.292	1.356	1.586
	Spring	4.511	3.072	2.443	2.865	6.429	3.785	3.007	3.572	1.541	1.831	1.839	4.396
	Summer	2.956	3.395	3.553	2.666	3.196	3.244	4.867	3.911	2.469	4.429	3.879	2.456
	Fall	1.786	1.755	1.845	1.958	1.256	1.528	2.244	2.190	1.282	1.969	1.731	1.793
	Ann[1]	10.184	10.145	9.044	8.639	11.818	9.732	11.315	11.387	6.629	9.521	8.805	10.232
	Ann[2]	10.863	9.767	8.985	8.854	11.933	9.596	11.628	11.233	6.744	9.414	8.980	10.061
PA30	Winter	-----	-----	-----	-----	1.600	2.588	0.985	1.066	1.813	1.283	1.635	1.435
	Spring	-----	-----	-----	-----	2.041	3.588	2.872	3.580	1.603	2.023	1.819	2.029
	Summer	-----	-----	-----	3.895	1.988	1.879	4.180	3.858	3.024	2.590	2.950	4.006
	Fall	-----	-----	-----	2.756	2.050	2.167	2.337	1.693	2.747	2.998	1.832	1.698
	Ann[1]	-----	-----	-----	-----	7.678	10.222	10.374	10.197	9.188	8.894	8.237	9.169
	Ann[2]	-----	-----	-----	-----	7.939	9.778	10.390	10.727	8.980	8.977	8.119	9.632
PA37	Winter	-----	-----	-----	1.271	1.005	1.129	0.779	0.979	1.548	0.931	1.091	-----
	Spring	-----	-----	0.016	3.505	2.464	3.818	3.716	3.193	1.883	2.208	2.144	-----
	Summer	-----	-----	2.817	3.354	4.179	3.258	6.283	3.792	2.628	3.340	3.949	-----
	Fall	-----	-----	1.961	1.405	1.576	1.353	2.116	2.399	1.630	2.566	1.515	-----
	Ann[1]	-----	-----	-----	9.536	9.224	9.558	12.895	10.363	7.689	9.045	8.700	-----
	Ann[2]	-----	-----	-----	9.563	9.523	9.151	12.609	10.374	7.890	8.828	8.963	-----

[1] Annual Period (December-November).

[2] Annual Period (January-December).

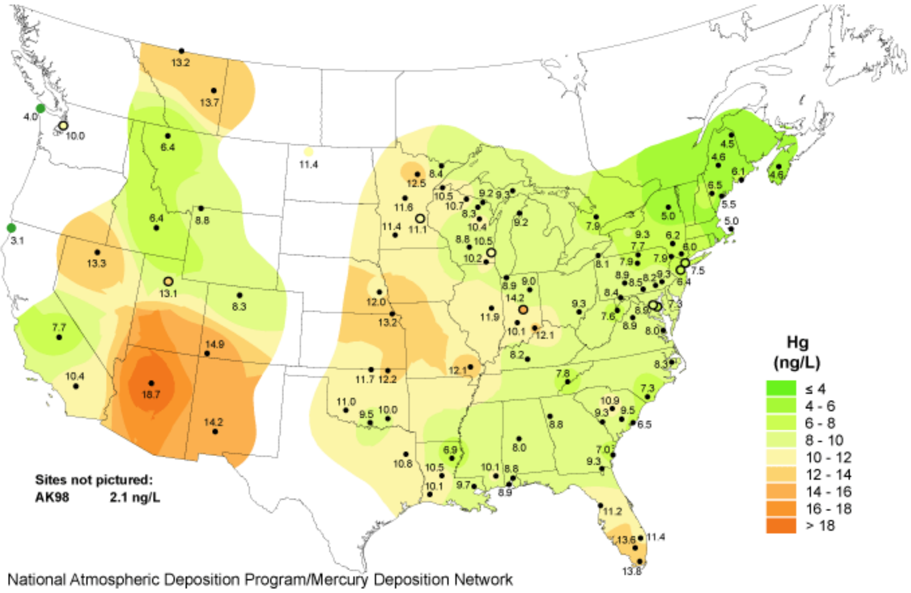
***Table 5** (continued).*

		Wet Deposition (µg/m^2)											
Site	Season	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
PA47	Winter	-----	-----	-----	-----	-----	-----	1.294	1.330	1.307	1.137	0.898	1.630
	Spring	-----	-----	-----	-----	-----	-----	2.154	3.411	1.866	1.724	1.921	2.939
	Summer	-----	-----	-----	-----	-----	-----	4.044	4.226	3.444	4.628	3.413	2.403
	Fall	-----	-----	-----	-----	-----	0.052	2.780	1.758	1.525	2.463	1.283	1.629
	Ann[1]	-----	-----	-----	-----	-----	-----	10.273	10.725	8.142	9.951	7.515	8.601
	Ann[2]	-----	-----	-----	-----	-----	-----	10.422	10.502	8.348	9.886	7.814	8.837
PA52	Winter	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	1.504
	Spring	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	2.776
	Summer	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	1.226	2.782
	Fall	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	1.753	1.206
	Ann[1]	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	8.268
	Ann[2]	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	8.168
PA60	Winter	-----	-----	-----	1.691	2.951	1.147	1.786	1.446	2.055	2.269	1.862	2.970
	Spring	-----	-----	-----	4.023	2.898	3.704	3.402	4.772	1.767	3.193	6.234	3.709
	Summer	-----	-----	-----	3.263	2.352	2.562	4.453	4.467	2.456	4.274	3.596	3.038
	Fall	-----	-----	0.315	2.865	0.851	1.647	3.519	2.277	3.308	3.691	2.179	2.053
	Ann[1]	-----	-----	-----	11.842	9.051	9.060	13.160	12.962	9.586	13.426	13.870	11.771
	Ann[2]	-----	-----	-----	12.613	8.447	9.843	12.779	12.521	9.910	13.439	12.351	11.395
PA72	Winter	-----	-----	-----	-----	1.867	1.213	1.292	0.989	1.630	1.383	1.038	1.917
	Spring	-----	-----	-----	-----	2.181	5.184	2.214	2.658	1.826	2.384	2.231	3.530
	Summer	-----	-----	-----	-----	3.309	2.667	4.928	5.611	2.606	3.438	4.102	3.855
	Fall	-----	-----	-----	1.172	1.422	1.242	2.987	3.416	2.046	3.164	1.570	1.824
	Ann[1]	-----	-----	-----	-----	8.778	10.306	11.420	12.674	8.108	10.370	8.941	11.127
	Ann[2]	-----	-----	-----	-----	8.399	9.892	11.726	12.673	8.172	10.109	8.378	11.020
PA90	Winter	0.505	1.179	2.051	0.798	0.560	0.950	0.651	0.625	0.927	0.810	0.917	1.312
	Spring	1.985	2.754	1.401	2.023	1.469	1.836	1.808	2.354	0.965	1.451	1.549	2.009
	Summer	3.182	2.668	2.120	3.024	1.782	2.599	4.196	3.642	3.530	5.241	3.420	2.844
	Fall	1.230	1.085	1.303	1.394	1.153	0.939	1.378	1.666	1.300	1.351	1.480	1.083
	Ann[1]	6.902	7.685	6.875	7.239	4.964	6.323	8.033	8.287	6.721	8.853	7.367	7.248
	Ann[2]	7.217	7.500	6.853	7.599	4.929	6.213	7.838	8.343	6.743	8.570	7.579	7.077

[1] Annual Period (December-November).
[2] Annual Period (January-December).

Figure 9. *Volume-weighted mean annual total mercury concentrations (ng/L) and estimated wet depositions ($\mu g/m^2$) at all Mercury Deposition Network sites in the United States and southern Canada that met the 75% data completeness criteria in 2008.*

Volume-weighted mean annual mercury concentrations in precipitation in the United States in 2008
National Atmospheric Deposition Program / Mercury Deposition Network



Annual total wet atmospheric mercury deposition in the United States in 2008
National Atmospheric Deposition Program / Mercury Deposition Network

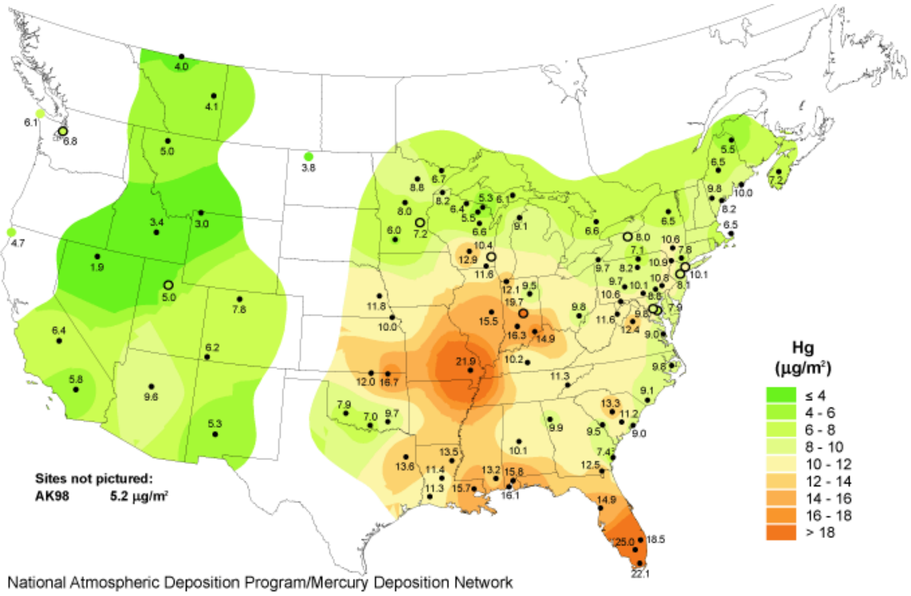
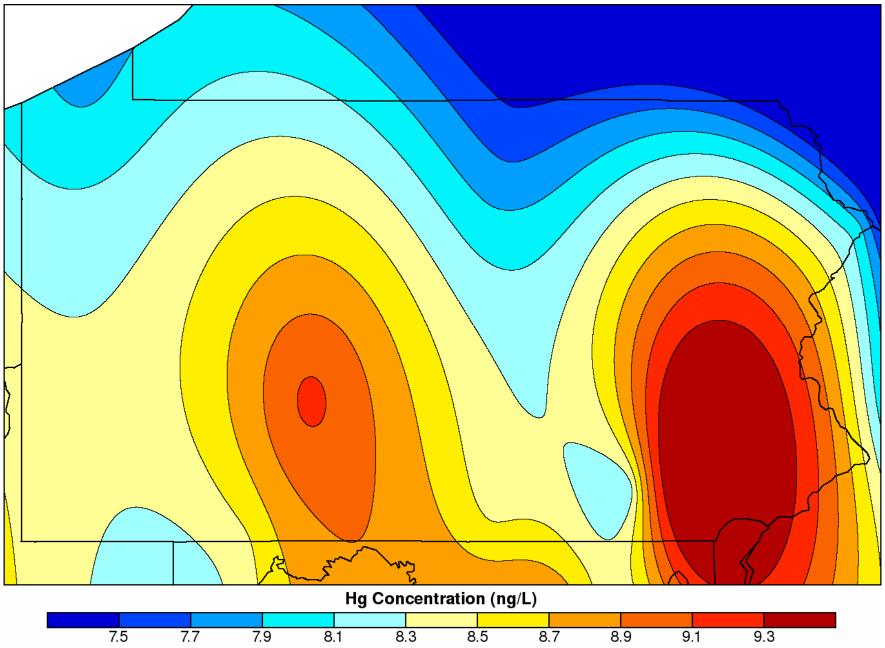


Figure 10. *Annual patterns of volume-weighted mercury concentrations in precipitation (ng/L) and wet mercury depositions (µg/m^2) based on interpolated data from Mercury Deposition Network sites in Pennsylvania and peripheral states.*

Volume-weighted mean annual mercury concentrations in precipitation in PA in 2008



Annual total wet atmospheric mercury deposition in PA in 2008

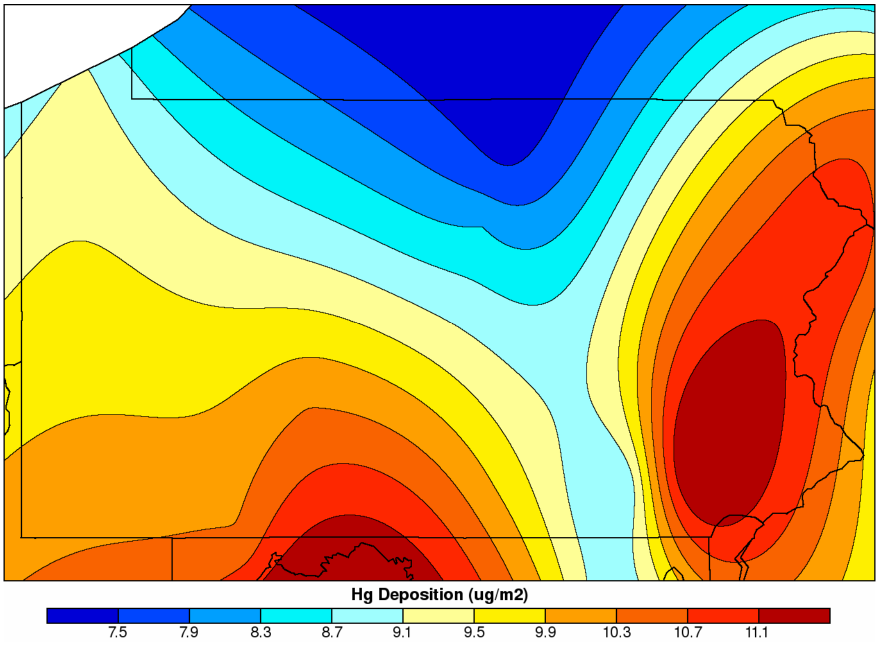


Figure 11. *Seasonal (quarterly) patterns of volume-weighted mean mercury concentration (ng/L) in precipitation across Pennsylvania in 2008.*

