# Temporal and regional variation in the wet deposition of mercury in the New York State area

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## Abstract

Mercury advisories have been issued by the EPA for sportfish found in all major fishing waters around the New York metropolitan area. Wet deposition of mercury has been linked to rising methyl mercury levels in affected ecosystems. Regulations on mercury emissions in the region have made monitoring mercury a priority. The Mercury Deposition Network maintains sites around the United States to monitor wet deposition of mercury. This study focuses on MDN sites in and around New York State, including Hills Creek State Park (PA90), Erie County (PA30), Milford (PA72), Chittinden County (VT99), West Point (NY99), Biscuit Brook (NY68), Essex County (NY20), and New Brunswick (NJ30). Quarterly averages at each site were investigated for temporal and spatial trends. All sites were found to display peak deposition in quarters corresponding to warmer months and lowest deposition levels in traditionally colder months. Mercury deposition patterns at VT99 significantly deviated from other sites in 2007. In 2008, both PA72 and NJ30 deviated significantly. Poor correlation was found for year to year data at each site, with NJ30 (r = 0.402512) and VT99 (r = 0.370893) having the highest correlation coefficients. Poor correlation was also found between daily maximum and minimum temperatures and mercury in precipitation at NY99.

Increased deposition of mercury in warmer months may reveal an important trend in seasonal wet deposition, but poor correlation between temperatures and concentration in precipitation suggests temperature is far from the only contributor. While the factors affecting mercury deposition are complex, investigating patterns and trends can aid in the awareness and control of mercury exposure.

## Introduction

Currently, the U.S. EPA has mercury advisories on sportfish found in each of the 27 waterway regions throughout New York City, Rockland County, Westchester County, and Long Island (EPA 2009). Because stricter policies have been put in place to reduce and ultimately eliminate emissions in the northeastern United States, monitoring mercury levels has become imperative.

The toxicity of mercury arises from the methylated form, commonly known as methyl mercury (MHg), which is a neurotoxin (Mergler et. al, 2007). Mercury is initially emitted into the atmosphere in three main forms: elemental mercury ($Hg^0$), gaseous oxidized mercury (GOM), and particulate bound mercury (Hgp). The elemental form is emitted from both natural and anthropogenic sources and travels long distances in the atmosphere due to its volatility. GOM and Hgp, being less volatile and water soluble or easily suspended in water, are the species primarily found in wet and dry deposition (Schroeder and Munthe, 1998).

Deposition of GOM and Hgp to aquatic environments has been linked to a rise in levels of MHg in organisms within the affected areas (Orihel, 2006; Harris et al., 2007; Munthe et. al., 2007). Bioaccumulation of MHg in the food chain results in levels that are toxic to both humans and larger wildlife (Driscoll, 2007).

Wet deposition has been shown to be a large contributing factor to the deposition of mercury to terrestrial surfaces (Sorensen, 1990; Lamborg, 2005; Landis and Keeler, 2002; Lai, 2007). Monitoring concentrations in precipitation has proven to be an effective method of gauging the amount of mercury entering terrestrial ecosystems. The Mercury Deposition Network (MDN), an outgrowth of the National Atmospheric Deposition Program, monitors concentrations in precipitation at several sites throughout the United States and Canada.

Most studies point to a general decline of mercury in precipitation throughout the northeastern region of the United States. During a ten-year period from 1996 to 2005, the northeast exhibited a lower mercury concentration than regions investigated in the south as well as the western U.S. (Prestbo and Gay, 2009). Between the years of 1998 and 2005, trends in the northeast region of North America exhibited a similar decline (Butler et. al, 2005). During a study between the years of 1996 and 2002, higher deposition rates were linked with coastal sites and summer months. The northeastern region of the United States was also found to have higher deposition rates than those of southeastern Canada (Van Arsdale et. al, 2005).

This study focuses on MDN sites in and around New York State, including Hills Creek State Park (PA90), Erie County (PA30), Milford (PA72), Chittinden County (VT99), West Point (NY99), Biscuit Brook (NY68), Essex County (NY20), and New Brunswick (NJ30). Data from each of these sites was studied for temporal and spatial trends throughout the years of 2007 and 2008. At NY99, the relationship between average monthly deposition and temperature, as well as time of year, was explored.

