The statistically significant decreasing total mercury concentration trends at Hills Creek (PA90), Allegheny-Portage NHS (PA13), and Holbrook (PA37) are similar to observed decreasing seasonal sulfate concentration trends at these sites (Figures 25-27), although the seasonal sulfate concentrations trends are not statistically significant ($p<0.05$). Given the close association 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 his site. This would not necessarily be the case at either the Allegheny-Portage or Holbrook sites, because of their relative close proximity to major point sources. In addition, the stepwise regression analysis at each site with the possible exception of PA13 (Table 7) suggests multiple mercury emissions sources which may account for the lack of concurrent statistically significant trends in both mercury and sulfate concentrations at these sites. As stated earlier, sources of mercury emissions to the atmosphere in the United States can be broadly classified as natural mercury emissions, anthropogenic mercury emissions and re-emitted mercury. Re-emitted mercury is mercury that was previously deposited on the Earth's surface following either anthropogenic or natural releases and is re-emitted to the atmosphere by natural, biologic or geologic processes. Multiple sources of mercury at the Valley Forge site (Figure 28) where sulfate concentrations are decreasing ($p=0.023$) would also help to explain the lack of a concurrent decrease in mercury concentrations at this site.

Summary

Annual total mercury wet deposition at all MDN sites in the United States and southern Canada that met data completeness criteria for 2005 and 2006 ranged from 2.5 μg/m^2 in New Mexico to 21.5 μg/m^2 in west central Florida in 2005 (Figure 5) and from 2.1 μg/m^2 in Nevada to 18.8 μg/m^2 in southern Florida (Figure 7) in 2006. Wet mercury deposition in Pennsylvania in 2005 ranged from 6.7 μg/m^2 in Tioga and Cambria counties to 9.9 μg/m^2 in Montgomery County (Table 5). Wet mercury deposition in 2006 was lowest (8.1 μg/m^2) in Adams County and highest (10.1μg/m^2) in Pike County (Table 5). Because the Montgomery County site did not meet MDN data completeness criteria because of a large number of invalid samples it was not included in this comparison despite the fact that mercury deposition at the site measured 13.4 μg/m^2 in 2006. Volume-weighted mean annual concentrations of total mercury in precipitation in the United States ranged from 3.5 ng/L (southeast Canada) to 17.5 ng/L (New Mexico) in 2005 and from 3.6 ng/L (Oregon) to 20.7 ng/L (New Mexico) in 2006 (Figures 5 and 7). The volume-weighted mean concentrations of total mercury in Pennsylvania ranged from 6.4 ng/L in Tioga County to 8.7 ng/L in Montgomery County in 2005 and from 7.5 ng/L in Pike and Adams counties to 8.7 ng/L in Greene County in 2006 (Table 4). Total mercury concentrations and wet deposition estimates in the United States as well as in Pennsylvania in 2005 and 2006 were similar to values reported since network monitoring began. Although some differences were evident, these differences can be attributed to an annual increase in new MDN sites and to fluctuations in precipitation volumes within and between regions as well as possible fluctuations in mercury emissions.

In general, mercury concentrations and wet depositions in the United States are lowest in New England and southeastern Canada and higher in Florida and other Gulf states and around the Great Lakes. Mercury depositions in Pennsylvania are, for the most part, in the middle of this range, although annual observations at some sites in Pennsylvania (e.g., Hills Creek in Tioga County where mercury deposition is generally lower than most eastern sites) do not always fit into this general spatial pattern. Mean annual mercury concentrations (Figure 15) and wet depositions (Figure 16) in Pennsylvania the last four years have not demonstrated any consistent spatial pattern. In 2003 the highest concentrations were measured in western Pennsylvania; in 2004 the highest concentrations were in the eastern region of the state; in 2005 mercury concentrations were highest in northwestern Pennsylvania; and, in 2006 the highest concentrations were reported in the extreme southeast and southwest corners of the state. Wet deposition patterns show the same type of variability, confounded even more by regional differences in precipitation patterns.

Seasonal mercury concentrations and wet depositions in the United States are generally highest during the summer months and lowest during the winter. This seasonal pattern has been evident in Pennsylvania for most but not all years at most but not all sites. Seasonally variable mercury concentrations and precipitation volumes have resulted in very inconsistent seasonal mean concentration and wet deposition patterns at individual sites as well as across the state. Some of this variability can be associated with one or more unusually high weekly mercury concentrations and wet depositions that account for a substantial percentage of the volume-weighted mean seasonal concentration wet deposition.

Correlation and stepwise regression analyses were conducted between weekly mercury concentrations and wet depositions and the concentrations and depositions of the major cations and anions found in precipitation samples collected at each of the MDN sites. The results of these analyses indicated that sulfate was significantly correlated with mercury concentrations at all sites in Pennsylvania. Calcium and/or magnesium concentrations were also significantly correlated with mercury concentrations at all sites and were the most significantly correlated at the Adams County (Arendtsville) and Lancaster County (Millersville) sites. Results from the stepwise regression analysis were very similar to the correlation analysis. At all sites, sulfate deposition was the most significant variable for predicting total mercury wet deposition followed by the wet deposition of one or more of the major cations, usually calcium. All of the models were statistically very significant with r-squared values around 0.70 (Table 9).

Trend analyses at four sites (Allegheny-Portage, Hills Creek, Holbrook, and Valley Forge) indicate statistically significant decreasing mercury concentration trends at each site except Valley Forge. The concentration trends do not appear to be influenced by precipitation at any of the sites. However, precipitation volumes did have significant influence over the wet mercury deposition trends. It is interesting to note that decreasing total mercury concentration patterns at Hills Creek, Allegheny-Portage and Holbrook are similar to observed decreasing patterns in sulfate concentrations at these sites, even though the quarterly sulfate concentration trends are not statistically significant. What these comparisons might suggest is that multiple sources of mercury likely influence mercury concentration patterns at these sites as well as across the network. 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. The association of sulfate concentrations with mercury concentrations as illustrated by the correlation coefficients, stepwise regression models, and trend analyses, appears to indicate that at least some of the mercury in precipitation at Pennsylvania MDN sites is from combustion sources, most likely coal-fired power plants. We also know that wind blown soil particles are an important source of cations in precipitation, particularly calcium and magnesium. The close association of these cations with mercury concentrations would seem to indicate that terrestrial/agricultural sources are potentially important at all sites as well. The fact that calcium is the most significant variable in predicting mercury concentrations at the Arendtsville (Adams County) and Millersville (Lancaster County) sites would tend to support this position. Both of these sites are located in areas that are dominated by agricultural activities, particularly Lancaster County where calcium concentrations explain more than 50% of the variance in weekly mercury concentrations. 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.

Although the results of seasonal 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 2007 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 a MDN site in Lycoming County at Little Pine State Park in 2007 and the possible establishment of another site in west central Pennsylvania 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.