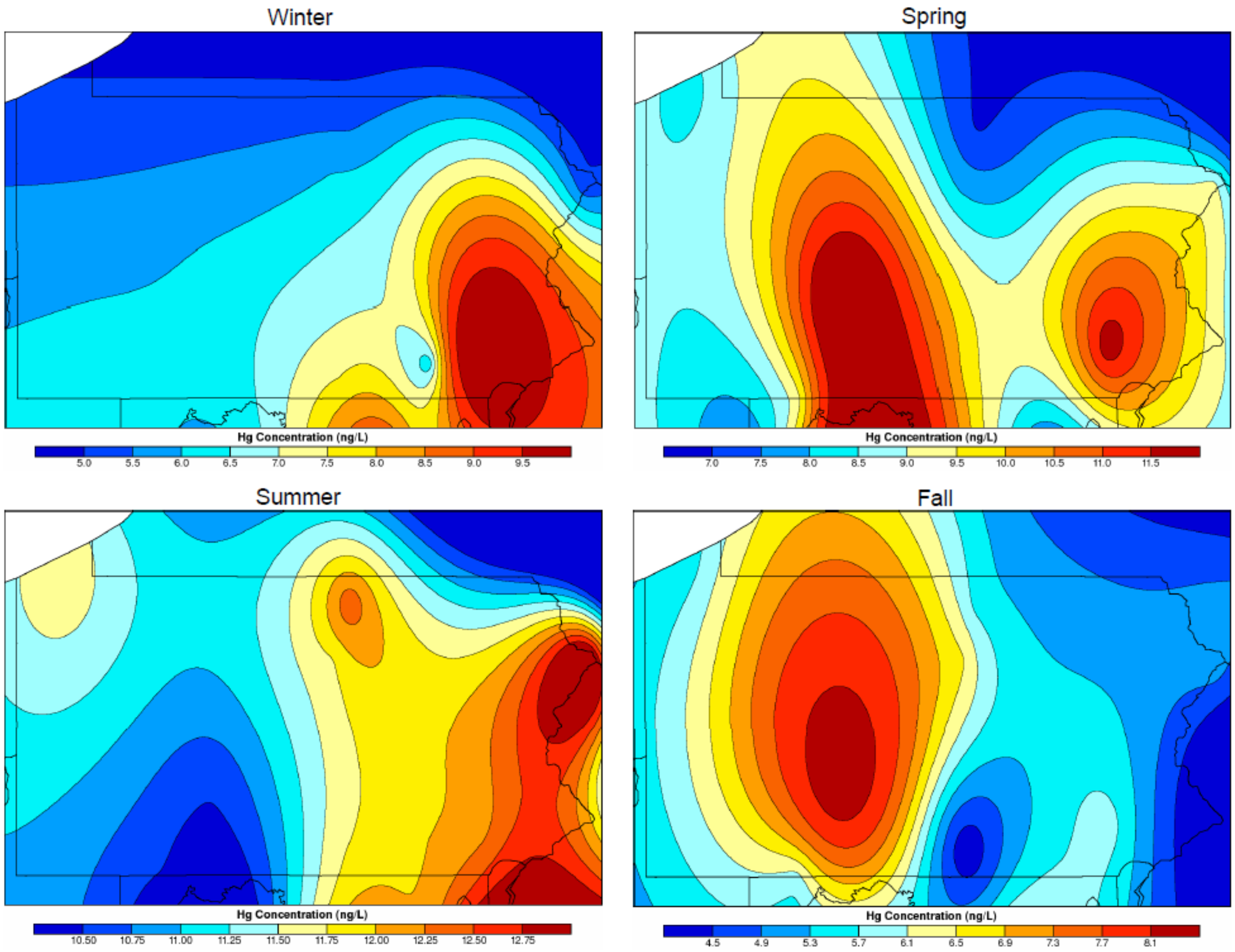


Figure 12. *Seasonal (quarterly) patterns of wet atmospheric mercury deposition (µg/m^2) across Pennsylvania in 2008.*

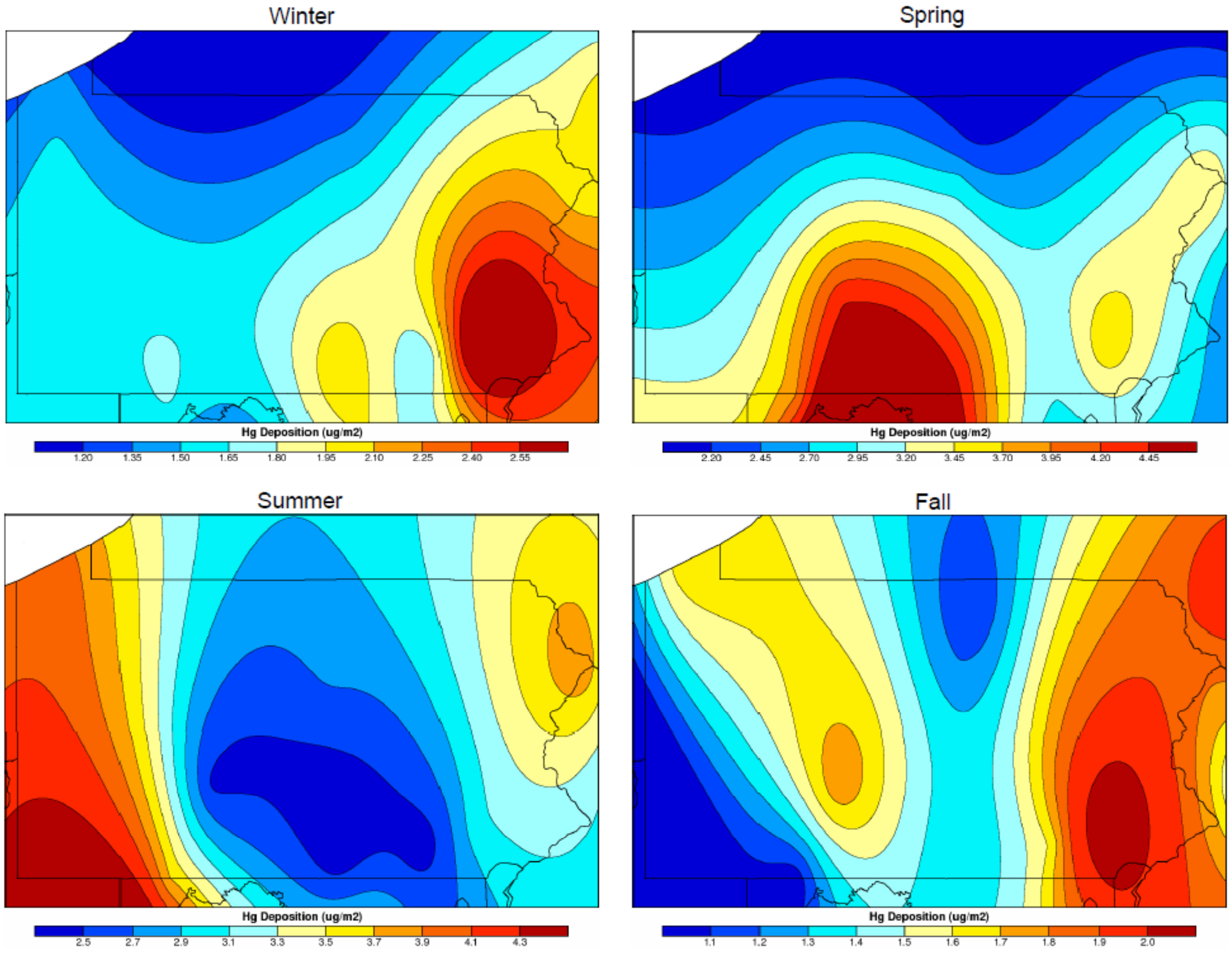


Figure 13. *Spatial interpolations of volume-weighted mean annual mercury concentrations (ng/L) across Pennsylvania in 2003-2008.*

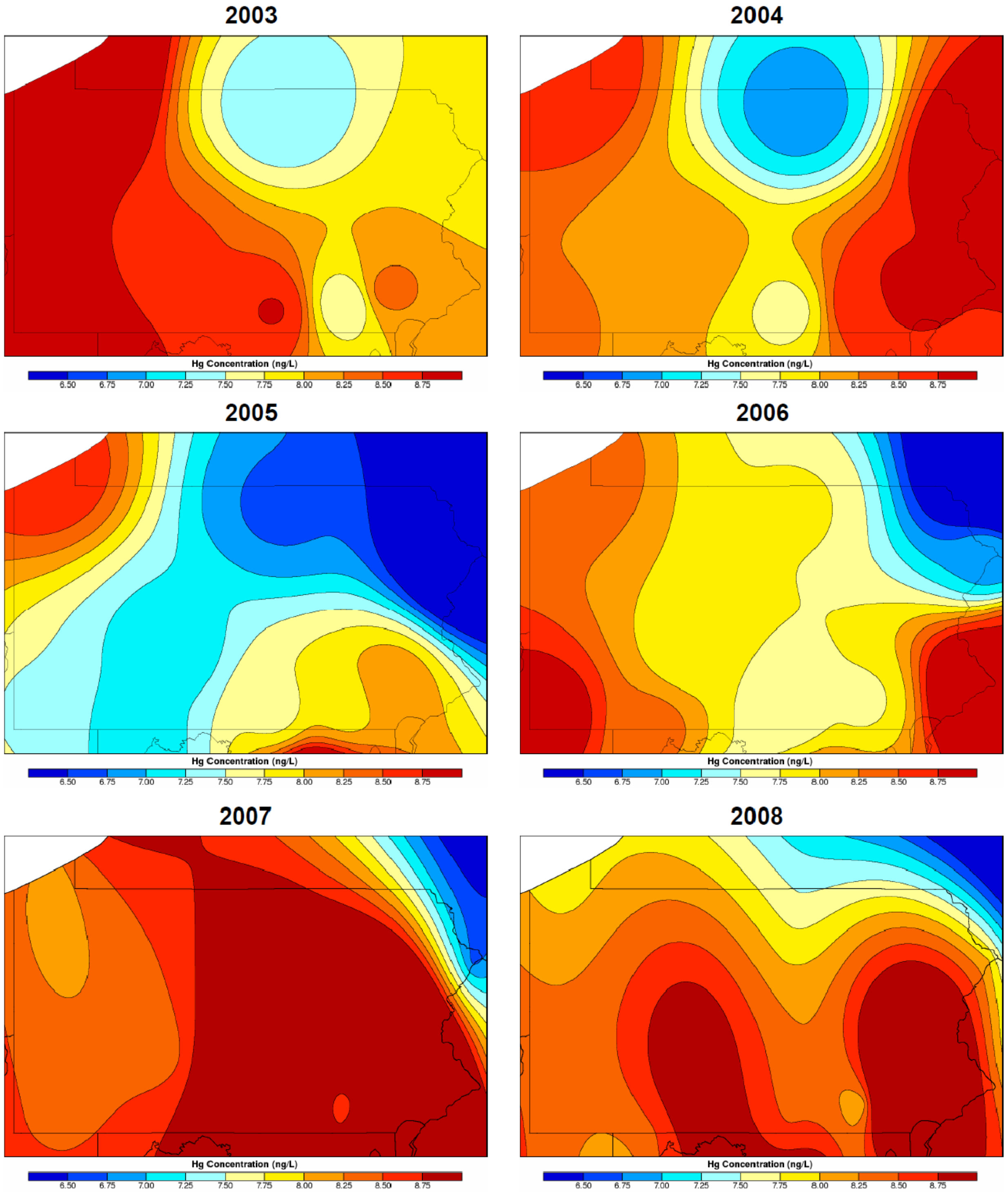
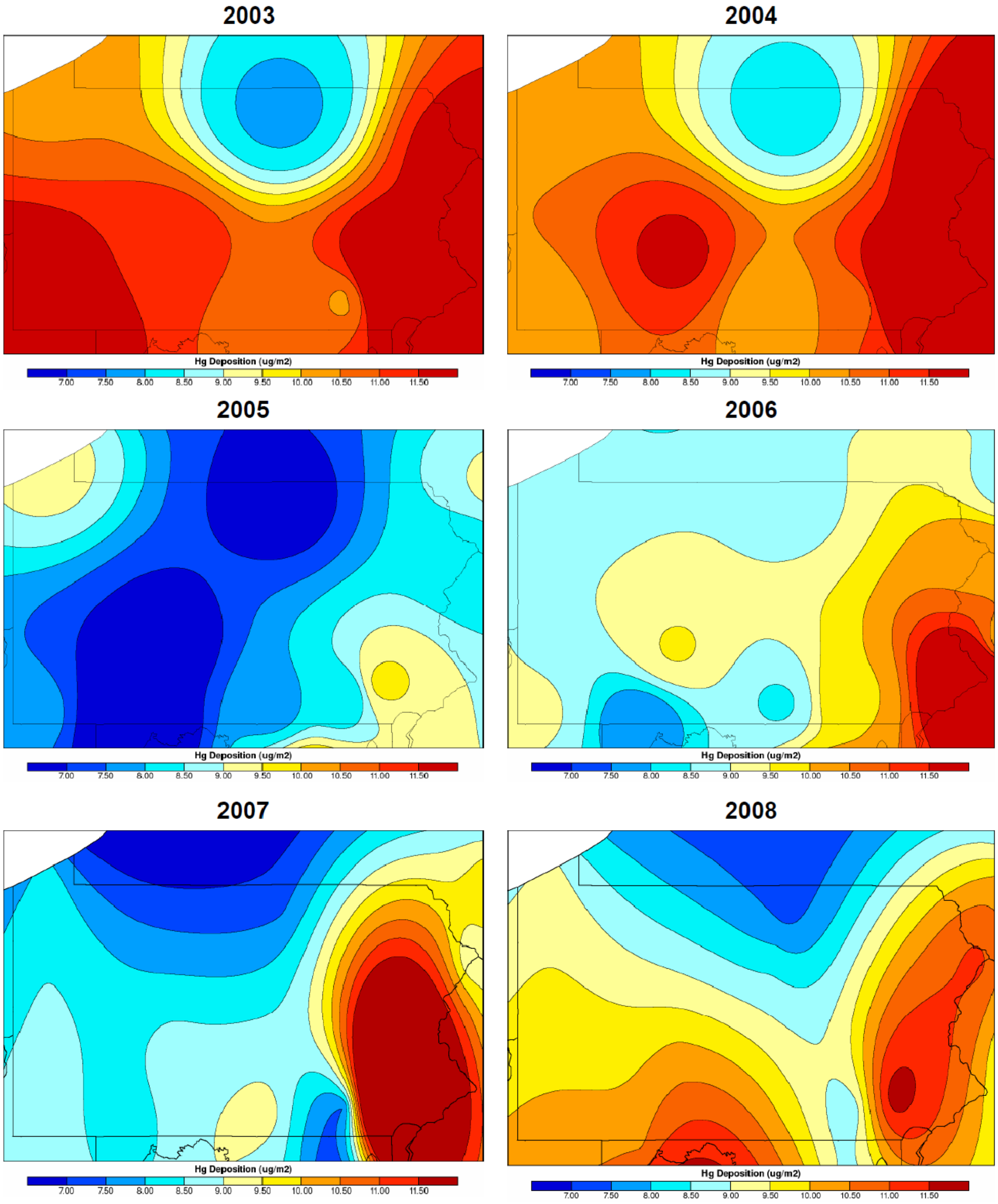