## Methods and Materials

Data from sites in Chittinden County Vermont (VT99), Hills Creek State Park Pennsylvania (PA90), Pike County Pennslyvania (PA72), Erie County Pennsylvania (PA30), Orange County New York (NY99), Ulster County New York (NY68), Essex County New York (NY20), and Middlesex County New Jersey (NJ30) (Figure 1) were gathered from the MDN online database for the years 2006, 2007 and 2008. Precipitation at each site is collected in an MDN model raincatcher, consisting of a borosilicate funnel for collection of precipitation, a capillary tube with an inner diameter of 3 mm leading to a 1 L borosilicate bottle, and a heater to melt frozen precipitation. Samples were treated to reduce all mercury present to the divalent form, these were then purged onto gold traps with $N_2$ gas for 20 minutes at 400 mL/min and analyzed by cold vapor atomic fluorescence spectroscopy (Vermette et. al 1995).

Yearly data was divided into quarters, with the first quarter defined as December through February, the second quarter as March through May, and so on. Weeks with missing information were removed. Total nanograms of mercury deposited each week was calculated from measured concentration and precipitation volumes. Quarterly averages of total nanograms deposited ($Q_{avg}$) at each site were calculated and graphed by year. $Q_{avg}$ were also used in a stepwise ANOVA test to determine a central tendency for the years 2007 and 2008. Central tendency elements were discovered by removing sites after successive ANOVA tests until results showed no significant deviation by any site included in the sample. These central tendency elements were then compared

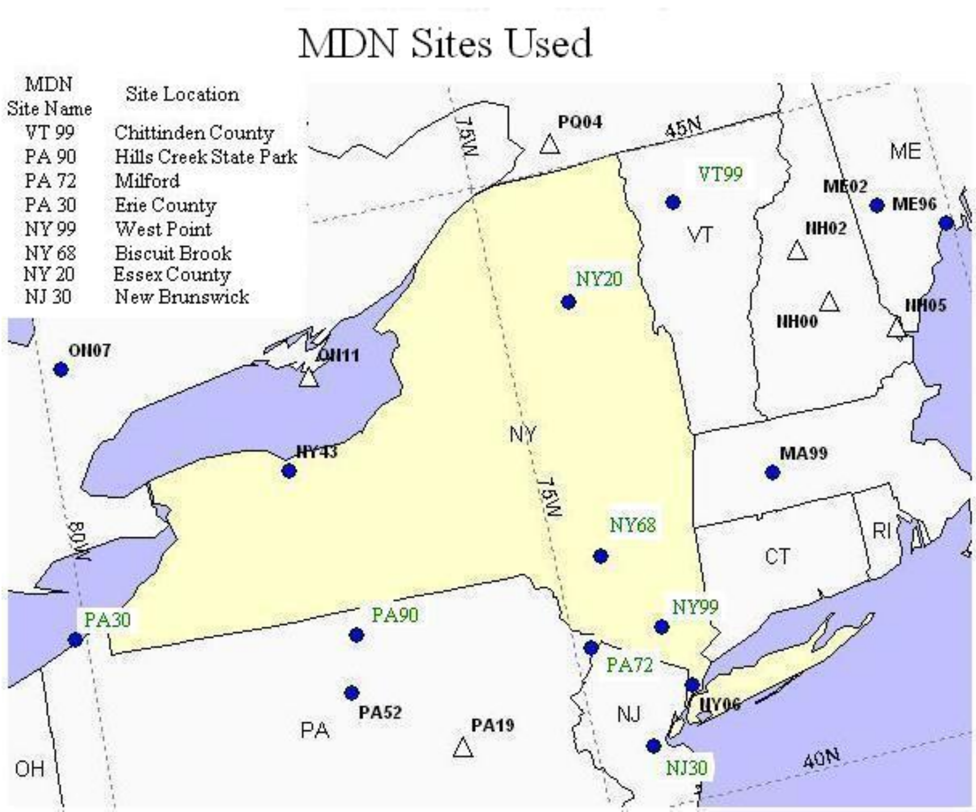


Figure 1 shows the location of each MDN site used. Weekly data was taken from each site and exported to Excel 2007 for statistical analysis. Sites were chosen based on availability of data for years 2007 and 2008.

to single sites in stepwise ANOVA calculations to detect sites that exhibited significant deviations from the central tendency.

Correlation tests using weekly data were performed between 2007 and 2008 data for each site. Weeks with missing data were removed. Daily maximum ($T_{max}$) and minimum ($T_{min}$) temperatures at NY99 were averaged by week. A correlation test was performed between MDN deposition data with both weekly temperature averages. Monthly deposition values at NY99 were also calculated from weekly data and represented in a yearly overlay. Excel 2007 Data Analysis ToolPak was used to perform all statistical tests.

