

**Reductions in Acidic Wet Deposition Following Implementation of the  
Clean Air Act Amendments of 1990: 1995-2004**

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The work upon which this report is based was supported by funds from The Pennsylvania Department of Environmental Protection through Contract Number ME359494.

Penn State Institutes of the Environment  
The Pennsylvania State University  
University Park, Pennsylvania 16802

December 2005

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## **Reductions in Acidic Wet Deposition Following Implementation of the Clean Air Act Amendments of 1990: 1995-2004**

### **Introduction**

The deposition of acidic substances from atmospheric sources was first recognized as a potential environmental threat in the United States in the mid-1970s. This recognition led to the establishment of The National Atmospheric Deposition Program/National Trends Network (NADP/NTN), a monitoring program initiated in 1978 to collect weekly precipitation samples for chemical analyses at 22 sites, mostly in the eastern United States, including one site located on the Allegheny National Forest near Kane, Pennsylvania (Lamb and Bowersox, 2000; Lynch and Kerchner, 2005). The original and continuing goal of this program is to provide data on temporal trends and the geographic distribution of the wet deposition of acidic compounds, nutrients, and base cations. Data from the initial couple of years of operation of this network indicated that precipitation over the Mid-Atlantic and Northeast regions of the United States, especially eastern Ohio and western Pennsylvania, was very acidic. The pH of precipitation samples collected in this region was frequently below 4.0, while annual sulfate and nitrate concentrations averaged above 3.5 mg/L and 2.0 mg/L, respectively. The very high acidity and nitrate and sulfate concentrations were attributed to sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) emissions, the principal precursors of acid rain, from sources located within the region and in upwind Midwestern states, particularly states along the Ohio River Valley.

Because of the geographic location of Pennsylvania to major emission sources in the Ohio River Valley, the preliminary indication that precipitation in Pennsylvania was more acidic than most, if not all, regions of the eastern United States, and the presence of numerous acid sensitive ecosystems in the Commonwealth, The Pennsylvania Department of Environmental Resources (currently The Department of Environmental Protection) established a long-term atmospheric deposition monitoring network in Pennsylvania in 1981 under a cooperative agreement with The Pennsylvania State University. The objectives of this project and subsequent revisions were: (1) to determine the magnitude and distribution of wet atmospheric deposition and associated toxic and nutrient elements in Pennsylvania, (2) to assess their potential environmental impacts, (3) to determine temporal trends in the chemistry of precipitation in the state, (4) to evaluate the influence of local emissions and variations in precipitation volume on wet deposition patterns, (5) to determine the optimum number of sites needed to define spatial variability in atmospheric deposition in Pennsylvania, and (6) to provide a quantitative means of evaluating the effectiveness of present and future air pollution control legislation, such as the Clean Air Act Amendments of 1990, aimed at reducing atmospheric deposition in the United States.

The current long-term atmospheric deposition monitoring network in Pennsylvania includes eight sites supported by The Pennsylvania Department of Protection (DEP) and four NADP/NTN sites (Figure 1). The DEP sites are located in Mercer (M.K. Goddard State Park), Armstrong (Crooked Creek Lake), Somerset (Laurel Hill State Park), Tioga (Hills Creek State Park), Lycoming (Little Pine State Park), Perry (Little Buffalo State Park), Luzerne (Frances Slocum

# Pennsylvania Atmospheric Deposition Monitoring Network

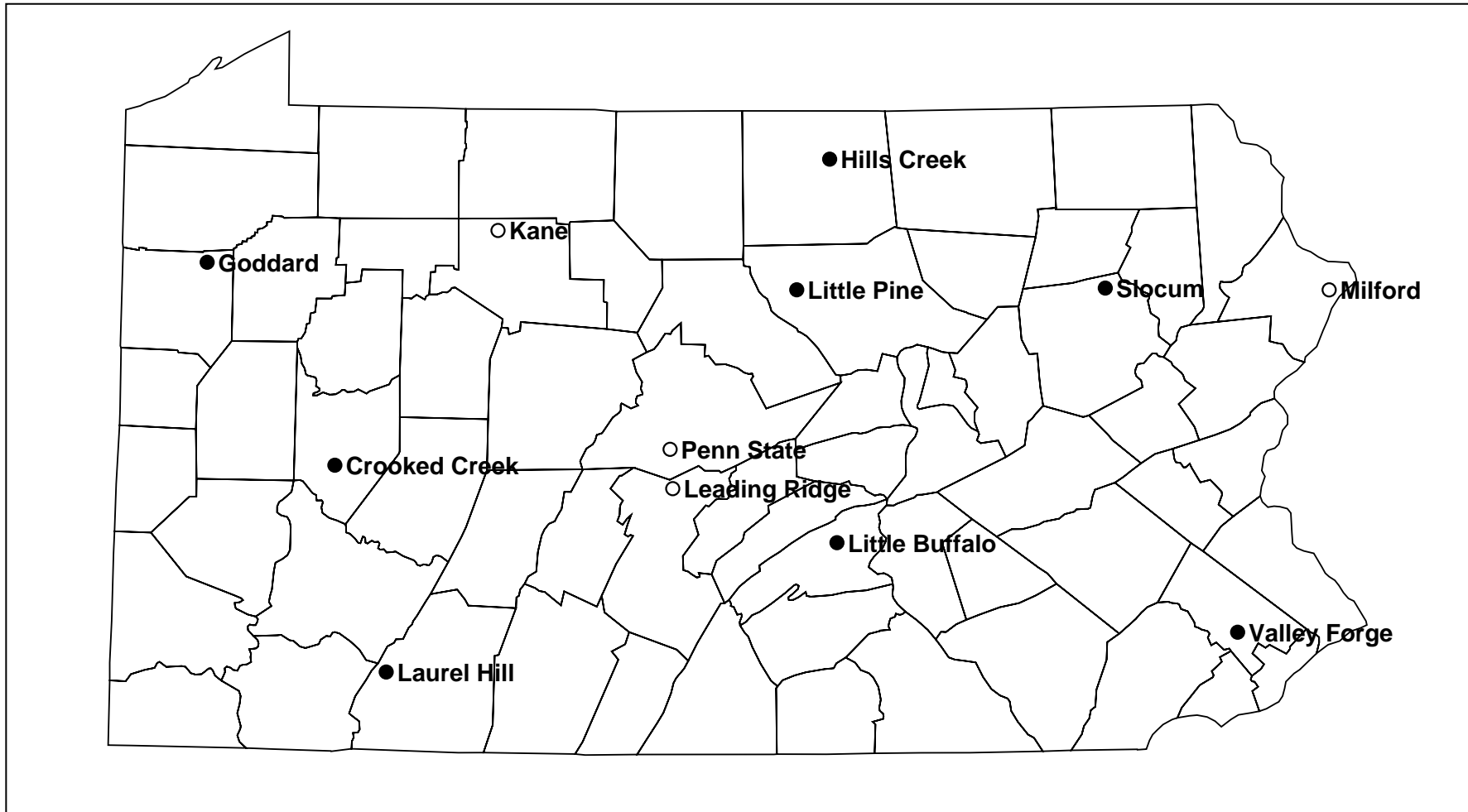


Figure 1. Locations of long-term sites in the Pennsylvania Atmospheric Deposition Monitoring Network. Sites marked with an empty circle are part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN).



State Park), and Montgomery (Valley Forge National Historic Park) counties. The four NADP/NTN sites are located in Elk County near Kane, in Huntingdon County on the Leading Ridge Experimental Watersheds, in Centre County near Penn State University, and in Pike County near Milford. The U.S. Forest Service, Northern Forest Experiment Station, supports the NADP/NTN sites near Kane and Milford. The Pennsylvania Agricultural Experiment Station through National Research Support Project-3 (NRSP-3) supports the Leading Ridge site and The National Oceanic and Atmospheric Administration supports the Penn State site.