Figure 14. *Spatial interpolations of wet atmospheric mercury deposition (μg/m^2) across Pennsylvania in 2003-2008.*



Correlation and Stepwise Regression Analyses

Correlation and stepwise regression analyses between mercury and cation and anion concentrations in precipitation are useful toward generating hypotheses about sources and source areas that affect mercury at the monitoring sites. Each MDN site in Pennsylvania is collocated with a precipitation sampler that provides weekly samples for analysis of the concentrations of major cations and anions in precipitation (Boyer et al. 2010). Pearson correlation coefficients between weekly mercury concentrations and the concentrations of the major cations (calcium, magnesium, potassium, ammonium and sodium), anions (sulfate, nitrate, and chloride), and precipitation volumes are shown in Table 6 for all MDN sites in the state. The results illustrate that sulfate and nitrate are positively correlated with total mercury concentrations at each site and all of the coefficients are statistically significant ($p<0.05$) (Table 6). The same is also true for calcium, magnesium and potassium concentrations. The correlation coefficients between weekly mercury concentrations and sodium and chloride are much weaker, although still statically significant at a few sites. Ammonium concentrations are positively correlated with mercury concentrations at all sites, although the coefficients are not statistically significant at several sites. As might be expected, precipitation volumes are inversely correlated with mercury concentrations at the sites (Table 6).

Concentration

Log_{10} transformed weekly cation and anion concentrations were included in a stepwise regression analyses with dependent variable $\log_{10}$ mercury concentrations. The statistically significant ($p<0.05$) variables and their order of selection are shown in Table 7. The first and most statistically significant variable in predicting mercury concentrations at most of the monitoring sites (6 of 8) was sulfate concentrations. At the other two sites, calcium concentrations were selected first followed by sulfate. At the sites where sulfate was the primary variable, the second most important variable in each model was calcium, magnesium, or potassium. Four sites had three variables in their predictive model, all with sulfate and calcium as predictors, but also including chloride, potassium, or ammonium. The model r-squared values, a measure of the amount of explained variation between dependent and independent variables, ranged from 0.22 at PA37 to 0.49 at PA72 (Table 7). When included in model development, precipitation volume was a significant (though not the primary) predictive variable at two sites, PA30 and PA60, replacing one of the cations (Table 7).

Sulfate concentrations in precipitation result from the oxidation of sulfur dioxide released to the atmosphere during combustion. The primary source of sulfur dioxide in Pennsylvania is from coal-fired power plants. We also know that sulfate concentrations in precipitation are highest during the summer and lowest during the winter months, the same temporal pattern that is frequently observed for mercury concentrations at all MDN sites in Pennsylvania. We also know that coal combustion is one of the primary sources of mercury emissions to the atmosphere in the eastern United States (EPA, 2002). The close association of sulfate concentrations with mercury concentrations as illustrated by the correlation coefficients (Table 6) and stepwise regression models (Table 7) appears to indicate that at least some of the mercury in precipitation at all Pennsylvania MDN sites is from combustion sources, including likely contributions from coal-fired power plants. At PA13 (Allegheny-Portage) sulfate is the only variable that is significantly associated with mercury concentrations at that site. This site is located on top of Cresson Mountain and is downwind of several large coal-fired utilities located in western Pennsylvania and the largest mercury emission sources in the state (Figure 14).

Wind-blown soil particles are an important source of cations in precipitation, particularly calcium and magnesium. The calcium and magnesium could come from a range of sources, for example they are released in small amounts during the combustion of fossil fuels, and they are entrained in the air from altering the soil such as in agricultural operations. The close association of calcium and magnesium with mercury concentrations might suggest the notion that potential terrestrial/agricultural sources are important at some sites. The fact that calcium is the most significant variable in predicting mercury concentrations at the Arendtsville (PA00) and Millersville (PA47) sites would tend to support this position. Both of these sites are located in areas that are dominated by agricultural activities, particularly at PA47 were calcium concentrations explain more than 50% of the variance in weekly mercury concentrations. Lindberg et al. (1998) reported that mercury is constantly recycled between terrestrial ecosystems and the atmosphere. How agricultural activities would affect the release of mercury cannot be determined by this analysis. However, mercury has been used extensively in agriculture for many years and may be a contributing factor. In addition, soil disturbance in agricultural areas and the subsequent increase in wind erosion may also be factor at some sites.

Deposition

Correlation and stepwise regression analyses were also conducted on weekly wet mercury depositions and the depositions of major cations and anions measured at each MDN sites. The correlation coefficients are presented in Table 8, while the results of the stepwise regression analyses are presented in Table 9. Results from the wet deposition analysis are similar to the concentration analysis in that sulfate concentrations are the primary and most statistically significant predictive variable in the regression models at all MDN sites. With the exception of the Holbrook site (PA37), wet sulfate deposition accounted for over 60% of the variability in wet mercury deposition at each MDN site (Table 9). The much higher r-squared values for the wet deposition analyses versus the concentration analyses results from the fact that precipitation volumes used to calculate wet deposition is the same for both sulfate and mercury wet deposition calculations. It should also be noted that although cation wet depositions were important in each site's model, they were not the primary variable at any site as they were for the concentration analysis. In addition, other ions such as sodium and nitrate were significant tertiary variables at some sites. The significance of these variables in explaining wet mercury deposition is not clear, although in all cases, their contribution (based on partial r-squared values) to each model is relatively small and may be indicative of broad regional land use activities or a function of long-range transport of pollutants including mercury to individual sites.

Table 6. *Pearson correlation coefficients (r) between total mercury and the major cation and anion concentrations in precipitation as measured at eight Pennsylvania collocated mercury (MDN) and acid rain monitoring sites during 2003 through 2008. All concentrations were log-transformed. Precipitation was transformed by taking its square root.*

Site	sulfate	nitrate	chloride	calcium	magnesium	potassium	sodium	ammonium	precipitation
PA00									
r	0.640	0.594	0.053	0.640	0.543	0.511	0.145	0.260	-0.477
Prob>|r|	0.0001	0.0001	0.4221	0.0001	0.0001	0.0001	0.0335	0.0001	0.0001
No. Obs.	215	215	228	215	215	215	215	228	250
PA13									
r	0.574	0.406	-0.084	0.398	0.349	0.326	0.016	0.124	-0.354
Prob>|r|	0.0001	0.0001	0.1689	0.0001	0.0001	0.0001	0.8039	0.0415	0.0001
No. Obs.	254	254	272	251	251	251	251	272	275
PA30									
r	0.637	0.455	-0.004	0.490	0.478	0.329	0.272	0.147	-0.453
Prob>|r|	0.0001	0.0001	0.9503	0.0001	0.0001	0.0001	0.0001	0.0164	0.0001
No. Obs.	252	252	267	252	252	252	252	267	271
PA37									
r	0.471	0.233	0.198	0.335	0.424	0.301	0.211	0.326	-0.163
Prob>|r|	0.0001	0.0007	0.0034	0.0001	0.0001	0.0001	0.0022	0.0001	0.0157
No. Obs.	210	210	217	210	210	210	210	217	218
PA47									
r	0.615	0.603	-0.020	0.674	0.569	0.543	0.099	0.003	-0.425
Prob>|r|	0.0001	0.0001	0.7476	0.0001	0.0001	0.0001	0.1559	0.9614	0.0001
No. Obs.	208	208	250	208	208	208	208	250	260
PA52									
r	0.657	0.462	0.072	0.556	0.408	0.332	0.141	0.310	-0.368
Prob>|r|	0.0001	0.0002	0.5731	0.0001	0.0010	0.0085	0.2749	0.0135	0.0026
No. Obs.	62	62	63	62	62	62	62	63	65
PA60									
r	0.622	0.556	0.147	0.535	0.428	0.465	0.174	0.362	-0.500
Prob>|r|	0.0001	0.0001	0.0262	0.0001	0.0001	0.0001	0.0116	0.0001	0.0001
No. Obs.	214	214	228	211	211	211	211	228	229
PA72									
r	0.697	0.585	0.118	0.668	0.530	0.559	0.011	0.484	-0.459
Prob>|r|	0.0001	0.0001	0.0590	0.0001	0.0001	0.0001	0.8687	0.0001	0.0001
No. Obs.	229	229	255	229	229	229	229	255	262
PA90									
r	0.690	0.541	0.199	0.609	0.651	0.410	0.354	0.462	-0.318
Prob>|r|	0.0001	0.0001	0.0008	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	271	271	281	270	270	270	270	281	284

Table 7. *Summary of stepwise regression analyses of* log_{10}*-transformed mercury concentration against* log_{10}*-transformed major cation and anion concentrations in precipitation collected at eight Pennsylvania collocated mercury and acid rain monitoring sites during 2003 through 2008. All predictors in the models are significant at* $p < 0.05$*.*