**Results**

In 2007, almost all sites exhibited the highest deposition in the third quarter, corresponding to the months of June, July, and August. Sites at PA72 and NY20 deviate from this pattern, with the highest average deposition in the second quarter. The lowest average deposition for NJ30 occurred in the last quarter. The lowest average deposition for all other sites occurred in the first quarter.

In 2008, average deposition peaks in the third quarter for all sites with the exception of PA72, which exhibits slightly larger average deposition values in the second quarter. The lowest average deposition for most sites occurs once again in the first quarter, with the

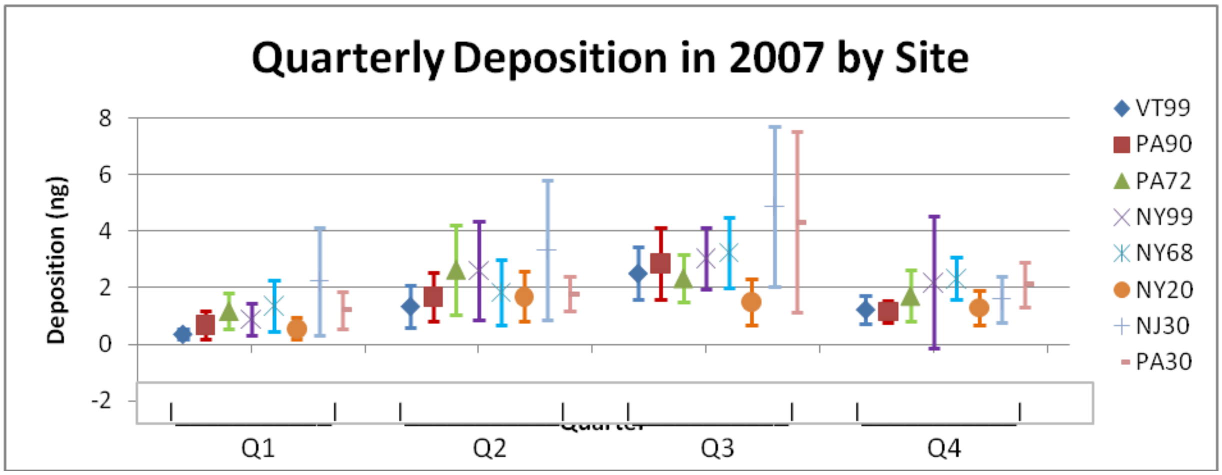


Figure 2a

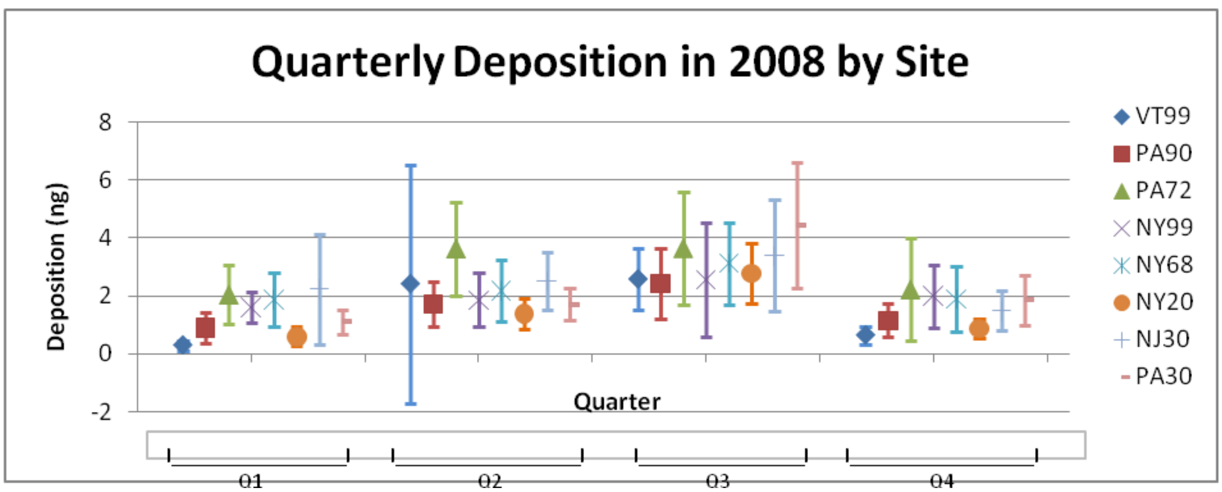


Figure 2b

Figure 2 shows the average deposition per site plotted by quarter with 95% confidence intervals. The data was split between two graphs; figure 2a represents 2007 and 2b represents 2008. The large confidence interval in the second quarter of 2008 is the result of an average derived from only two usable data points at VT99.

exception of NJ30 in the fourth quarter. A large confidence interval for VT99 in the second quarter resulted from a lack of data - only 2 of 12 weeks of data were recorded.