Although both networks operate independent of one another, both employ identical sampling equipment and sampling and analytical protocols. Network design and operation of all DEP sites are discussed in Lynch et al. (2004) which can be viewed over the internet at <http://www.dep.state.pa.us>. Precipitation chemistry data and wet deposition estimates for all DEP sites for all years of operation are available at this web address. Network design and operation of all NADP/NTN sites in Pennsylvania and all other locations in the United States are also available over the internet at <http://nadp.sws.uiuc.edu>. Concentration measurements and wet deposition estimates for all NADP/NTN sites are also accessible at this web address.

### **Emissions Trends**

Following a 10-year assessment of the impacts of acidic deposition on aquatic and terrestrial ecosystems, cultural and material resources, and human health (NAPAP, 1990), Congress amended the Clean Air Act (P.L 101-549) and included in the amendments Title IV that seeks to reduce the adverse effects of acidic deposition in the United States through phased reductions in sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) emissions. Phase I of the SO<sub>2</sub> reduction program was implemented on 1 January 1995. On that date additional limitations were imposed on SO<sub>2</sub> emissions at 110 electric utility plants (263 units) in 21 states of which 17 are east of the Mississippi River (P. L. 101-549, Table A). Phase II of the SO<sub>2</sub> emissions reduction program targeted over 2000 sources at existing utilities servicing generators with an output capacity of greater than 25 megawatts and all new utility units located throughout the United States. Phase II was implemented on 1 January 2000.

Sulfur dioxide emissions at the 110 utilities affected by Phase I dropped 3.4 million tons (39%) in 1995 when compared to 1990 emissions (Figure 2). From 1995 through 1999 (Phase I), emissions from these 110 utilities averaged 5.3 million tons, 3.4 million tons less than 1990 levels; emissions from all Phase I and II affected sources averaged 12.6 million tons over this period. Emissions in 1999 were reported at 4.9 million tons at Phase I sites and 12.5 million tons at all Title IV affected sources (EPA, 2005b). Some of the decrease in emissions between 1998 and 1999 and between 1999 and 2000 (Figure 2) were likely the result of Phase II requirements. In some cases, utilities implemented emissions reduction programs prior to the mandatory date of 1 January 2000. This was also the case in 1994-1995 for some Phase I affected sources. Since 2000, annual sulfur dioxide emissions from all Title IV affected sources ranged from 11.2 million tons to 10.2 million tons and averaged 10.6 million tons. In 2004, emissions from Title IV affected sources measured 10.3 million tons, a decrease of 0.3 million tons over 2003 emissions, but 0.1 million tons higher than 2002 emissions (Figure 2). The higher emissions in 2003 were attributed to an increase in the combustion of coal as utilities sought to reduce fuel

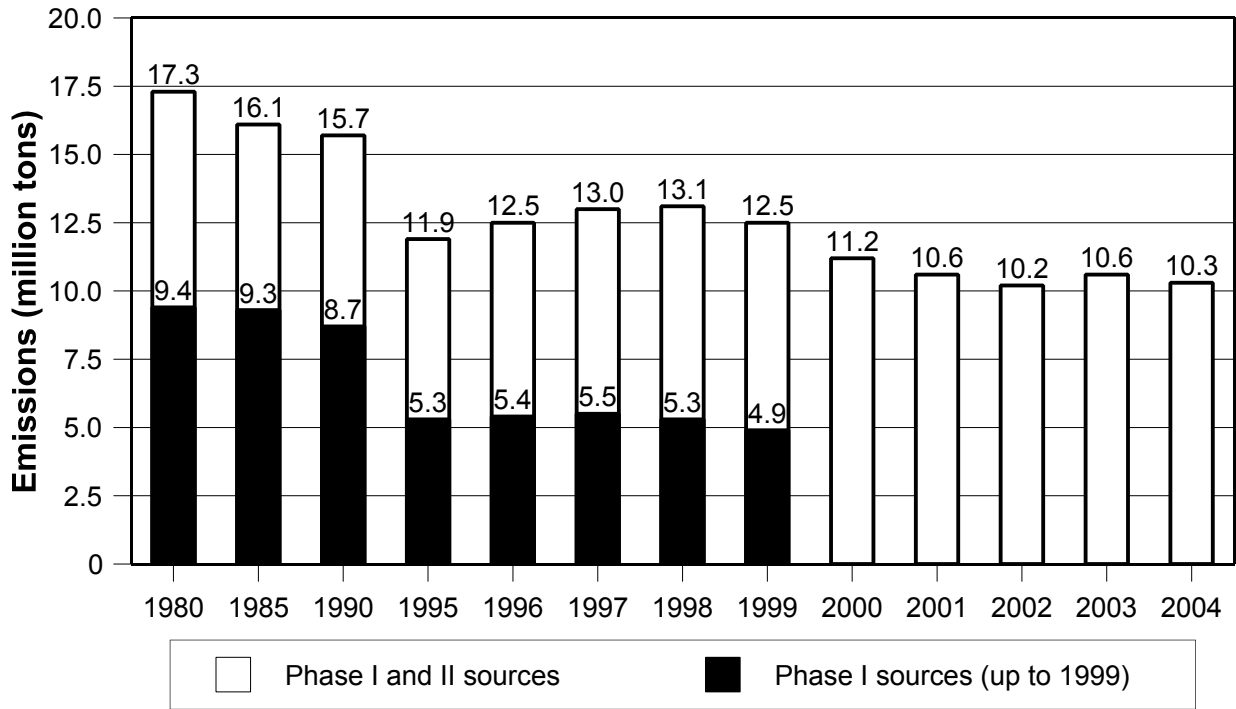


Figure 2. Sulfur dioxide emissions from Title IV affected sources of the Clean Air Act Amendments of 1990 for 1980, 1985, 1990, and 1995 through 2004 (EPA Acid Rain Program, <http://www.epa.gov/airmarkets/emissions/index.html>).