Site	Variables In Model	Partial R-square	Model R-square	C(p) Value	F-value	p > F
PA00	Ca^{2+}	0.410	0.410	31.128	147.85	<0.0001
	SO_4^{2-}	0.077	0.486	1.641	31.69	<0.0001
PA13	SO_4^{2-}	0.337	0.337	4.129	126.70	<0.0001
PA30	SO_4^{2-}	0.406	0.406	25.068	170.65	<0.0001
	Mg^{2+}	0.047	0.453	5.267	21.60	<0.0001
	Na^{2+}	0.009	0.462	3.173	4.11	0.0438
PA37	SO_4^{2-}	0.222	0.222	16.248	59.31	<0.0001
	Mg^{2+}	0.043	0.265	5.882	12.20	0.0006
PA47	Ca^{2+}	0.455	0.455	17.414	171.77	<0.0001
	SO_4^{2-}	0.031	0.486	6.650	12.54	0.0005
PA52	SO_4^{2-}	0.432	0.432	11.418	45.68	<0.0001
	Ca^{2+}	0.046	0.478	7.773	5.22	0.0259
	Cl^{2-}	0.061	0.540	2.273	7.73	0.0073
PA60	SO_4^{2-}	0.378	0.378	21.517	127.15	<0.0001
	K^{+}	0.044	0.423	7.212	15.98	<0.0001
	Ca^{2+}	0.019	0.441	2.348	6.92	0.0092
PA72	SO_4^{2-}	0.485	0.485	46.871	214.06	<0.0001
	Ca^{2+}	0.078	0.563	7.816	40.20	<0.0001
	Cl^{2-}	0.012	0.574	3.350	6.48	0.0116
PA90	SO_4^{2-}	0.477	0.477	62.258	244.22	<0.0001
	Mg^{2+}	0.092	0.569	6.263	57.29	<0.0001
	NH_4^{+}	0.010	0.579	2.065	6.24	0.0131
----------If the square root of precipitation is included as an independent variable----------						
PA30	SO_4^{2-}	0.406	0.406	34.698	170.65	<0.0001
	Pcp	0.048	0.454	13.768	21.98	<0.0001
	Mg^{2+}	0.022	0.476	5.336	10.38	0.0014
PA60	SO_4^{2-}	0.378	0.378	31.971	127.15	<0.0001
	Pcp	0.064	0.442	9.161	23.92	<0.0001
	K^{+}	0.030	0.473	0.568	11.99	0.0006

Table 8. *Pearson correlation coefficients (r) between wet total mercury deposition and cation and anion wet depositions as measured at eight Pennsylvania collocated mercury (MDN) and acid rain monitoring sites during 2003 through 2008. All depositions were log-transformed. Precipitation was transformed by taking its square root.*

Site	sulfate	nitrate	chloride	calcium	magnesium	potassium	sodium	ammonium	precipitation
PA00									
r	0.820	0.770	0.555	0.728	0.714	0.729	0.509	0.601	0.761
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	215	215	228	215	215	215	215	228	250
PA13									
r	0.776	0.641	0.442	0.484	0.478	0.467	0.364	0.595	0.773
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	254	254	272	251	251	251	251	272	275
PA30									
r	0.833	0.662	0.447	0.565	0.561	0.520	0.545	0.517	0.752
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	252	252	267	252	252	252	252	267	271
PA37									
r	0.594	0.391	0.330	0.384	0.486	0.399	0.375	0.417	0.780
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	210	210	217	210	210	210	210	217	218
PA47									
r	0.860	0.819	0.488	0.778	0.756	0.731	0.484	0.460	0.781
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	208	208	250	208	208	208	208	250	260
PA52									
r	0.845	0.724	0.656	0.656	0.608	0.542	0.568	0.674	0.780
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	62	62	63	62	62	62	62	63	65
PA60									
r	0.796	0.692	0.539	0.580	0.636	0.543	0.511	0.633	0.777
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	214	214	228	211	211	211	211	228	229
PA72									
r	0.815	0.728	0.553	0.712	0.685	0.688	0.427	0.648	0.724
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	229	229	255	229	229	229	229	255	262
PA90									
r	0.841	0.750	0.552	0.649	0.701	0.520	0.589	0.677	0.744
Prob>|r|	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
No. Obs.	271	271	281	270	270	270	270	281	284

Table 9. *Summary of stepwise regression analyses of* $\log_{10}$*-transformed wet deposition of mercury against* $\log_{10}$*-transformed major cation and anion wet depositions measured at eight Pennsylvania collocated mercury and acid rain monitoring sites during 2003 through 2008. All predictors the models are significant at* $p<0.05$*.*

Site	Variables In Model	Partial R-square	Model R-square	C(p) Value	F-value	p > F
PA00	SO_4^{2-}	0.672	0.672	18.964	436.51	<0.0001
	Ca^{2+}	0.022	0.694	5.356	15.44	0.0001
	NO_3^-	0.007	0.701	2.416	4.98	0.0267
PA13	SO_4^{2-}	0.604	0.604	8.876	379.84	<0.0001
	Na^{2+}	0.008	0.612	5.508	5.31	0.0220
PA30	SO_4^{2-}	0.694	0.694	16.651	567.95	<0.0001
	Na^{2+}	0.019	0.713	2.568	16.11	0.0001
PA37	SO_4^{2-}	0.352	0.352	14.655	113.16	<0.0001
	K^+	0.023	0.375	8.829	7.61	0.0063
PA47	SO_4^{2-}	0.740	0.740	21.093	584.64	<0.0001
	K^+	0.020	0.759	5.834	17.02	<0.0001
	NO_3^-	0.006	0.766	2.617	5.25	0.0229
PA52	SO_4^{2-}	0.714	0.714	1.667	149.96	<0.0001
PA60	SO_4^{2-}	0.644	0.644	13.849	378.16	<0.0001
	K^+	0.019	0.663	4.000	11.79	0.0007
	Na^{2+}	0.009	0.672	0.201	5.91	0.0159
PA72	SO_4^{2-}	0.665	0.665	33.033	450.51	<0.0001
	Ca^{2+}	0.034	0.699	8.918	25.45	<0.0001
	K^+	0.008	0.707	4.436	6.47	0.0116
PA90	SO_4^{2-}	0.702	0.702	41.164	631.55	<0.0001
	Mg^{2+}	0.030	0.732	12.267	29.86	<0.0001
	NO_3^-	0.010	0.742	3.498	10.79	0.0012

Trends in Total Mercury Deposition

Eleven years of observations exist at the Hills Creek (PA90) and Allegheny-Portage (PA13) sites. These sites with the longest periods of record in the state represent the best opportunity to consider trends in mercury concentrations in precipitation and the associated wet depositions.

First, we explore trends in mercury (Hg) from a seasonal least-squares generalized linear model fit of each species quarterly concentration values (from Table 4) or deposition values (from Table 5), using the equation: Hg concentration or deposition = b0 + b1*date + [b2]*[quarter], where: date is the decimal year expression of the mid-point of the quarterly summary period (e.g., 2005.0417 is the date value for the 1st quarter of 2005); and quarter is a 3-level categorical covariate array representing quarters of the climatological year (Dec-Feb, Mar-May, Jun-Aug, Sep-Nov). In Figures 15 and 16 below, these are indicated as the predicted mercury concentration (Figures 15a and 16a) or predicted mercury deposition (Figures 15b and 16b). This very simple linear model is not intended to accurately reproduce the variability in the observed patterns, but rather is used strictly as a first approximation to assess linear trends in mercury concentration and deposition. Similarly, in the context of considering relationships among patterns of mercury and sulfate deposition, we quantify trends in sulfate (SO_4) from a seasonal least-squares generalized linear model fit of each species quarterly concentration values (from Table 4) or deposition values (from Table 5), using the equation: SO4 concentration or deposition = b0 + b1*date + [b2]*[quarter], where date and quarter are defined as above.

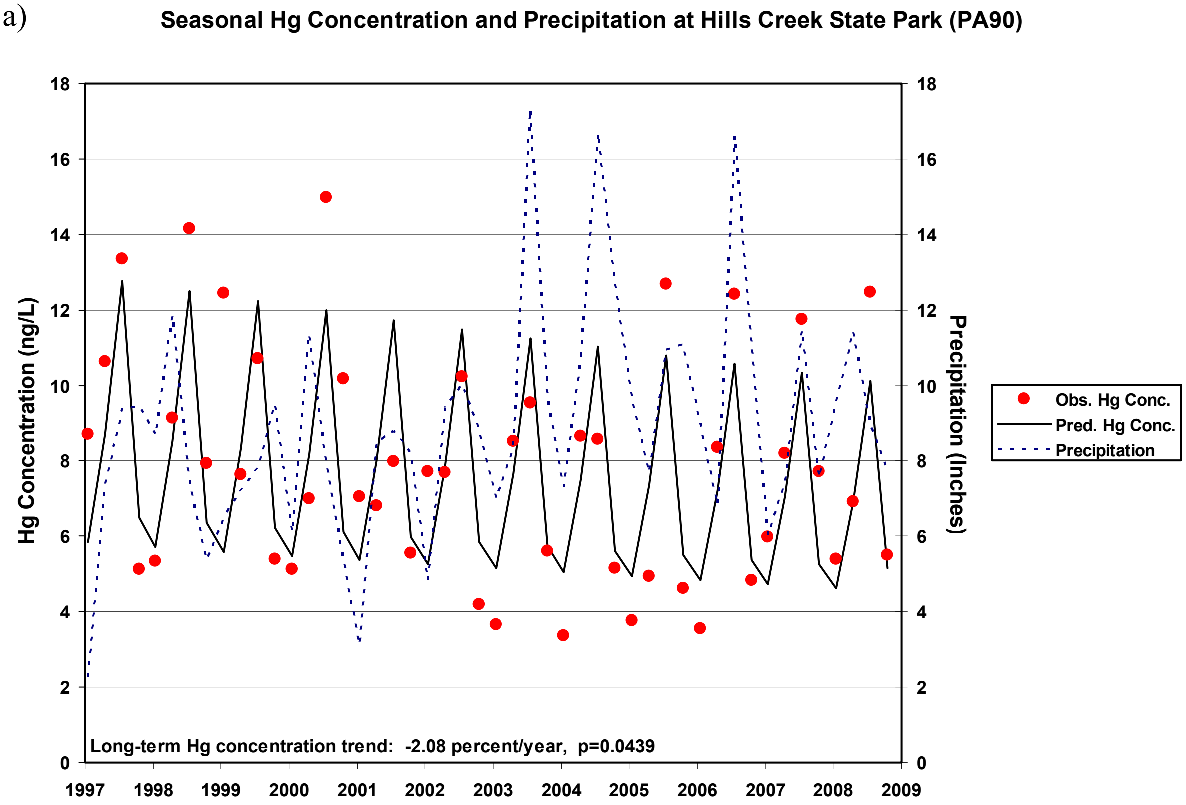
At the Hills Creek site, total mercury concentrations in precipitation have decreased from 1997 through 2008 (Figure 15a). The decreasing trend (2.08% per year) is statistically significant ($p=0.0435$, and $p<0.05$). Despite the decline in mercury concentrations at this site, wet mercury deposition has actually increased (1.39% per year) though the trend is not statistically significant ($p=0.2166$) (Figure 15b). Similarly, at the Allegheny Portage Site, total mercury concentrations in precipitation have decreased from 1997 through 2008 (Figure 16a). The decreasing trend (2.59% per year) is statistically significant ($p=0.0023$, $p<0.05$). Despite the decline in mercury concentrations at this site, wet mercury deposition has actually increased slightly (0.09% per year) though the trend is not statistically significant ($p=0.9270$) (Figure 16b). The lack of a significant wet mercury deposition trends at these sites is influenced by high precipitation volumes and wet depositions in some years of record.

The statistically significant decreasing total mercury concentration trends at Hills Creek (PA90) and Allegheny-Portage NHS (PA13) are similar to observed decreasing seasonal sulfate concentration trends at these sites (Figures 17 and 18), although the seasonal sulfate concentrations trends are not statistically significant ($p<0.05$). Given the close correlations between sulfate and mercury concentrations at these sites (Table 6 and 7), it is reasonable to assume that some of the decline total mercury concentrations would be related to reductions in sulfate concentrations that are in turn directly related to decreasing sulfur dioxide emissions in the eastern half of the United States following implementation in 1995 of Title IV of the Clean Air Act Amendments of 1990 (CAAA). Sulfur emissions reductions were achieved through a combination of scrubber technology, fuel switching (e.g., oil or natural gas for coal), the use of lower sulfur coal for Mid-western sources, and/or emissions trading. It is possible that this combination of approaches to reduced sulfur dioxide emissions has resulted in a concurrent reduction in mercury emissions as well. Given the location of the Hills Creek site and the lack of nearby mercury and sulfur emissions sources, it is reasonable to assume that long range transport of pollutants from upwind sources are the likely sources that were affected by the CAAA emissions reductions and are thus likely the sources also contributing to the reductions in mercury concentrations and deposition at this site. This would not necessarily be the case at the Allegheny-Portage site, because of its relative close proximity to major point sources.

Although the results of seasonal linear trend analyses as well as correlation and stepwise regression analyses for both mercury and sulfate concentrations suggest a positive relationship between sulfate and mercury concentration in precipitation, verification of this relationship and the reasonable assumptions presented in this report can only be achieved through the use of transport modeling to target source-receptor relationships. In addition, mercury deposition monitoring should continue in Pennsylvania in 2009 and beyond in order to establish a database of sufficient length to more accurately describe spatial and temporal patterns across the Commonwealth and to assess how these patterns are related to mercury emissions, climatic variability, and land cover/land use patterns. The establishment of additional MDN sites in some under-represented regions of the state (see Figure 1) will help to better define spatial patterns across the state as well as quantify mercury deposition inputs to surface waters of the Commonwealth. The additional sites will also help to evaluate the impact of any mercury emissions reduction programs in Pennsylvania and neighboring states.