Successive ANOVA tests were used to determine sites that exhibited comparable mercury deposition concentrations when blocked by quarter. In 2007, PA90, PA72, PA30, NY99, and NY68 showed no significant deviation from another in an ANOVA test. In 2008, VT99, PA90, PA30, NY99, NY68, NY20 showed no significant deviation in an ANOVA test. These sites were applied as the central tendency in stepwise ANOVA for their respective years.

Stepwise ANOVA tests of $Q_{avg}$ in 2007 showed almost no significant deviation in site behavior, with the exception of VT99. Sites at NY20 and NJ30 were found to be only marginally not significant. In 2008, PA72 and NJ30 were found to behave significantly different than other sites in terms of seasonal mercury trends. The sites PA30, PA90, NY20, NY68, and NY99 appeared in the central tendency for both years. No sites were found to deviate significantly both years.

A correlation test compared MDN measurements in 2007 to those of 2008 for each of the sites. NJ30 has the strongest year-to-year correlation, followed by VT99. The other sites have fairly low year-to-year correlation coefficients. Correlation tests run between $T_{min}$ and $T_{max}$ with NY99 MDN deposition values yielded correlation coefficients of 0.235 and 0.206, respectively.

Table 1 shows all sites and respective p-values, when entered into an ANOVA with central tendency elements in each year. NY20 and NJ30 were found to deviate significantly from the central tendency by a small margin. Values that were not significant (ns) were labeled as such.

| | 2007 | 2008 |
|---|---|---|
| Site | p- Value | p- Value |
| VT99 | 0.037959 | ns |
| PA30 | ns | ns |
| PA72 | ns | 0.004715 |
| PA90 | ns | ns |
| NY20 | 0.050715 | ns |
| NY68 | ns | ns |
| NY99 | ns | ns |
| NJ30 | 0.056446 | 0.033655 |

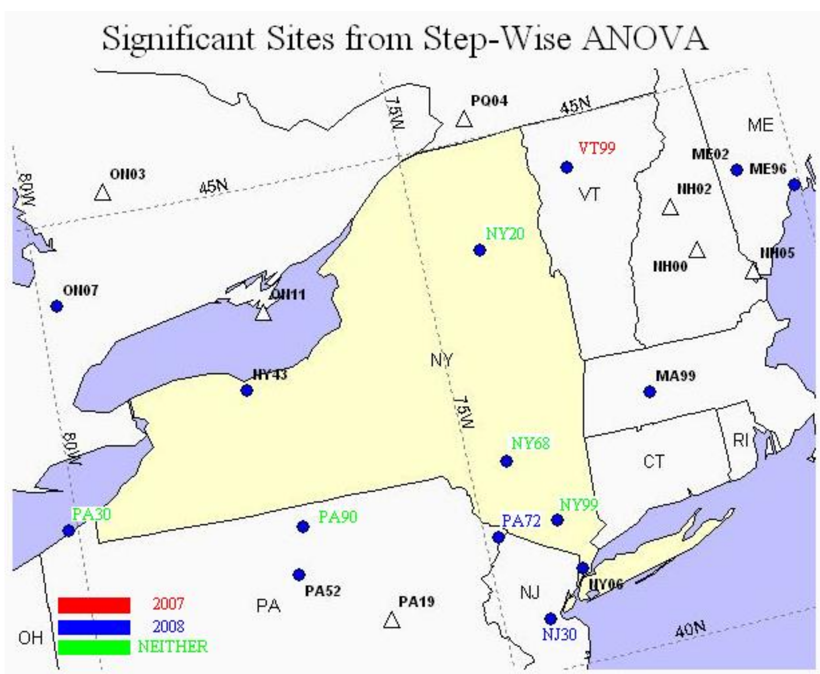

Figure 3 shows sites exhibiting significant differences in each year. Sites found to deviate from the central tendency in 2007 are highlighted in red; those deviating in 2008 are highlighted in blue. Sites that consistently appeared in the central tendency are in green.