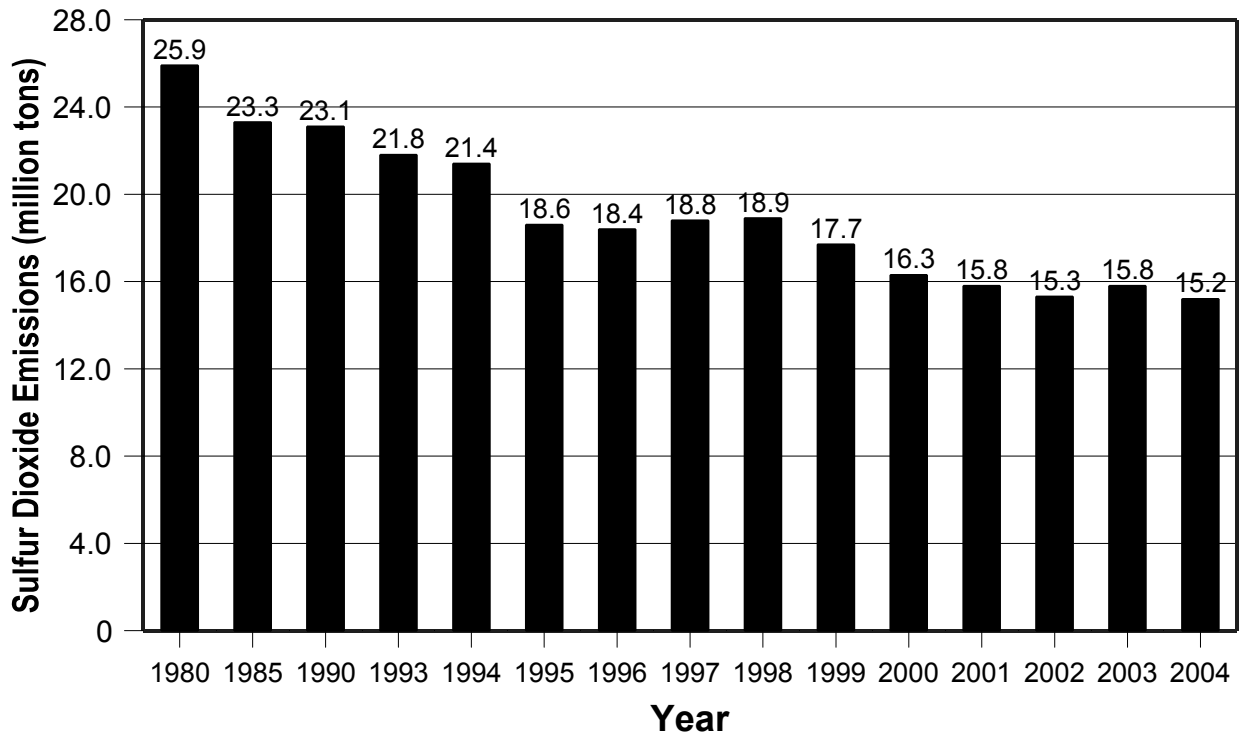


Figure 3. Sulfur dioxide emissions trend from all point and area sources in the United States (EPA AirData, <http://www.epa.gov/airmarkets/emissions/index.html>). Emission estimates for 2004 are preliminary.

costs by switching from oil or gas to lower cost coal as their primary source of energy (EPA, 2004b). The average annual reduction in sulfur emissions from all Title IV sources since 1995 has been 4.1 million tons (26.1%) when compared to 1990 emission (Figure 2).

Total SO<sub>2</sub> emissions from all point and area sources in the United States totaled 23.1 million tons in 1990 (Figure 3). In 1995, total SO<sub>2</sub> emissions dropped to 18.6 million tons. From 1995 through 1999, SO<sub>2</sub> emissions averaged 18.5 million tons (Figure 3). In 2004, SO<sub>2</sub> emissions totaled 15.2 million tons, 7.9 million tons below 1990 levels and 0.6 million tons below 2003 levels of 15.8 million tons. The decrease in total SO<sub>2</sub> emissions from 1995 through 1999 and from 2000 through 2004 resulted from implementation of Phase I and Phase II, respectively, of Title IV of the CAAA. The increase in 2003 over 2002 levels was largely due to fuel switching at Title IV affected sources as discussed above.

Many of the SO<sub>2</sub> emission sources targeted by Phase I and Phase II of the CAAA are located in Pennsylvania, Ohio, West Virginia, Kentucky, Indiana, and Maryland. Sulfur dioxides and NO<sub>x</sub> emissions within these states are likely to have a direct impact on precipitation chemistry in Pennsylvania. Annual SO<sub>2</sub> emissions from affected units in these states for 1990 and from 1995 through 2004 are shown in Table 1. Sulfur dioxide emissions from within these states in 2004 totaled 4.2 million tons, a reduction of 40.4% from 1990 levels. The average percent reduction in emissions from these sources since 1995 was 35.3%. Sulfur dioxide emissions at Pennsylvania units affected by Phase I and II were slightly less than one million tons in 2004, 2.2 million tons below 1990 levels but 0.03 million tons above 2003 levels. Since 1995, SO<sub>2</sub> emissions from Phase I and II affected units in Pennsylvania averaged 0.99 million tons, an 18.3% reduction over 1990 emissions (Table 1). Percentage reductions in SO<sub>2</sub> emissions since 1995 averaged 43.1% in Ohio, 39.1% in West Virginia, 34.6% in Kentucky, 41.1% in Indiana, and 6.9% in Maryland (Table 1).

Title IV of the CAAA also specifies a two-part strategy to reduce nitrogen oxides (NO<sub>x</sub>) emissions (Krolewski and Mingst, 2000). The first stage of this program was implemented 1 January 1996; the second phase began 1 January 2000. Actual NO<sub>x</sub> emissions from all Title IV affected sources during Phase I (1996 through 1999) averaged 5.25 million tons annually, a decrease of 0.15 million tons over 1995 levels (Figure 4). From 2000 through 2004 (Phase II), NO<sub>x</sub> emissions averaged 4.1 million tons, 1.3 million tons below 1995 levels and 0.7 million tons below 1999 emissions (Figure 4). Nitrogen oxides emissions from all Title IV affected sources in 2004 were 3.8 million tons, 0.7 million tons lower than 2003 emissions and 2.9 million tons lower than 1990 levels (Figure 4). The reductions in NO<sub>x</sub> emissions are primarily from high temperature combustion sources, such as those that occur in automobiles and power plants (EPA, 2005a).

Nitrogen oxides emissions reductions in Pennsylvania and in selected upwind states are listed in Table 1 (EPA, 2005a). The average percent reduction in NO<sub>x</sub> emissions in PA, OH, MD, WV, KY, and IN from 1996 through 2004 relative to 1995 emissions was 18.0% (range 3.9% to 29.4%). The percent reduction in 2004 NO<sub>x</sub> emissions relative to 1995 emissions averaged 43.5% (range 17.9% to 58.1%). The largest overall reduction in NO<sub>x</sub> emissions occurred in Kentucky. The substantial increase in the percent reductions in 2004 relative to the 1996-2003

Table 1. Sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) emissions (1000 tons) from all Phase I and Phase II affected sources in Pennsylvania, Ohio, West Virginia, Kentucky, Indiana and Maryland since implementation of the Title IV of the Clean Air Act Amendments of Phase I SO<sub>2</sub> reductions were implemented 1 January 1995; Phase II was implemented 1 January 2000. Phase I NO<sub>x</sub> reductions were implemented on 1 January 1996; Phase II was implemented 1 January 2000 (from EPA, 2005b).

Year	PA	OH	WV	KY	IN	MD	Total
<u>Sulfur Dioxide Emissions from Phase I and II Affected Sources</u>							
1990	1213.4	2211.6	968.6	905.1	1499.2	282.5	7080.4
1995	1054.5	1199.9	606.8	676.3	894.6	230.0	4662.1
1996	1013.7	1479.0	658.3	642.3	933.6	253.7	4980.6
1997	1071.7	1448.5	663.6	671.4	977.4	259.8	5092.4
1998	1072.9	1415.0	667.9	625.1	968.3	289.0	5038.2
1999	964.2	1309.9	694.5	659.0	941.9	281.8	4851.3
2000	935.2	1209.5	593.3	584.9	874.6	254.5	4450.3
2001	944.9	1125.5	498.1	535.4	795.5	254.5	4153.9
2002	889.9	1132.1	507.1	482.7	778.9	255.4	4046.0
2003	967.2	1175.9	539.9	531.5	803.6	269.0	4287.1
2004	997.3	1091.5	473.8	514.8	862.9	281.7	4222.0
Mean							
1995-2004	991.2	1258.7	590.3	592.3	883.1	262.9	4578.4
Average % Reduction <sup>1</sup>	18.3	43.1	39.1	34.6	41.1	6.9	35.3
<u>Nitrogen Oxides Emissions from Phase I and II Affected Sources</u>							
1995	264.6	528.7	276.8	372.7	354.9	97.8	1895.5
1996	254.5	555.9	296.5	368.3	364.7	106.0	1945.9
1997	244.6	538.2	321.6	363.1	383.2	109.0	1959.7
1998	239.4	516.0	292.5	319.4	363.6	120.5	1851.4
1999	198.0	426.8	285.0	308.3	347.5	106.0	1671.6
2000	209.4	375.2	258.4	246.1	334.1	80.7	1503.9
2001	203.3	332.9	204.3	231.8	315.3	71.9	1359.2
2002	217.8	368.7	226.3	198.5	281.1	86.4	1378.8
2003	174.3	350.2	203.5	174.8	254.0	84.8	1241.6
2004	176.4	266.8	172.5	156.2	218.3	80.3	1070.6
Mean							
1995-2004	213.1	414.5	251.2	262.9	318.0	94.0	1553.6
Average % Reduction <sup>2</sup>	19.5	21.6	9.3	29.4	10.4	3.9	18.0
% Reduction <sup>3</sup>	33.3	49.5	37.7	58.1	38.5	17.9	43.5

<sup>1</sup>Average % reduction in SO<sub>2</sub> emissions from 1995-2004 relative to 1990 emissions.