Figure 15. *Seasonal (quarterly) trends in at the Hills Creek State Park MDN site in Tioga County, Pennsylvania from 1997 through 2008. a) total mercury concentrations and precipitation and b) total mercury deposition and precipitation.*

a)



b)

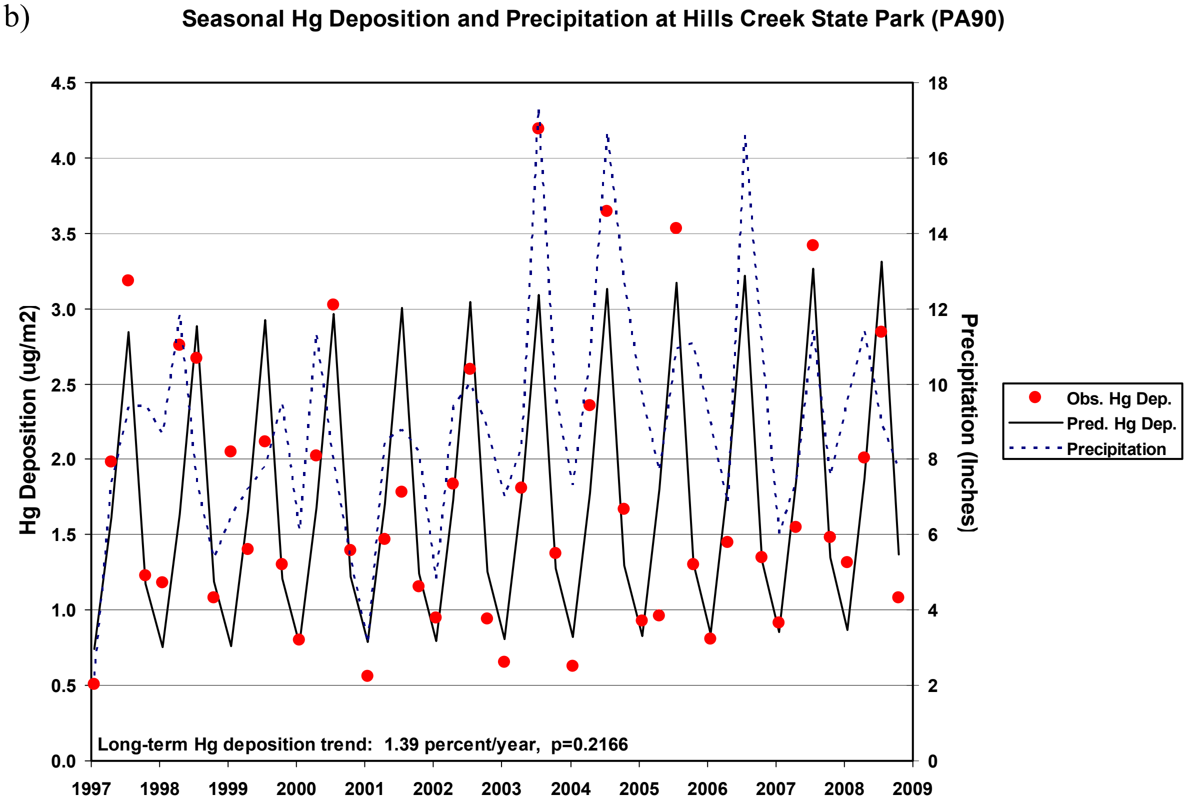
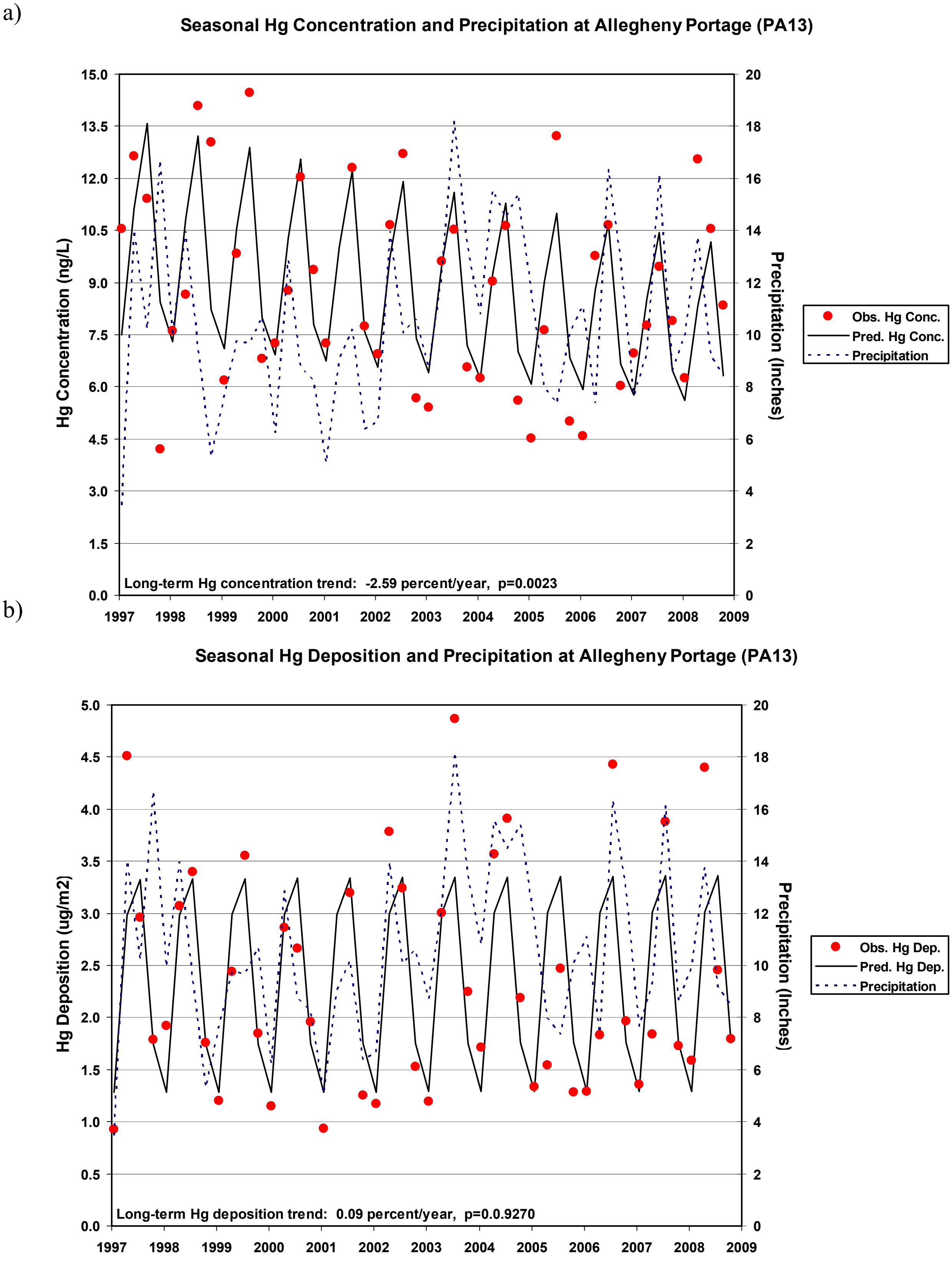


Figure 16. *Seasonal (quarterly) trends in at the Allegheny Portage MDN site in Cambria County, Pennsylvania from 1997 through 2008. a) total mercury concentrations and precipitation and b) total mercury deposition and precipitation.*


a)

Seasonal Hg Concentration and Precipitation at Allegheny Portage (PA13)

Long-term Hg concentration trend: -2.59 percent/year, p=0.0023

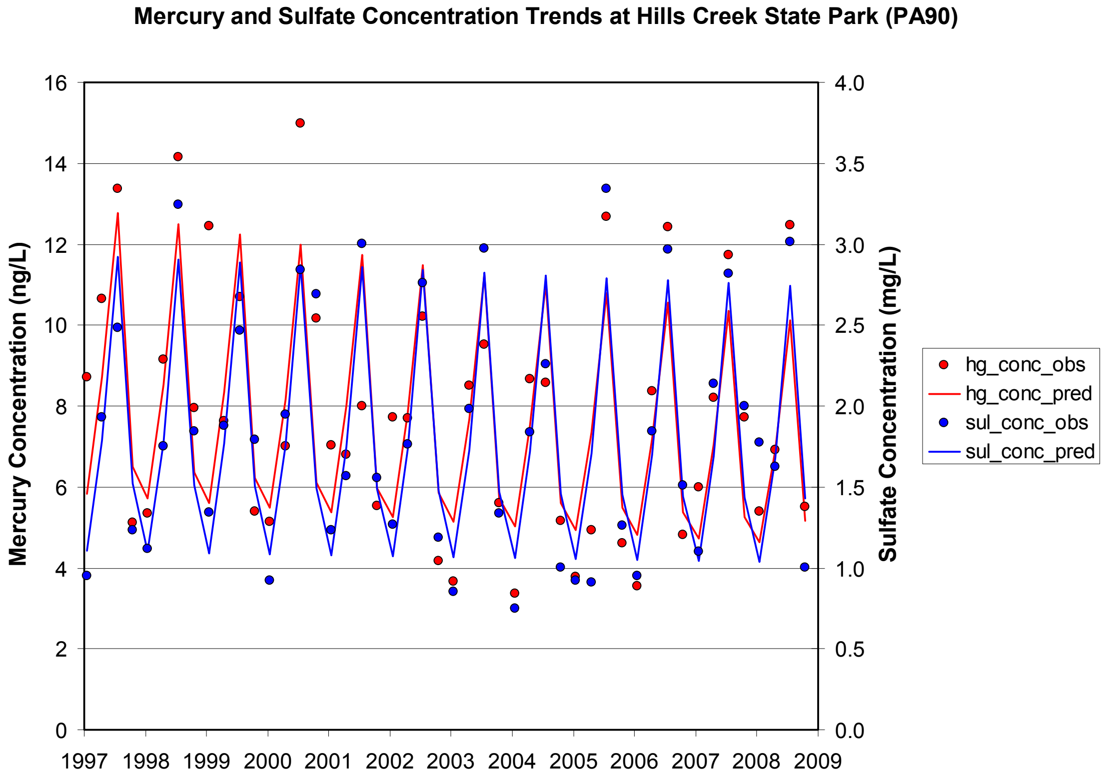
b)

Seasonal Hg Deposition and Precipitation at Allegheny Portage (PA13)

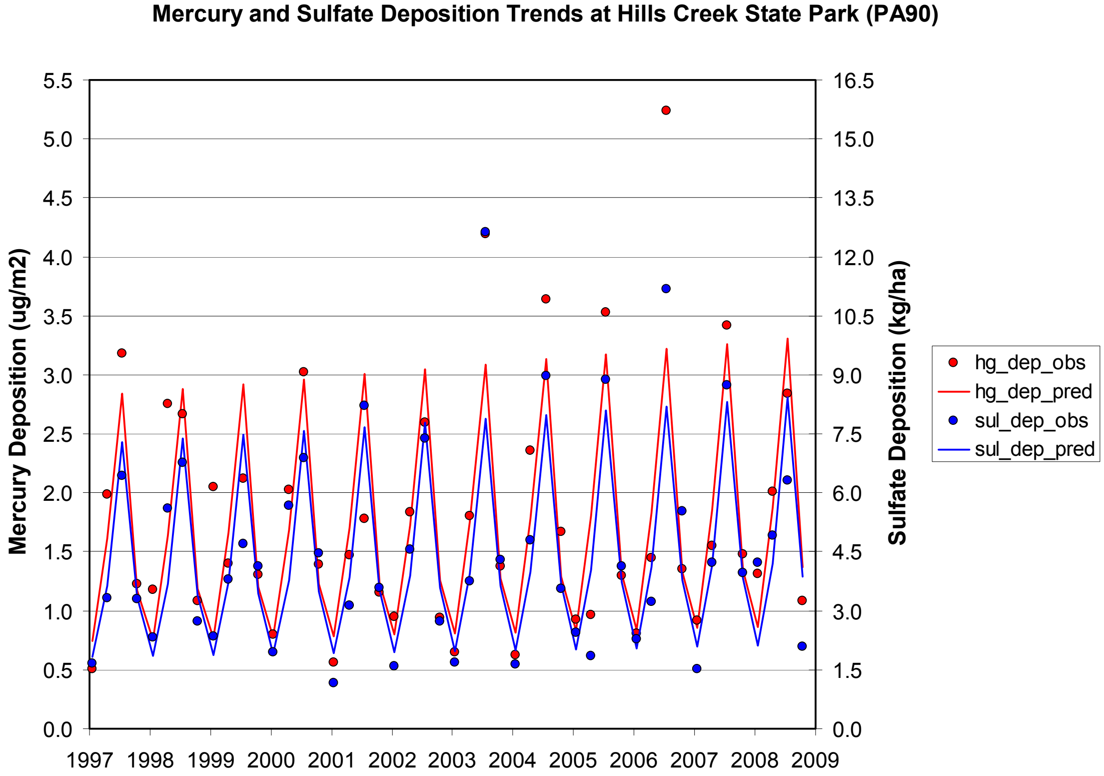
Long-term Hg deposition trend: 0.09 percent/year, p=0.9270