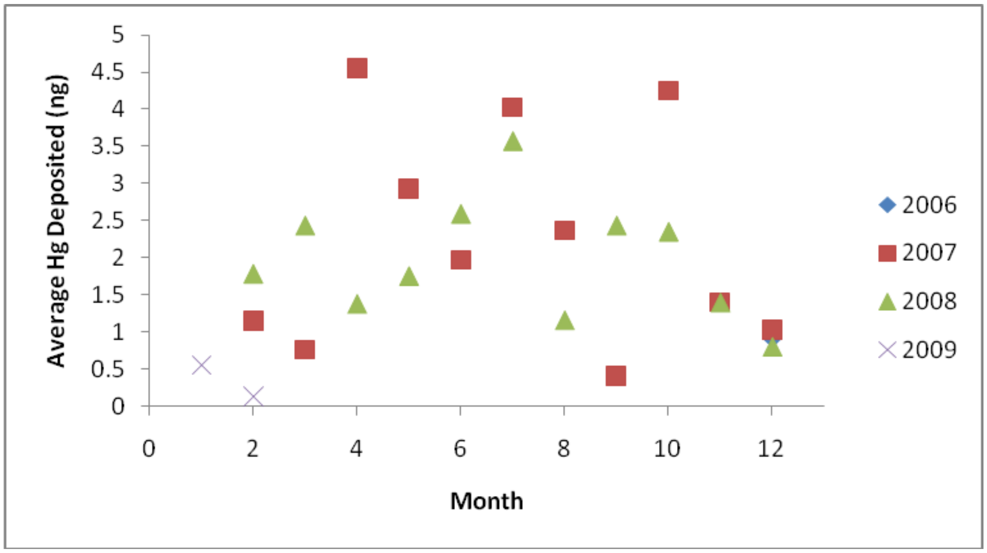


Figure 4 displays a yearly overlay of average monthly mercury deposition in total nanograms. There are no records before December 2006, and data after February 2009 was not taken into account.

Table 2 represents year-to-year correlation coefficients for weekly data comparing the years 2007 and 2008 at each site.

| Site | Correlation Coefficient (r) |
|---|---|
| VT 99 | 0.370893 |
| PA 30 | 0.072834 |
| PA 90 | 0.0265 |
| PA 72 | -0.04662 |
| NY 99 | -0.12644 |
| NY 68 | 0.167045 |
| NY 20 | 0.04786 |
| NJ 30 | 0.402512 |

**Discussion**

While regional trends in wet deposition have been found to decline over time, the effects of mercury already introduced to the atmosphere still remain relevant. Investigation of precipitation in the New York area generally maintains the decline mentioned in previous studies, but with a more erratic pattern between the years of 2007 and 2008.

Low correlation coefficients for yearly data describe low consistency between each year. However, certain sites (PA30, PA90, NY20, NY68, NY99) were discovered to behave with a central tendency with one another in both years. This may be representative of changing weather patterns affecting the region as a whole. Their similar behavior also suggests that they are affected by a global or regional phenomenon rather than a local source. Sites at NJ30 and VT99 showed the strongest consistency between years, but they deviate significantly from the other sites mentioned in the central tendency. NJ30 demonstrated higher levels of deposition compared to the central tendency sites, while VT99 demonstrated lower deposition values. VT99 is located in northern Vermont and is an inland site and may not be subject to the weather patterns affecting sites at lower latitudes.

The proximity of NJ30 to the coast and large urban areas suggests that different weather patterns and a local source may be causing higher levels of deposition in this region. The coastal trend mentioned in Van Arsdale (2005) is not observed at the site PA30, while NJ30 does demonstrate higher deposition. This discrepancy is most likely due to NJ30 being on an ocean coastline, while PA30 borders Lake Ontario and does not suffer from the same weather patterns. At NY99, higher deposition is seen in the warmer months. However, correlation coefficients between weekly average maximum and minimum temperatures and mercury deposition are low. Wet deposition of mercury does not appear to be strongly related to surface temperature.

Quarterly data from each site does suggest a relationship between warmer months (represented by the second and third quarters) and higher wet deposition. Conversely, there is a consistent decline in mercury deposition during the first and fourth quarters. A mixture of factors could be causing this effect. Electrical demand peaks during the spring and summer months and so coal combustion for power generation would be expected to peak during the warmer months. Warm air currents could also carry $Hg^0$ into the region and cause higher deposition in the area. Lowered capacity of colder precipitation to capture mercury may also play a role in depressing deposition in colder months.

A longer term study could reveal more significant trends and provide more statistically robust analyses. Additionally, temperature data from each site would allow a better comparison between site deposition levels. Effects of geography at each site were not considered. Many of the sites in the region are fairly new, with less than three years of data. Sites maintained for longer may provide better records of both deposition and temperature trends. It is likely that a future study, including more years of data, would yield stronger evidence for relationships between mercury deposition and the multitude of variables that affect it.

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