<sup>2</sup>Average percent reduction in NO<sub>x</sub> emissions from 1996-2004 relative to 1995 emissions.

<sup>3</sup>Percent reduction in 2004 NO<sub>x</sub> emissions relative to 1995 emissions.

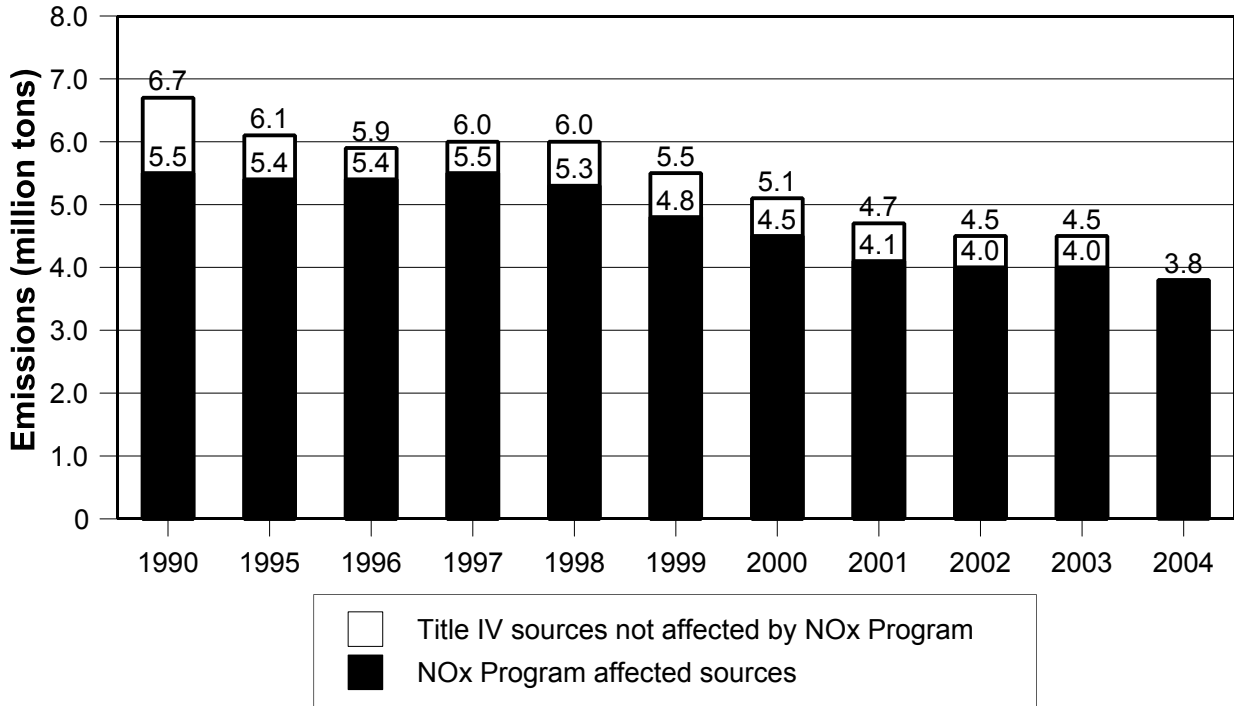


Figure 4. Nitrogen oxides emissions from Title IV affected sources of the Clean Air Act Amendments of 1990 for 1990 and 1995 through 2004 (EPA Acid Rain Program, <http://www.epa.gov/airmarkets/emissions/index.html>). Emissions estimates for Title IV sources not affected by the NOx program during 2004 were not available at the time of publication.

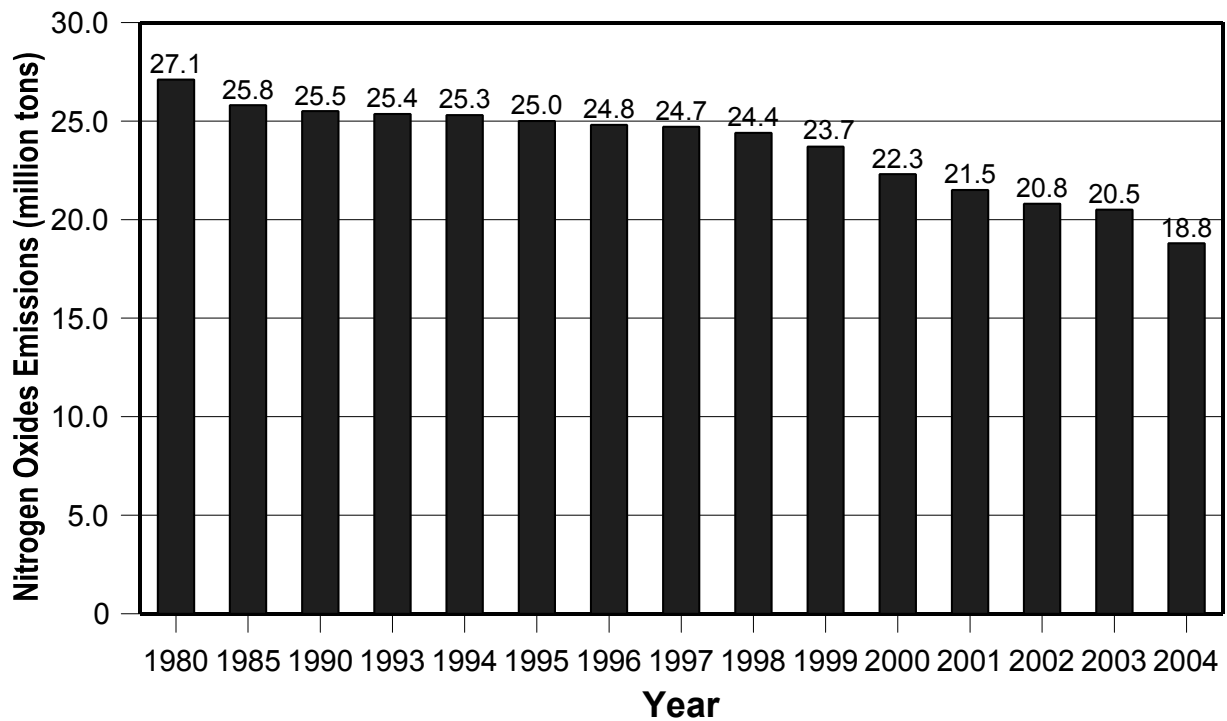


Figure 5. Nitrogen oxides emissions trends from all point and area sources in the United States (EPA AirData, <http://www.epa.gov/airmarkets/emissions/index.html>). Emission estimates for 2004 are preliminary.

mean percent reductions reflects changes since implementation of Title IV Phase II controls, as well as other emissions control programs aimed at reducing ozone levels. In Pennsylvania, the average reduction in NO<sub>x</sub> emissions since 1996 was 19.5% (51,500 tons). Nitrogen oxides emissions at all Title IV affected sources in PA in 2004 were 88,200 tons lower than in 1995, but slightly higher than reported emissions in 2003 (Table 1).