***Figure 17.** Seasonal (quarterly) trends in at the Hills Creek State Park MDN site in Tioga County, Pennsylvania from 1997 through 2008. a) mercury and sulfate concentrations and b) mercury and sulfate deposition.*

a)



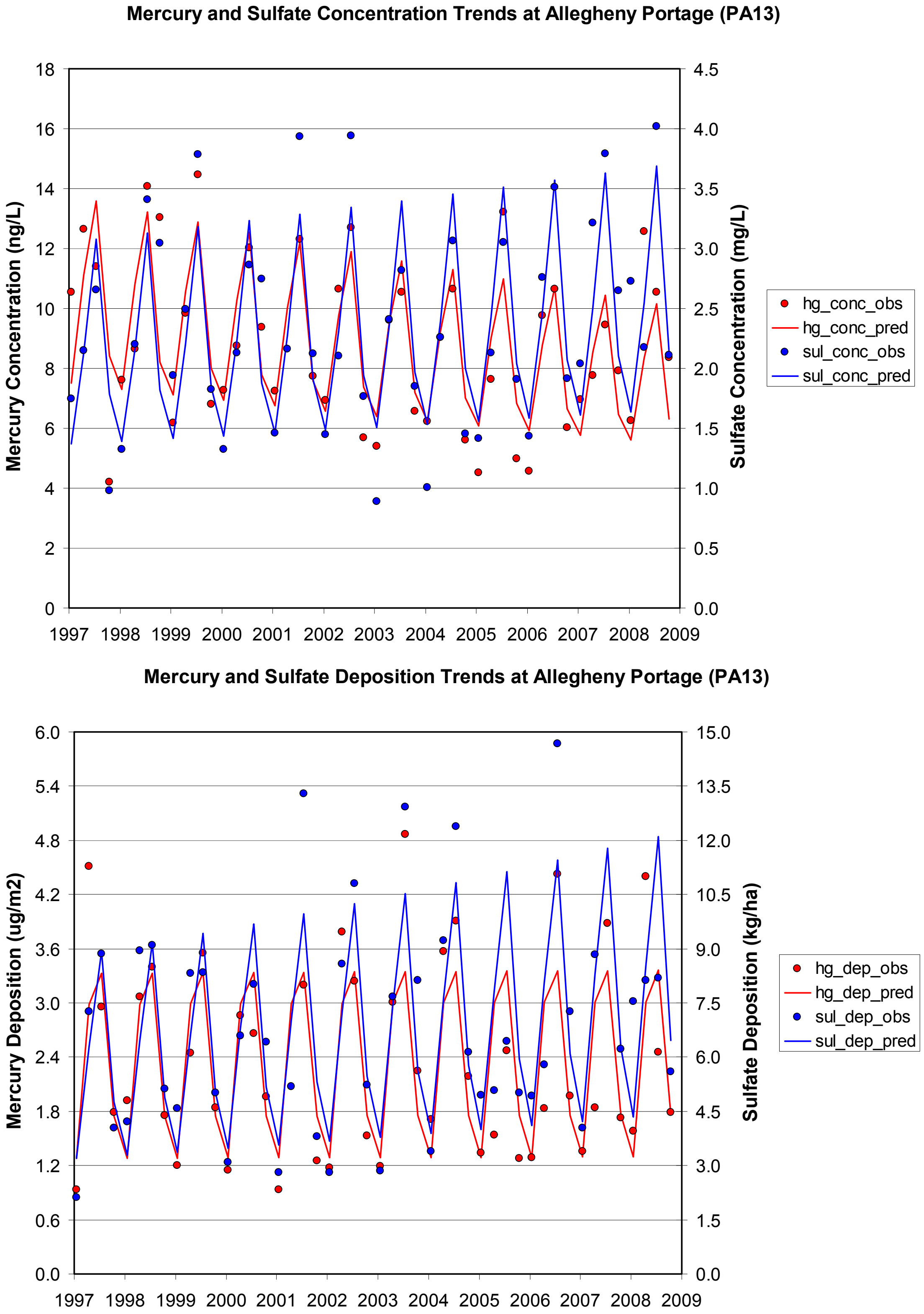
Mercury and Sulfate Concentration Trends at Hills Creek State Park (PA90)



Mercury and Sulfate Deposition Trends at Hills Creek State Park (PA90)

Figure 18. *Seasonal (quarterly) trends in at the Allegheny Portage MDN site in Cambria County, Pennsylvania from 1997 through 2008. a) mercury and sulfate concentrations and b) mercury and sulfate deposition.*

a)



ACKNOWLEDGEMENTS

We thank Donald Torsello, Nick Lazor, and Jeff Miller of the Pennsylvania Department of Environmental Protection for their continued interest in this work, and for financial support. We also express our appreciation to the many observers, partners, and cooperators who make our work at the monitoring sites possible.

LITERATURE CITED

Boyer, E.W., J.A. Lynch, J.W. Grimm, and K.S. Horner (2008-2010). Atmospheric Deposition in Pennsylvania: Spatial and Temporal Variations 2008. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, within Penn State Institutes of Energy and The Environment. 247pp.

Driscoll, C.T., D. Evers, K.F. Lambert, N. Kamman, T. Holsen, Y-J. Han, C. Chen, W. Goodale, T. Butler, T. Clair, and R. Munson (2007a). Mercury Matters: Linking Mercury Science with Public Policy in the Northeastern United States. Hubbard Brook Research Foundation. Science Links Publication. Vol. 1, no. 3.

Driscoll, C.T., Y. J.Han, C.Y. Chen, D.C. Evers, K.F. Lambert, T.M. Holsen, N.C. Kamman, and R.K. Munson (2007b). Mercury Contamination in Forest and Freshwater Ecosystems in the Northeastern United States. *BioScience,* 57(1):17-28.

EPRI (2006a). Frequently asked questions about mercury. Environment Mercury Fact Sheet, Document number 1014576, Electric Power Research Institute.

EPRI (2006b). Mercury in the environment: its sources and deposition. Environment Mercury Fact Sheet, Document number 1014425, Electric Power Research Institute.

Evers D.C., Y.J. Han, C.T. Driscoll, N.C. Kamman, M.W. Goodale, K.F. Lambert, T.M. Holsen, C.Y. Chen, T.A. Clair, and T. Butler. Biological mercury hotspots in the northeastern United States and Southeastern Canada. *BioScience*, 57(1):29-43.

M.J. Bradley & Associates (2010). Benchmarking air emissions of the 100 largest electric power producers in the United States. Report by Ceres and others, 74pp. Online URL:// http://www.ceres.org/Page.aspx?pid=1259.

NADP (2006). Quality Assurance Plan, Mercury Analytical Laboratory. National Atmospheric Deposition Program, 39pp. Online URL: http://nadp.sws.uiuc.edu/lib/qaplans/qapHAL2006.pdf.

NADP (2008). National Atmospheric Deposition Program. Monitoring mercury deposition: a key tool to understanding the link between emissions and effects. NADP Brochure 2005-01, revised 2008. Illinois State Water Survey, 4pp. Online URL: http://nadp.sws.uiuc.edu/lib/brochures/mdn.pdf.

NRC (2000). Toxicological effects of methylmercury. Committee on the Toxicological Effects of Methylmercury, Board on Environmental Studies and Toxicology, National Research Council. 344pp.

NRC (2009). Global sources of local pollution: An assessment of long-range transport of key air pollutants to and from the United States. Committee on the Significance of International Transport of Air Pollutants, Board on Atmospheric Sciences and Climate, National Research Council. 234pp.

Pacyna, E.G., J.M Pacyna, K. Sundseth, J. Munthe, K. Kindborn, S. Wilson, F. Steenhuisen, and P. Maxson (2010). Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmospheric Environment,* 44:2487-2499, doi:10.1016/j.atmosenv.2009.06.009.

Seigneur, C., K. Jayaraghavan, K. Lohman, P. Karamchandani, and C. Scott (2004). Global source attribution for mercury deposition in the United States. *Environmental Science & Technology,* 38:555-569.

USEPA (2009). Electronic Report on the Environment for 2008, mercury indicator. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-07/045F (NTIS PB2008-112484). Online URL: http://cfpub.epa.gov/eroe/index.cfm?fuseaction=detail.viewInd&lv=list.listByAlpha&r=188199&subtop=341.

USEPA (2010a). Inventories and Emissions Factors (web data clearinghouse). U.S. Environmental Protection Agency. Online URL: http://www.epa.gov/ttn/chief/.

USEPA (2010b). Mercury (web portal). U.S. Environmental Protection Agency. Online URL: http://www.epa.gov/mercury/.

USEPA (2010c). Toxics Release Inventory Program (web data clearinghouse), data for 2000-2010. U.S. Environmental Protection Agency. Online URL: http://www.epa.gov/tri/tridata/index.htm.

USGS (2000). Mercury in the Environment. U.S. Geological Survey, Fact Sheet 146-100. Online URL: http://www.usgs.gov/themes/factsheet/146-00/.

USGS (2010). Mercury (web portal). U.S. Geological Survey. Online URL: http://www.usgs.gov/mercury/.

USHHS (2010). Mercury (web portal). U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry. Online URL: http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=24.

APPENDIX: 2007 Monitoring Data for Pennsylvania: Weekly precipiation, mercury concentration, and deposition

Data Availability

All of the PA MDN monitoring data presented in this report are publicly available via the MDN web site (http://nadp.sws.uiuc.edu/mdn) and the PA DEP web site (http://www.dep.state.pa.us/dep/deputate/airwaste/aq/acidrain/acidrain.htm). They are also available upon request from the authors of this report.

Monitoring Data

Weekly precipitation, mercury concentration in precipitation, and atmospheric mercury deposition at Pennsylvania Sites of the National Atmospheric Deposition Program, Mercury Deposition Network, for 2008

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg Dep (ng/m2)	Sample Type	Quality Rating	Notes
PA00	20080108	0.02	--	--	W	C	v
PA00	20080115	0.77	29.84	583.61	W	B	z
PA00	20080122	0.35	3.03	26.94	W	A	
PA00	20080129	0.07	62.77	111.61	W	B	i
PA00	20080205	2.13	6.17	333.81	W	B	z
PA00	20080212	0.62	9.38	147.72	W	B	z
PA00	20080219	1.23	7.72	241.19	W	A	
PA00	20080226	0.79	--	--	W	C	zv
PA00	20080304	0.57	15.05	217.89	W	B	mz
PA00	20080311	3.23	8.08	662.90	W	A	
PA00	20080318	0.21	54.00	288.04	W	A	
PA00	20080325	0.79	12.78	256.44	W	B	h
PA00	20080401	0.30	11.09	84.51	W	B	dz
PA00	20080408	0.52	22.09	291.76	W	A	
PA00	20080415	0.65	10.19	168.24	W	B	h
PA00	20080422	2.05	9.06	471.75	W	A	
PA00	20080429	2.53	6.46	415.13	W	A	
PA00	20080506	0.02	52.86	26.85	W	B	i
PA00	20080513	3.08	8.20	641.50	W	A	
PA00	20080520	1.65	9.22	386.41	W	B	z
PA00	20080527	0.22	11.12	62.14	W	B	z
PA00	20080603	1.50	8.49	323.47	W	B	dz
PA00	20080610	1.15	4.44	129.69	W	A	
PA00	20080617	0.11	19.74	55.15	W	B	dmh
PA00	20080624	0.35	14.72	130.86	W	A	
PA00	20080701	0.58	9.05	133.32	W	B	dm
PA00	20080708	0.75	11.89	226.50	W	A	
PA00	20080715	0.88	13.98	312.48	W	A	
PA00	20080722	0.01	--	--	T	A	