Nitrogen oxides emissions from all sources in the United States for 1980, 1985, 1990, and 1993 through 2004 are shown in Figure 5. Clearly, NO<sub>x</sub> emissions from all Title IV affected sources represent a relatively small percentage (approximately 24% on average) of total NO<sub>x</sub> emissions from all sources (Figures 4 vs. Figure 5). Likewise, reductions in NO<sub>x</sub> emissions from Title IV sources from 1996 to 1999 (0.60 million tons) represent a very small percentage reduction when compared to total NO<sub>x</sub> emissions from all sources over this period. Since 2000, NO<sub>x</sub> emissions from all Title IV sources declined from 4.8 million tons in 1999 to 3.8 million tons in 2004 (Figure 4). Nitrogen oxides emissions from all sources (except fire) in 2004 totaled 18.8 million tons, 6.0 million tons below 1996 emissions (EPA, 2005a). The greater reduction in total NO<sub>x</sub> emissions relative to reductions from Title IV sources represents a decrease in NO<sub>x</sub> emissions from other non-Title IV sources, primarily mobile sources. In 1990, fuel combustion sources accounted for 43.3% of all NO<sub>x</sub> emissions in the United States; in 2003 these sources represented 38.3%. In contrast, on-road and non-road mobile emission sources in 1990 accounted for 53.1% of the annual total; in 2003 these sources accounted for 56.0% of all NO<sub>x</sub> emissions. Although both fuel combustion and on-road and non-road sources decreased in 2003 relative to 1995 (EPA, 2005a), the percent reductions were much greater from fuel combustion sources (-26.5%) than on-road and non-road sources (-11.6%). When compared to 1990 emissions the percent reductions are 26.9% and 14.1%, respectively. Clearly, Title IV and other Titles in the CAAA have reduced NO<sub>x</sub> emissions in the United States, with relatively larger reductions occurring from fuel combustion sources (industries/utilities) than from other sources. Consequently, the mix of emissions sources and their relative importance have changed since 1990 and even 1995 with on-road and non-road sources accounting from a larger percentage of all NO<sub>x</sub> emissions. Changes in the relative contribution of emission sources in a region likely influence the distribution and magnitude of nitrate reductions in precipitation across that region.

## Methods

Evaluation of the effects of changes in time series data, such as the sharp reduction in SO<sub>2</sub> emissions in the eastern United States since implementation of the CAAA, requires a reference period for comparison. The reference period (pre-CAAA) used in this analysis included precipitation chemistry data from both Pennsylvania and NADP/NTN network sites from 1983 through 1994. This reference period was selected because it provides the longest continuous measure of precipitation chemistry in Pennsylvania and neighboring states while avoiding potential start-up problems with field sampling and laboratory protocols often associated with environmental monitoring programs.

In the trend analysis of the pre-CAAA reference period (1983-1994) and the post-CAAA effects period (1995-2004), weekly precipitation volume and ionic concentration measurements were accumulated into bi-monthly precipitation totals and volume-weighted mean concentrations and

wet depositions for each ionic species (i.e.,  $H^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $NH_4^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and  $Na^+$ ). Only valid weekly samples with a complete set of analyses were used to calculate bi-monthly volume-weighted mean concentrations.

Trends in ionic concentrations and wet depositions at each site were evaluated using a two-stage, least-squares general linear model (SAS Institute, Inc, 1998). This model was developed by the authors for detecting and quantifying trends in precipitation chemistry data that exhibit strong seasonal patterns (Lynch et al., 1995). The form of the model for both stages was:

$$\log_{10}(C_y+1.0) = b_0 + b_y*y + \sum_{s=1}^6 b_s I_s$$

- where,  $c_y$  = estimated concentration of a given ion at time  $y$ .  
 $b_0$  = intercept.  
 $b_y$  = slope of the long-term log-concentration trend.  
 $y$  = mid-point of the bi-monthly observation period expressed as decimal years. For example,  $y$  for a May-June 1990 observation was coded as  $90+(5/12)$  or 90.4167.  
 $b_s$  = adjustment to estimate for bimonthly period,  $s$ . The array of 6  $b_s$  coefficients account for the seasonal variation in precipitation chemistry.  
 $I_s$  = an element of an array of 6 indicator variables set to 1 for bimonthly periods,  $s$ , and set to 0, otherwise.

Log-transformed concentrations and depositions were used to normalize the distribution of the model residuals (Lynch et al., 1995). After initially fitting the model to a site's concentration or deposition observations (expressed as  $\mu\text{eq/L}$  or  $\text{kg/ha}$ , respectively) for a given ion, studentized residuals were calculated. Bi-monthly observations having a studentized residual  $>3.5$  in absolute value were eliminated from the data set and a second calculation of model coefficients was performed using the remaining observations. The selected cut-off value applied to the studentized residuals would be exceeded by chance at a rate less than 0.001 under the assumption of normally distributed residuals of constant variance. Results from this analysis provided the baseline against which concentrations and deposition trends from 1995 through 2004 were compared to assess the effects of Title IV of the CAAA on precipitation chemistry.

To determine whether trends in ionic concentrations and depositions following implementation of Phases I and II emissions reductions differed from those during the pre-CAAA reference period, the seasonalized trend described above was applied to observations for each site from 1983 through 1994 (pre-CAAA) and the resulting coefficients were used to produce estimates for each of the observations during the 1995 through 2004 (post-CAAA) period. Deviations for each of the observed values during the post-CAAA period from these estimates were then calculated. The seasonalized trend model was applied to these post-CAAA deviations to assess the change in concentration and deposition trends relative to the pre-CAAA period. The means

of log-transformed, bi-monthly ionic concentrations and wet depositions for each site were compared between the pre- and post-CAAA periods and tested for differences using a two sample t-test. A significant t-test ( $p < 0.05$ ) was considered evidence of change between periods.

## Results and Discussion

**Sulfate** - Sulfate concentrations (Figure 6) and wet deposition (Figure 7) have decreased substantially across Pennsylvania since implementation of the CAAA. These reductions are in response to lower  $\text{SO}_2$  emissions (Figures 2 and 3) following implementation of Phase I of CAAA, Title IV on 1 January 1995 and Phase II on 1 January 2000. A comparison of mean annual and seasonal sulfate concentrations and wet depositions (Table 2) at each of the long-term monitoring sites during pre- (1983-1994) and post-CAAA (1995-2004) periods illustrates the magnitude of the reductions. Statistically significant ( $p < 0.05$ ) reductions in mean annual sulfate concentrations are evident at all Pennsylvania sites and range from 0.603 mg/L at Laurel Hill (Somerset County) to 0.913 mg/L at Hills Creek (Tioga County). The average reduction is slightly greater in central Pennsylvania (0.792 mg/L) than in either the eastern (0.766 mg/L) or western (0.760 mg/L) regions of the state. The overall average reduction in mean annual sulfate concentrations across the state since 1995 has been 0.775 mg/L (Table 2).

The largest seasonal reductions in sulfate concentrations occurred during the growing season (Table 2). Average growing season reductions ranged from 0.945 mg/L at Slocum State Park in Luzerne County to 1.523 mg/L at the Leading Ridge NADP/NTN site in Huntingdon County with all sites exhibiting statistically significant ( $p < 0.05$ ) decreasing trends. As with annual concentration means, the mean growing season reduction in central Pennsylvania (1.270 mg/L) was slightly larger than in the western (1.198 mg/L) and eastern (1.023 mg/L) regions of the state (Table 2). The overall average growing season reduction in sulfate concentrations since 1995 was 1.183 mg/L, a 31% decrease when compared to the pre-CAAA mean (Table 2).

Mean dormant season sulfate concentrations also decreased since 1995 (Table 2), although the drop was not as large as they were for growing season concentrations. Reductions in mean dormant season concentrations ranged from 0.246 mg/L at M. K. Goddard State Park in Mercer County to 0.613 mg/L at the Slocum site. Reductions in mean dormant season concentrations were significant ( $p < 0.05$ ) at all sites (Table 2). However, unlike growing season reductions in sulfate concentrations, mean dormant season reductions since 1995 were actually greater in eastern Pennsylvania (0.541 mg/L) than in either the central (0.379 mg/L) or western (0.309 mg/L) portions of the state (Table 2). With some exceptions (e.g., Kane, Hills Creek, and Penn State) there is an increasing west to east pattern in the decline of dormant season sulfate concentrations since 1995. The reason for this pattern and its deviation from the growing season pattern is uncertain but may be associated with seasonal differences in the conversion of sulfur dioxide to sulfate as well as seasonal differences in emissions and long-range transport processes.

As would be expected given the large reductions in sulfate concentrations since 1995, wet sulfate deposition across the state has also decreased (Table 2, Figure 7). On an annual basis, the average reduction in sulfate deposition at each of the long-term monitoring sites ranged from



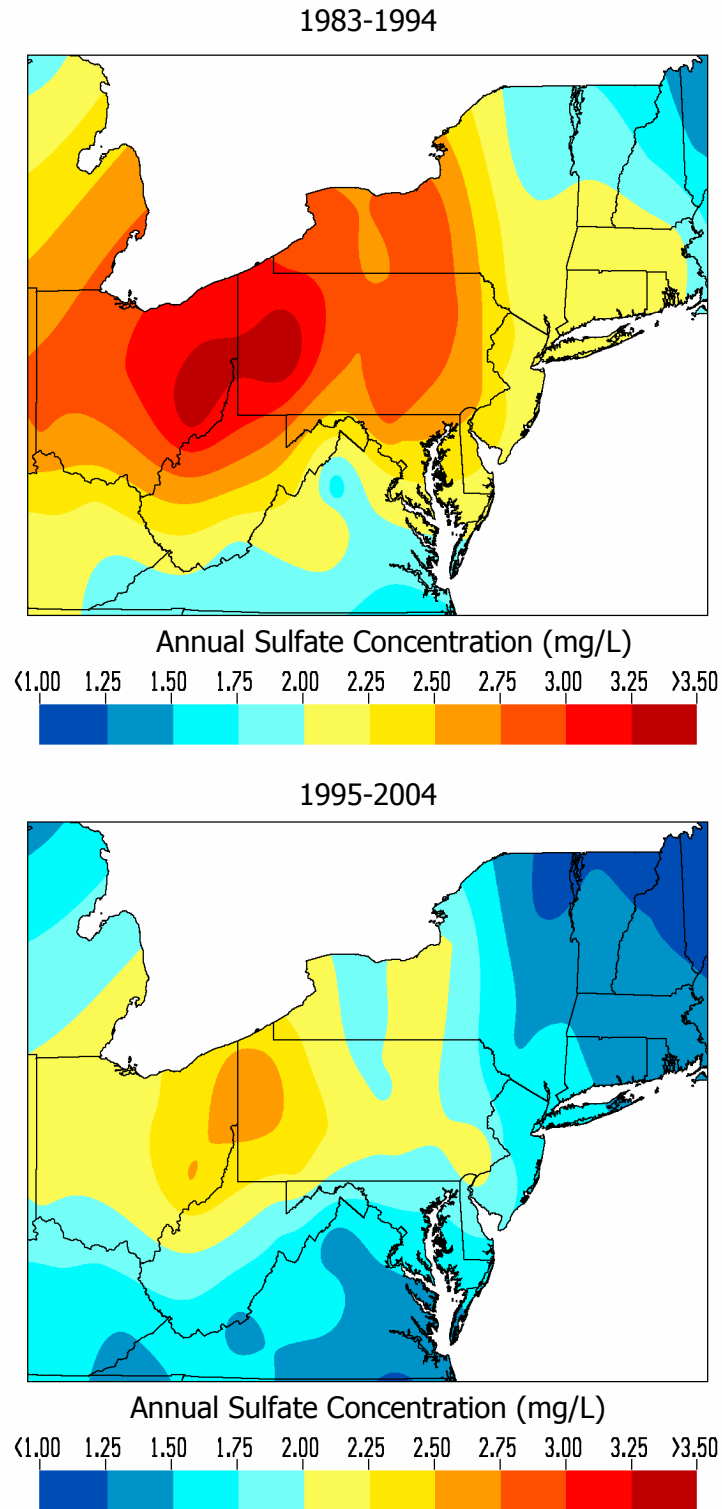


Figure 6. Mean annual sulfate concentrations across Pennsylvania and neighboring states before (1983-1994) and after (1995-2004) implementation of Title IV of the Clean Air Act Amendments of 1990.