PA00	20080729	1.63	12.84	531.60	W	A	
PA00	20080805	0.01	--	--	T	A	
PA00	20080812	1.16	21.13	622.57	W	B	m
PA00	20080819	0.10	28.23	71.70	W	A	
PA00	20080826	0.00	--	0.00	D	A	
PA00	20080902	1.15	4.07	118.88	W	B	d
PA00	20080909	2.61	3.47	230.04	W	A	
PA00	20080916	0.85	6.05	130.62	W	B	d
PA00	20080923	0.00	--	0.00	D	A	
PA00	20080930	3.81	4.06	392.90	W	A	
PA00	20081007	0.00	--	0.00	D	A	
PA00	20081013	0.00	--	0.00	D	A	
PA00	20081021	0.07	19.13	34.01	W	A	
PA00	20081028	1.79	3.28	149.13	W	A	
PA00	20081104	0.00	--	0.00	D	A	
PA00	20081111	0.12	12.24	37.31	W	A	
PA00	20081118	1.81	--	--	W	C	zvf
PA00	20081125	0.36	--	--	W	C	zvf
PA00	20081202	0.91	--	--	W	C	zvf
PA00	20081209	0.08	28.00	56.90	W	B	mzi
PA00	20081216	2.87	2.63	191.72	W	B	mz
PA00	20081223	1.84	6.30	294.44	W	B	mz
PA00	20081230	1.04	--	--	W	B	mz
PA13	20080101	0.33	4.57	38.54	W	B	dm
PA13	20080108	0.21	12.08	64.43	W	A	
PA13	20080114	0.90	7.02	160.48	W	A	
PA13	20080122	0.32	2.99	24.30	W	A	
PA13	20080129	0.35	18.86	167.67	W	B	m
PA13	20080205	1.64	3.30	137.46	W	B	z
PA13	20080212	1.34	11.08	377.12	W	B	zh
PA13	20080219	0.42	15.01	160.13	W	A	
PA13	20080226	0.45	10.56	120.70	W	A	
PA13	20080304	1.10	14.20	396.75	W	C	ziv
PA13	20080311	1.71	11.48	498.62	W	A	
PA13	20080318	0.58	3.83	56.42	W	A	
PA13	20080325	1.16	19.63	578.38	W	B	m
PA13	20080401	0.35	16.73	148.73	W	B	d
PA13	20080408	0.42	9.39	100.17	W	B	m
PA13	20080414	0.66	10.58	177.36	W	A	
PA13	20080422	0.80	13.45	273.30	W	A	
PA13	20080429	1.14	11.84	342.84	W	B	d
PA13	20080506	0.62	4.33	68.19	W	C	zu
PA13	20080513	2.95	5.00	374.65	W	C	dzu
PA13	20080520	1.79	8.55	388.73	W	C	dzu
PA13	20080527	0.20	13.27	67.41	W	C	zu
PA13	20080603	0.30	11.23	85.57	W	C	zu

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg Dep (ng/m2)	Sample Type	Quality Rating	Notes
PA13	20080610	0.51	7.83	101.43	W	A	
PA13	20080617	1.43	11.44	415.52	W	B	d
PA13	20080624	0.52	19.11	252.40	W	A	
PA13	20080701	1.19	13.70	414.10	W	A	
PA13	20080708	0.35	8.35	74.23	W	A	
PA13	20080715	0.43	11.16	121.89	W	A	
PA13	20080722	0.66	12.25	205.36	W	A	
PA13	20080729	0.84	11.95	254.97	W	A	
PA13	20080805	0.15	17.79	67.78	W	A	
PA13	20080812	1.18	11.35	340.18	W	A	
PA13	20080819	0.05	48.47	61.56	W	B	i
PA13	20080826	0.00	--	0.00	D	B	h
PA13	20080902	1.86	3.10	146.46	W	B	h
PA13	20080909	1.76	17.23	770.25	W	A	
PA13	20080915	1.57	6.82	271.97	W	B	h
PA13	20080923	0.02	--	--	W	C	v
PA13	20080930	0.54	7.22	99.03	W	A	
PA13	20081007	0.33	5.01	41.99	W	A	
PA13	20081014	0.13	8.38	27.67	W	A	
PA13	20081021	0.18	6.58	30.08	W	A	
PA13	20081028	1.13	5.97	171.35	W	A	
PA13	20081104	0.30	7.15	54.48	W	A	
PA13	20081112	0.10	14.19	36.04	W	A	
PA13	20081118	0.91	7.18	165.96	W	A	
PA13	20081125	0.59	2.68	40.16	W	A	
PA13	20081202	0.89	3.54	80.03	W	A	
PA13	20081209	0.17	7.06	30.49	W	A	
PA13	20081216	1.90	4.19	202.21	W	B	h
PA13	20081223	2.14	5.77	313.63	W	A	
PA13	20081230	2.35	4.53	270.40	W	B	d
PA30	20080108	0.46	6.77	79.10	W	B	mh
PA30	20080115	1.14	14.26	412.91	W	C	dhf
PA30	20080122	0.30	6.99	53.26	W	A	
PA30	20080129	0.44	15.58	174.12	W	A	
PA30	20080205	0.90	6.48	148.13	W	B	d
PA30	20080212	1.14	3.50	101.35	W	B	h
PA30	20080219	1.10	6.26	174.90	W	A	
PA30	20080226	0.30	4.16	31.70	W	A	
PA30	20080304	0.99	6.49	163.20	W	A	
PA30	20080311	1.89	4.71	226.11	W	A	
PA30	20080318	0.15	15.63	59.55	W	A	
PA30	20080325	0.80	4.89	99.36	W	A	
PA30	20080401	0.87	7.51	165.96	W	A	
PA30	20080408	0.70	9.06	161.09	W	A	
PA30	20080414	0.60	20.39	310.74	W	A	

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg Dep (ng/m2)	Sample Type	Quality Rating	Notes
PA30	20080422	0.00	--	0.00	D	A	
PA30	20080429	0.78	12.35	244.68	W	B	m
PA30	20080505	0.89	7.40	167.28	W	B	dm
PA30	20080513	0.76	6.00	115.82	W	B	m
PA30	20080520	0.94	8.00	191.01	W	B	m
PA30	20080527	0.08	14.86	30.20	W	B	m
PA30	20080603	0.22	16.87	94.27	W	B	m
PA30	20080610	1.05	18.63	496.86	W	A	
PA30	20080618	2.67	13.28	900.62	W	B	dm
PA30	20080625	0.20	10.43	52.98	W	A	
PA30	20080701	1.29	13.53	443.32	W	B	d
PA30	20080708	0.61	10.79	167.18	W	C	mu
PA30	20080715	2.72	9.86	681.21	W	B	d
PA30	20080721	0.40	15.48	157.28	W	A	
PA30	20080730	1.07	10.75	292.16	W	B	e
PA30	20080805	0.97	14.43	355.53	W	B	h
PA30	20080812	2.10	6.47	345.11	W	B	dh
PA30	20080819	0.15	15.79	60.16	W	A	
PA30	20080827	0.00	--	0.00	D	C	f
PA30	20080902	0.15	10.06	38.33	W	B	d
PA30	20080909	1.09	8.24	228.13	W	B	dh
PA30	20080917	1.10	6.87	191.95	W	B	dh
PA30	20080923	0.00	--	0.00	D	A	
PA30	20080930	0.05	37.46	47.57	W	B	di
PA30	20081007	3.20	3.70	300.74	W	B	dmh
PA30	20081014	0.10	20.17	51.23	W	A	
PA30	20081022	0.99	9.79	246.18	W	A	
PA30	20081028	0.45	2.27	25.95	W	B	d
PA30	20081104	0.63	3.50	56.01	W	B	d
PA30	20081112	1.00	8.44	214.38	W	C	hf
PA30	20081118	1.89	4.60	220.83	W	B	em
PA30	20081125	0.66	4.60	77.11	W	B	em
PA30	20081202	1.19	3.81	115.16	W	A	
PA30	20081209	0.50	10.57	134.24	W	A	
PA30	20081216	2.10	7.01	373.91	W	A	
PA30	20081223	1.20	2.68	81.69	W	B	zh
PA30	20081230	1.65	7.11	297.98	W	B	d
PA47	20080102	1.15	5.30	154.81	W	A	
PA47	20080108	0.06	2.86	4.36	W	A	
PA47	20080115	0.31	11.01	86.69	W	A	
PA47	20080122	0.50	2.32	29.46	W	A	
PA47	20080129	0.05	97.57	123.91	W	B	mi
PA47	20080205	2.20	6.01	335.84	W	A	
PA47	20080212	0.16	11.08	45.59	W	B	dm
PA47	20080219	2.18	5.62	311.19	W	A	

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg Dep (ng/m2)	Sample Type	Quality Rating	Notes
PA47	20080226	0.26	7.59	50.12	W	B	m
PA47	20080304	0.33	9.93	83.49	W	B	m
PA47	20080311	1.70	8.86	382.57	W	B	mh
PA47	20080318	0.23	10.24	59.82	W	B	m
PA47	20080325	1.30	6.06	200.10	W	B	m
PA47	20080401	0.15	17.17	65.42	W	B	m
PA47	20080408	0.42	4.79	51.10	W	B	dm
PA47	20080415	0.60	9.38	142.95	W	B	m
PA47	20080422	0.06	24.38	37.16	W	A	
PA47	20080429	2.05	10.62	552.98	W	B	mh
PA47	20080506	0.06	21.67	33.03	W	B	dm
PA47	20080513	1.78	12.51	565.60	W	B	dmh
PA47	20080520	1.70	10.90	470.66	W	B	mh
PA47	20080527	0.70	5.64	100.28	W	B	m
PA47	20080603	1.15	6.65	194.25	W	B	dm
PA47	20080610	0.61	5.93	91.88	W	B	mz
PA47	20080617	1.00	26.12	663.45	W	B	m
PA47	20080624	0.29	18.01	132.66	W	B	m
PA47	20080701	1.00	10.19	258.83	W	B	z
PA47	20080708	0.55	4.93	68.87	W	B	m
PA47	20080715	1.51	9.87	378.55	W	B	m
PA47	20080722	0.08	39.22	79.70	W	B	mz
PA47	20080729	1.15	11.55	337.38	W	B	dm
PA47	20080805	0.05	16.95	21.53	W	B	m
PA47	20080812	0.34	12.50	107.95	W	B	m
PA47	20080819	0.34	17.48	150.96	W	B	h
PA47	20080826	0.01	--	--	W	C	v
PA47	20080902	0.95	4.47	107.86	W	A	
PA47	20080909	4.35	5.52	609.90	W	B	h
PA47	20080916	0.78	7.65	151.56	W	A	
PA47	20080923	0.00	--	0.00	D	A	
PA47	20080930	1.67	4.52	191.73	W	B	d
PA47	20081007	0.14	10.28	36.56	W	B	h
PA47	20081014	0.00	--	0.00	D	B	z
PA47	20081021	0.00	--	0.00	D	B	z
PA47	20081028	2.05	4.02	209.32	W	B	dh
PA47	20081104	0.08	5.55	11.28	W	A	
PA47	20081111	0.05	10.89	13.83	W	A	
PA47	20081118	1.10	8.21	229.39	W	A	
PA47	20081125	0.35	7.35	65.34	W	A	
PA47	20081202	0.90	4.80	109.73	W	A	
PA47	20081209	0.04	7.88	8.01	W	B	i
PA47	20081216	2.60	4.04	266.80	W	B	dm
PA47	20081223	1.76	6.41	286.55	W	C	f
PA47	20081230	0.57	16.42	237.73	W	A	

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg dep (ng/m2)	Sample Type	Quality Rating	Notes
PA52	20080108	0.15	13.63	51.93	W	A	
PA52	20080115	0.76	8.65	166.98	W	A	
PA52	20080122	0.14	--	--	W	C	v
PA52	20080129	0.09	20.19	46.15	W	A	
PA52	20080205	2.20	5.53	309.02	W	A	
PA52	20080211	1.10	9.01	251.74	W	B	h
PA52	20080219	0.91	10.24	236.69	W	A	
PA52	20080225	0.34	3.88	33.51	W	A	
PA52	20080304	0.57	4.32	62.54	W	A	
PA52	20080311	3.69	6.29	589.54	W	A	
PA52	20080318	0.25	6.75	42.86	W	A	
PA52	20080325	1.09	6.09	168.61	W	A	
PA52	20080401	1.56	11.27	446.56	W	A	
PA52	20080408	0.34	8.46	73.06	W	A	
PA52	20080415	0.43	16.86	184.14	W	A	
PA52	20080422	0.77	6.87	134.36	W	A	
PA52	20080429	1.38	8.37	293.39	W	B	h
PA52	20080506	0.79	3.01	60.40	W	A	
PA52	20080513	1.43	7.48	271.69	W	A	
PA52	20080520	1.59	8.84	357.01	W	A	
PA52	20080527	0.12	29.43	89.70	W	B	i
PA52	20080603	0.01	--	--	W	C	v
PA52	20080610	0.47	20.42	243.77	W	B	h
PA52	20080617	0.70	20.48	364.13	W	A	
PA52	20080624	1.66	12.93	545.18	W	A	
PA52	20080701	0.47	14.88	177.64	W	A	
PA52	20080708	0.40	8.85	89.92	W	A	
PA52	20080715	2.04	6.76	350.28	W	A	
PA52	20080722	0.69	15.29	267.97	W	B	h
PA52	20080729	0.85	9.47	204.46	W	A	
PA52	20080805	0.64	--	--	W	C	zv
PA52	20080812	0.87	8.23	181.87	W	B	h
PA52	20080819	0.00	--	0.00	D	A	
PA52	20080826	0.02	--	--	W	C	v
PA52	20080902	0.54	9.44	129.48	W	C	f
PA52	20080909	0.48	10.76	131.19	W	A	
PA52	20080916	0.79	8.50	170.56	W	B	d
PA52	20080923	0.00	--	0.00	D	A	
PA52	20080930	1.50	5.89	224.41	W	B	d
PA52	20081007	0.13	5.42	17.90	W	A	
PA52	20081014	0.03	17.65	13.45	W	B	i
PA52	20081021	0.03	31.31	23.86	W	B	i
PA52	20081028	1.85	3.01	141.44	W	A	
PA52	20081104	0.15	4.16	15.85	W	B	h
PA52	20081111	0.23	26.13	152.65	W	A	