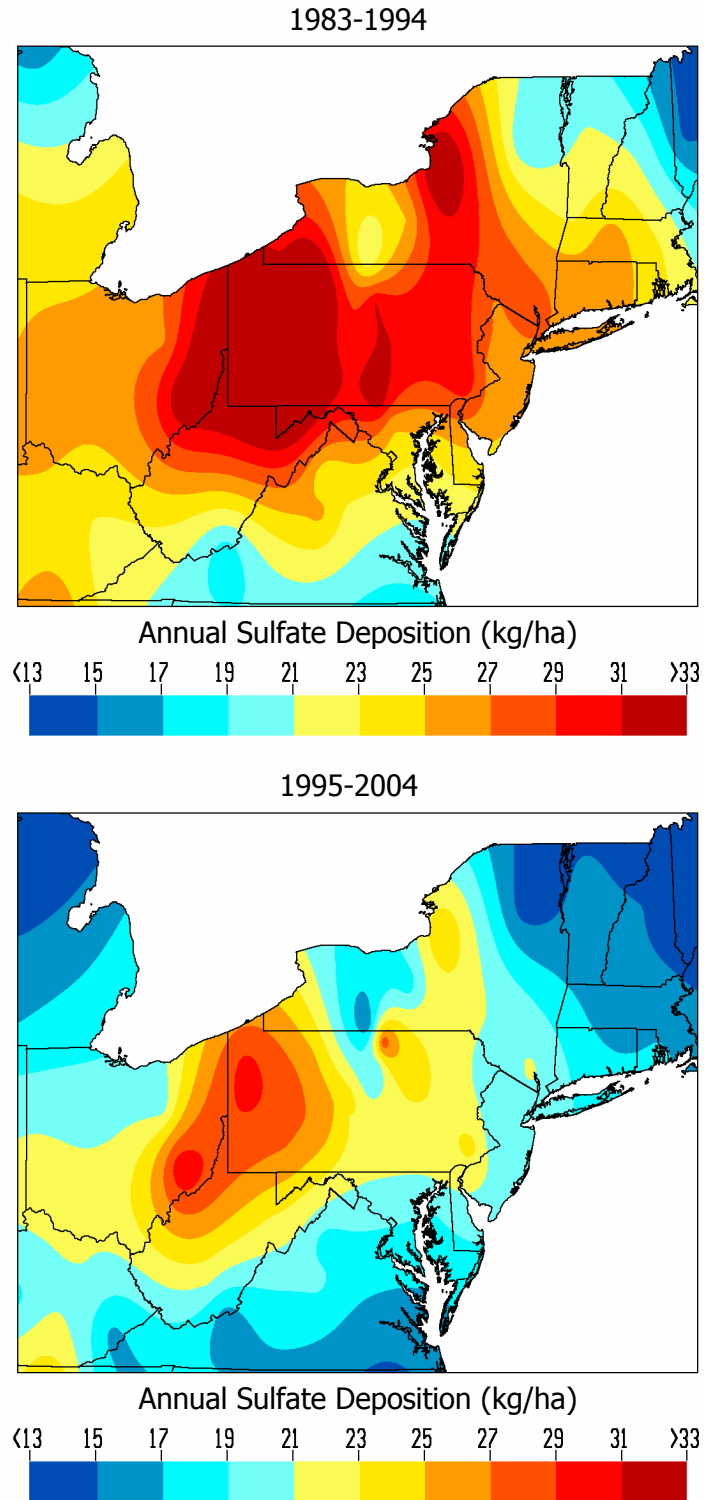


Figure 7. Mean annual sulfate deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2004) implementation of Title IV of the Clean Air Act Amendments of 1990.

Table 2. Comparison of mean annual and seasonal sulfate ion concentrations and depositions at 12 atmospheric deposition monitoring stations in Pennsylvania before (1983-1994) and after (1995-2004) implementation of the Clean Air Act Amendments, Title IV (CAAA).

Site/Region	Sulfate Ion Concentrations (mg/L)								
	Annual			Growing Season			Dormant Season		
	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference
LAURHILL	2.943	2.339	-0.603*	4.022	2.971	-1.050*	1.977	1.727	-0.250*
GODDARD	3.179	2.404	-0.775*	3.957	2.779	-1.178*	2.211	1.965	-0.246*
CROOKCRK	3.558	2.755	-0.803*	4.746	3.474	-1.272*	2.242	1.932	-0.310*
KANE	3.032	2.173	-0.858*	3.909	2.618	-1.291*	2.118	1.689	-0.428*
<b>Western Region</b>	3.178	2.418	-0.760*	4.158	2.960	-1.198*	2.137	1.828	-0.309*
LITTBUFF	2.917	2.244	-0.673*	3.889	2.750	-1.140*	1.982	1.674	-0.308*
HILLSCRK	2.793	1.880	-0.913*	3.659	2.353	-1.306*	1.690	1.236	-0.455*
LEADRIDG	3.036	2.173	-0.864*	4.165	2.642	-1.523*	1.978	1.601	-0.378*
LITTPINE	2.965	2.260	-0.704*	3.894	2.792	-1.101*	1.951	1.645	-0.306*
PSUNADP	2.935	2.123	-0.812*	3.915	2.632	-1.283*	1.939	1.480	-0.458*
<b>Central Region</b>	2.928	2.136	-0.792*	3.904	2.634	-1.270*	1.906	1.527	-0.379*
VALLFORG	2.576	1.869	-0.707*	3.227	2.222	-1.005*	1.919	1.476	-0.443*
MILFORD	2.397	1.586	-0.811*	3.052	1.933	-1.119*	1.762	1.195	-0.567*
SLOCUM	2.797	2.017	-0.780*	3.504	2.559	-0.945*	1.968	1.355	-0.613*
<b>Eastern Region</b>	2.590	1.824	-0.766*	3.261	2.238	-1.023*	1.883	1.342	-0.541*
<b>Statewide</b>	2.927	2.152	-0.775*	3.827	2.644	-1.183*	1.979	1.581	-0.398*

Site/Region	Sulfate Ion Wet Depositions (kg/ha)								
	Annual			Growing Season			Dormant Season		
	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference
LAURHILL	39.132	30.866	-8.267*	25.335	19.547	-5.788*	13.797	11.316	-2.481*
GODDARD	35.841	26.452	-9.389*	24.701	16.952	-7.749*	11.142	9.500	-1.643
CROOKCRK	38.112	30.228	-7.884*	26.751	20.567	-6.184*	11.358	9.661	-1.696
KANE	38.584	25.383	-13.201*	25.792	16.231	-9.561*	12.790	9.151	-3.639*
<b>Western Region</b>	37.917	28.232	-9.685*	25.645	18.324	-7.321*	12.272	9.907	-2.365*
LITTBUFF	31.324	25.570	-5.754*	21.045	16.780	-4.265*	10.278	8.790	-1.488
HILLSCRK	26.186	17.652	-8.534*	19.372	12.758	-6.614*	6.813	4.892	-1.921*
LEADRIDG	32.865	23.178	-9.687*	22.624	15.607	-7.017*	10.238	7.570	-2.668*
LITTPINE	31.004	23.847	-7.157*	21.793	15.995	-5.798*	9.213	7.854	-1.359
PSUNADP	29.401	24.696	-4.705*	20.380	17.260	-3.120	9.019	7.435	-1.584*
<b>Central Region</b>	30.168	22.989	-7.179*	21.053	15.680	-5.373*	9.114	7.308	-1.806*
VALLFORG	30.327	22.539	-7.788*	19.238	14.177	-5.061*	11.090	8.360	-2.730*
MILFORD	28.733	18.943	-9.790*	19.062	12.358	-6.705*	9.671	6.583	-3.088*
SLOCUM	30.880	21.646	-9.234*	21.517	15.188	-6.329*	9.363	6.458	-2.905*
<b>Eastern Region</b>	29.980	21.043	-8.937*	19.939	13.908	-6.031*	10.041	7.134	-2.908*
<b>Statewide</b>	32.758	24.250	-8.508*	22.332	16.118	-6.213*	10.426	8.131	-2.295*

13.20 kg/ha at the Kane NADP/NTN site in Elk County to 4.71 kg/ha at the Penn State NADP/NTN site in Centre County. The ten-year average statewide reduction in sulfate deposition was 8.51 kg/ha. The smallest regional reductions in wet deposition occurred in central Pennsylvania (7.18 kg/ha) despite the fact that reductions in sulfate concentrations (Table 2) were actually greater in central Pennsylvania than other regions of the state. Reductions in central Pennsylvania were about 2.5 kg/ha less than those in western (9.69 kg/ha) and eastern (8.94 kg/ha) portions of Pennsylvania. This discrepancy between changes in concentrations and wet deposition is largely a result of variability in the timing and volume of precipitation across regions and summary periods.

Reductions in wet sulfate deposition during the growing season were significant ( $p < 0.05$ ) at all long-term network sites except the Penn State NADP/NTN site in Centre County. The largest average decrease during the past ten growing seasons (9.56 kg/ha) was measured at the Kane NADP/NTN site; the smallest significant ( $p < 0.05$ ) reduction (4.27 kg/ha) was measured at Little Buffalo State Park in Perry County (Table 2). The average statewide growing season reduction was 6.21 kg/ha. The smallest regional reduction in growing season sulfate deposition was measured in central Pennsylvania (5.37 kg/ha); the largest regional reduction (7.32 kg/ha) was observed in western Pennsylvania.