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg Dep (ng/m2)	Sample Type	Quality Rating	Notes
PA52	20081118	0.85	8.86	191.29	W	A	
PA52	20081125	0.48	5.50	67.06	W	A	
PA52	20081202	0.69	3.20	56.08	W	B	z
PA52	20081209	0.06	4.74	7.22	W	A	
PA52	20081216	2.16	3.53	193.67	W	A	
PA52	20081222	1.07	2.29	62.24	W	A	
PA52	20081230	1.09	4.81	133.17	W	A	
PA60	20080102	1.41	8.95	320.54	W	C	u
PA60	20080108	0.00	--	0.00	D	A	
PA60	20080115	0.64	10.73	174.43	W	A	
PA60	20080122	0.62	5.03	79.21	W	A	
PA60	20080129	0.00	--	0.00	D	B	h
PA60	20080205	1.48	10.92	410.50	W	A	
PA60	20080212	0.05	--	--	W	C	v
PA60	20080219	3.03	13.79	1061.31	W	B	m
PA60	20080226	0.49	12.99	161.67	W	A	
PA60	20080304	0.23	12.16	71.04	W	A	
PA60	20080311	2.83	11.63	835.99	W	B	d
PA60	20080318	0.15	--	--	W	C	v
PA60	20080325	1.03	11.77	307.93	W	B	h
PA60	20080401	0.21	25.56	136.34	W	A	
PA60	20080408	0.54	15.65	214.66	W	B	h
PA60	20080415	0.90	11.39	260.38	W	A	
PA60	20080422	0.00	--	0.00	D	C	hf
PA60	20080429	1.68	13.45	573.94	W	B	dh
PA60	20080506	0.00	--	0.00	D	B	i
PA60	20080513	2.01	8.81	449.79	W	B	dmz
PA60	20080520	1.64	11.97	498.62	W	B	d
PA60	20080527	0.52	5.82	76.87	W	A	
PA60	20080603	0.58	16.19	238.51	W	B	h
PA60	20080610	0.59	11.08	166.04	W	B	zh
PA60	20080617	0.41	37.95	395.21	W	A	
PA60	20080624	0.07	--	--	W	C	zhv
PA60	20080701	0.87	12.25	270.70	W	A	
PA60	20080708	0.82	7.11	148.09	W	A	
PA60	20080715	1.31	5.86	194.99	W	B	h
PA60	20080722	0.47	15.86	189.34	W	A	
PA60	20080729	3.34	11.33	961.19	W	A	
PA60	20080805	0.00	--	0.00	D	C	zf
PA60	20080812	1.69	14.02	601.82	W	B	h
PA60	20080819	0.00	--	0.00	D	C	f
PA60	20080826	0.00	--	0.00	D	A	
PA60	20080902	0.32	10.96	89.08	W	A	
PA60	20080909	3.39	4.89	421.06	W	B	m
PA60	20080916	1.31	7.06	234.91	W	A	

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg Dep (ng/m2)	Sample Type	Quality Rating	Notes
PA60	20080923	0.00	--	0.00	D	A	
PA60	20080930	2.34	6.25	371.48	W	B	m
PA60	20081007	0.18	13.62	62.27	W	A	
PA60	20081014	0.00	--	0.00	D	A	
PA60	20081021	0.00	--	0.00	D	A	
PA60	20081028	2.49	3.93	248.56	W	B	m
PA60	20081104	0.30	3.22	24.54	W	A	
PA60	20081111	0.41	9.69	100.91	W	A	
PA60	20081118	1.73	7.12	312.87	W	A	
PA60	20081125	0.51	8.61	111.53	W	B	m
PA60	20081202	1.03	6.30	164.82	W	B	m
PA60	20081209	0.02	6.47	3.29	W	B	i
PA60	20081216	3.08	3.86	301.98	W	B	m
PA60	20081223	2.08	5.00	264.16	W	B	m
PA60	20081230	0.34	16.32	140.94	W	B	m
PA72	20080102	1.58	5.88	235.98	W	A	
PA72	20080108	0.05	21.22	26.95	W	B	dmi
PA72	20080115	0.67	8.07	137.34	W	B	dm
PA72	20080122	0.39	2.45	24.27	W	A	
PA72	20080130	0.24	22.24	135.58	W	B	m
PA72	20080206	1.85	8.10	380.62	W	A	
PA72	20080212	0.55	11.75	164.15	W	B	h
PA72	20080219	4.35	3.67	405.50	W	A	
PA72	20080226	0.80	2.12	43.08	W	A	
PA72	20080305	3.75	5.84	556.26	W	A	
PA72	20080311	1.58	6.63	266.08	W	B	edm
PA72	20080318	1.58	6.63	266.08	W	B	edm
PA72	20080325	1.35	7.69	263.69	W	B	m
PA72	20080402	1.00	39.07	992.38	W	B	m
PA72	20080408	0.65	12.50	206.38	W	B	m
PA72	20080415	0.70	8.34	148.29	W	B	m
PA72	20080422	0.00	--	0.00	D	B	m
PA72	20080430	1.80	6.30	288.04	W	B	dm
PA72	20080506	0.45	9.80	112.01	W	A	
PA72	20080513	0.75	7.50	142.88	W	B	dm
PA72	20080521	1.45	7.83	288.38	W	B	dh
PA72	20080527	0.00	--	0.00	D	B	hi
PA72	20080604	1.22	10.46	324.13	W	B	dm
PA72	20080610	0.78	22.36	443.00	W	B	dm
PA72	20080617	0.55	23.66	330.53	W	B	dm
PA72	20080625	0.20	12.14	61.67	W	B	h
PA72	20080702	0.31	19.32	150.65	W	B	mh
PA72	20080710	0.64	10.74	174.59	W	B	m
PA72	20080715	0.65	9.16	151.23	W	B	mh
PA72	20080722	1.60	25.56	1038.76	W	B	h

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg Dep (ng/m2)	Sample Type	Quality Rating	Notes
PA72	20080730	2.40	7.57	461.47	W	B	h
PA72	20080805	0.31	19.21	151.26	W	B	m
PA72	20080812	2.10	8.77	467.79	W	B	h
PA72	20080820	0.16	21.07	85.63	W	A	
PA72	20080826	0.00	--	0.00	D	A	
PA72	20080903	0.10	5.79	14.71	W	A	
PA72	20080910	3.95	8.12	814.68	W	B	h
PA72	20080917	0.57	9.18	132.91	W	A	
PA72	20080923	0.00	--	0.00	D	B	h
PA72	20081002	2.35	2.33	139.08	W	B	emh
PA72	20081007	0.00	--	0.00	D	B	h
PA72	20081016	0.02	61.98	31.49	W	B	emhi
PA72	20081022	0.07	5.74	10.21	W	B	mh
PA72	20081028	3.50	2.41	214.25	W	B	m
PA72	20081106	0.14	--	--	W	C	hv
PA72	20081112	0.10	8.70	22.10	W	B	m
PA72	20081118	1.60	6.78	275.54	W	B	mh
PA72	20081125	0.75	3.66	69.72	W	B	m
PA72	20081203	0.82	4.58	95.39	W	B	m
PA72	20081210	1.00	5.39	136.91	W	A	
PA72	20081216	3.01	1.86	142.25	W	B	mz
PA72	20081223	1.49	1.96	74.18	W	B	mz
PA72	20081230	0.65	20.56	339.45	W	C	dziv
PA90	20080108	0.10	9.75	24.77	W	B	z
PA90	20080115	0.42	10.78	115.00	W	A	
PA90	20080122	0.15	5.95	22.67	W	A	
PA90	20080129	0.12	22.34	68.09	W	A	
PA90	20080205	1.70	4.66	201.22	W	A	
PA90	20080212	1.73	7.30	320.78	W	B	h
PA90	20080219	0.73	4.88	90.48	W	B	m
PA90	20080226	0.29	4.10	30.20	W	A	
PA90	20080304	0.64	9.19	149.39	W	A	
PA90	20080311	3.43	4.87	424.28	W	A	
PA90	20080318	0.43	8.67	94.69	W	B	h
PA90	20080325	0.95	4.05	97.73	W	B	h
PA90	20080401	1.98	4.17	209.72	W	A	
PA90	20080408	0.26	12.04	79.51	W	B	m
PA90	20080415	0.54	11.94	163.77	W	A	
PA90	20080422	0.06	12.99	19.80	W	A	
PA90	20080429	1.00	10.04	255.02	W	A	
PA90	20080506	0.41	6.43	66.96	W	B	z
PA90	20080513	0.45	12.40	141.73	W	B	z
PA90	20080520	1.13	8.75	251.14	W	B	z
PA90	20080527	0.06	8.56	13.05	W	A	
PA90	20080603	0.08	20.69	42.04	W	A	

Site	Date Off	Precip (inches)	Hg Conc (ng/L)	Hg Dep (ng/m2)	Sample Type	Quality Rating	Notes
PA90	20080610	0.22	11.25	62.87	W	A	
PA90	20080617	0.38	23.99	231.55	W	A	
PA90	20080624	1.91	10.94	530.74	W	A	
PA90	20080701	0.31	11.23	88.43	W	A	
PA90	20080708	0.28	9.90	70.41	W	B	h
PA90	20080715	2.40	11.14	679.09	W	A	
PA90	20080722	0.47	23.55	281.14	W	B	dh
PA90	20080729	0.35	9.85	87.57	W	A	
PA90	20080805	0.59	17.55	263.00	W	A	
PA90	20080812	0.57	16.37	237.00	W	A	
PA90	20080819	0.15	16.67	63.51	W	A	
PA90	20080826	0.44	7.52	84.04	W	A	
PA90	20080902	0.91	7.11	164.34	W	A	
PA90	20080909	0.38	6.80	65.63	W	B	h
PA90	20080916	0.58	7.81	115.06	W	A	
PA90	20080923	0.00	--	0.00	D	A	
PA90	20080930	1.55	5.34	210.24	W	B	h
PA90	20081007	0.52	5.39	71.19	W	A	
PA90	20081014	0.01	--	--	W	C	vf
PA90	20081021	0.11	6.13	17.13	W	A	
PA90	20081028	1.90	3.65	176.15	W	A	
PA90	20081104	0.22	3.89	21.74	W	B	h
PA90	20081110	0.24	14.64	89.25	W	A	
PA90	20081118	1.24	7.14	224.88	W	A	
PA90	20081125	0.39	4.07	40.32	W	C	zu
PA90	20081202	0.60	2.37	36.12	W	A	
PA90	20081209	0.05	--	--	W	C	v
PA90	20081216	1.65	3.21	134.53	W	A	
PA90	20081223	1.03	2.88	75.35	W	B	m
PA90	20081230	0.27	3.90	26.75	W	A	

Data Key

Site: Refers to MDN sites included in Table 1,

- Date Off: Samples are typically collected at weekly intervals. This is the end date of the sample, after exposure to precipitation for approximately 1 week.
- Precip: Total precipitation during the sampling period (as determined by the off dates; typically 1 week), in inches per sampling period.
- Hg Conc: Total mercury concentration reported by the lab in ng/L.
- Hg Dep: Total mercury wet deposition in ng/m^2.
- Sample Type, Quality Rating and Notes: see codes below.

Sample Type Code:

W	wet sample, measurable precipitation (≥ 0.01 in.) on the rain gauge (RG) or net bottle catch (BC) ≥ 1.5 mL if RG data are missing. Concentration and deposition data are reported unless the QR Code is C.
D	dry sample The RG measured a 0 precipitation amount net, or if the RG is missing, the BC < 1.5 mL . No concentration data are reported and are indicated by a -9.00. RGPPT, SUBPPT, and HGDEP are set to zero.
T	trace sample, used when the rain gage detects that an unmeasurable amount of precipitation occurred. No Hg concentration or depositions are shown. SUBPPT is set to 0.127 mm
--	unknown sample type. Precipitation amount is unknown.

Quality Rating Code:

A	fully qualified with no problems
B	valid data with minor problems, used for summary statistics
C	invalid data, not used for summary statistics
-	no sample submitted for this time period

Note Code:

Code	Description	Quality Rating (QR) code	Valid for Summary Statistics (Y/N)
e	Extended sample time (> 8days)	B	Y
d	debris present	B	Y
m	missing information	B	Y
z	site operations problems	B	Y
h	sample handling problems	B	Y
i	low volume sample (1.5 mL $\leq$ sample volume < 10 mL) (Hg conc. data are reported but they are less certain than samples with a sample volume of at least 10 mL	B	Y
b	bulk sample (sample exposed the whole time)	C	N
v	Rain gage indicates precipitation occurred but the sample volume was less than 1.5 mL, or the sample volume was less than 10% of indicated rain gage precipitation amount.	C	N
u	undefined sample (sample exposed for at least 6 hours without precipitation)	C	N
f	serious problems in field operations that compromise sample integrity	C	N
l	laboratory error	C	N
c	contamination of sample	C	N
p	no precipitation data from either the rain gage or the sample volume	C	N
n	no sample submitted	C	N