The average post-CAAA statewide decrease in sulfate deposition during the dormant season was 2.29 kg/ha (Table 2). Although all sites reported lower dormant season sulfate deposition since 1995, the reductions were significant ( $p < 0.05$ ) at only eight of the 12 long-term sites (Table 2). These sites included Hills Creek (1.92 kg/ha), Kane (3.64 kg/ha), Laurel Hill (2.48 kg/ha), Leading Ridge (2.67 kg/ha), Milford (3.09 kg/ha), Penn State (1.58 kg/ha), Slocum (2.91 kg/ha), and Valley Forge (2.73 kg/ha). Interestingly, the greatest regional reduction in sulfate deposition during the dormant season occurred in eastern Pennsylvania. This pattern is consistent with dormant season concentration trends at eastern sites but a departure from growing season sulfate deposition differences since 1995. As noted above, precipitation volume differences between sites as well as year to year variability strongly influence seasonal deposition trends and their significance. For example, significantly lower dormant season sulfate concentrations were evident at all sites since 1995; however, reductions in wet deposition at four sites (M.K. Goddard, Crooked Creek Lake, Little Buffalo, and Little Pine) were not significant ( $p < 0.05$ ). Consequently, when evaluating trends in wet deposition it is important that deviations in precipitation volumes between the pre- and post-CAAA periods as well as between sites and seasons be considered in assessing the impact of reductions in emissions on wet deposition.

Yearly reductions in post-CAAA sulfate concentrations and wet deposition relative to pre-CAAA levels are highly variable. The average annual decrease in sulfate concentrations and deposition over the 10-year post-CAAA period (Table 2) are largely the result of an initial step-function decrease in SO<sub>2</sub> emissions in 1995, followed by another step-function decrease in 1999 and 2000, not a gradual decrease in emissions over the 10-year post-CAAA period. Fluctuations in annual SO<sub>2</sub> emissions since 1995 (Figures 2 and 3) resulted in fluctuations in annual sulfate concentrations and wet deposition. Compounding this relationship is year to year variability in climatic patterns that also influence ionic concentrations and the amount and timing of wet deposition that falls on the Commonwealth.

Trend analyses of pre- and post-CAAA ionic concentrations and wet deposition are shown in Tables 3 and 4, respectively. Clearly, sulfate concentrations at all sites during the pre-CAAA period were decreasing and this trend changed in magnitude and, at some sites, direction since 1995 when SO<sub>2</sub> emission reductions mandated by the CAAA were implemented. At two of the long-term sites (Hills Creek and Slocum), post-CAAA trend analyses indicate that sulfate concentrations have increased over the past ten years, while at the remaining ten sites the pre-CAAA decreasing patterns continued into the post-CAAA period. Although only two of the post-CAAA trend patterns are statistically significant (Laurel Hill and Little Pine), the patterns are fairly consistent with SO<sub>2</sub> emissions (Figures 2 and 3). After the initial reduction in 1995, SO<sub>2</sub> emissions from Title IV affected sources increased until 1998 and did not fall below 1995 levels until 2000. After 2000 sulfur dioxide emissions declined to their lowest level in 2002 before increasing slightly in 2003. Emissions in 2004 were lower than 2003 levels but still slightly higher than 2002 (Figure 2). Increasing SO<sub>2</sub> emissions from 1995 to 1998 followed by a decreasing pattern from 1999 through 2002 has resulted in increasing sulfate concentration patterns during the post-CAAA period at some sites (Table 3). Also contributing to the temporal and spatial patterns is the fact that the impact of emissions and emissions reduction programs on sulfate concentrations are not uniform across the state or region. This latter observation is supported by the fact that pre- and post-CAAA mean annual sulfate concentrations (Table 2) are highly variable across the Commonwealth, differing by more than 1.5 mg/L during both the pre- and post-CAAA periods.

Pre- and post-CAAA wet sulfate deposition trends are even more variable than concentration patterns (Table 4). Pre-CAAA wet deposition patterns are decreasing at 10 of the long-term sites and increasing at two sites (Little Pine in Lycoming County and Crooked Creek Lake in Armstrong County). Post-CAAA trend analyses indicate that the increasing pattern at these sites was reversed, while decreasing pre-CAAA patterns continued at four sites but were reversed at six other sites. The decreasing pattern at Laurel Hill continued during the post-CAAA period and that this pattern is statistically significant ( $p < 0.05$ ). At Hills Creek, Slocum, and Leading Ridge, the post-CAAA trends are increasing and the trends are significant ( $P < 0.05$ ). With four exceptions (Little Buffalo State Park, Penn State, Kane, and Leading Ridge), wet sulfate deposition trends since 1995 are identical to the concentration trends. However, fluctuation in precipitation volumes between and within summary periods has been an influencing factor and the reason for the increasing deposition patterns at the four sites listed above while sulfate concentrations at these sites have decreased the past 10 years. Despite the fact that the average yearly precipitation in Pennsylvania between the pre- and post-CAAA periods is nearly identical, in six of the last 10 years annual precipitation was below the pre-CAAA mean. The four post-CAAA years that precipitation was above the pre-CAAA mean were some of the wettest on record including 2004 which averaged nearly 10 inches (53.37 inches versus 43.96 inches) above the pre-CAAA mean. Such variability in precipitation influences yearly concentration and wet deposition levels as well as trends. Consequently, the post-CAAA trend results should not be interpreted to mean that sulfate concentrations and wet deposition have not changed as a result of the CAAA. Instead they are included to illustrate that the trends between the pre- and post-CAAA periods changed since 1995 and that sulfate concentrations and wet deposition since then have been highly variable, reflecting to a great extent patterns in SO<sub>2</sub> emissions from Title IV

Table 3. Change in trends of ionic concentrations in precipitation in Pennsylvania before (1983-1994) and after (1995-2004) implementation of Title IV of the Clean Air Act Amendments of 1990.

Site	1983-94 trend (%/yr)	1995-2004 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2004 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2004 trend (%/yr)	Change in trends (%/yr)	p	
----- hydrogen ion -----					----- sulfate -----					----- nitrate -----			
CROOKCRK	-1.86	-5.89	-4.04	0.0004	-1.09	-2.62	-1.53	0.1611	-1.64	-4.27	-2.63	0.0295	
GODDARD	-3.11	-3.98	-0.88	0.3650	-1.54	-2.94	-1.40	0.1025	-2.40	-4.90	-2.50	0.0074	
HILLSCRK	-0.91	-1.51	-0.60	0.5605	-0.96	1.35	2.31	0.0663	-1.28	-0.91	0.37	0.7574	
LAURHILL	-2.06	-5.63	-3.57	0.0059	-0.96	-3.69	-2.73	0.0318	-2.16	-4.90	-2.74	0.0256	
LITTBUFF	-4.03	-2.69	1.34	0.3321	-1.80	-0.55	1.25	0.3400	-3.01	-3.65	-0.65	0.6360	
SLOCUM	-1.53	-2.18	-0.65	0.5872	-0.54	1.39	1.93	0.1610	-1.20	-1.38	-0.18	0.8921	
VALLFORG	-1.88	-2.13	-0.25	0.8586	-1.28	-1.27	0.01	0.9952	-2.42	-1.32	1.10	0.4147	
LITTPINE	-0.46	-8.53	-8.07	0.0001	-0.19	-3.95	-3.76	0.0187	-1.57	-6.76	-5.19	0.0014	
PSUNADP	-2.61	-1.61	0.99	0.3877	-2.43	-0.79	1.64	0.2103	-2.55	-2.24	0.31	0.8236	
KANE	-1.66	-2.80	-1.14	0.2390	-1.44	-1.37	0.08	0.9435	-0.59	-3.12	-2.53	0.0235	
LEADRIDG	-1.51	-1.91	-0.40	0.7393	-2.05	-0.21	1.84	0.2039	-1.55	-2.48	-0.93	0.5065	
MILFORD	-1.91	-3.33	-1.43	0.2998	-2.58	-2.25	0.33	0.8134	-1.33	-2.95	-1.62	0.1837	
----- ammonium -----					----- calcium -----					----- magnesium -----			
CROOKCRK	-0.14	-0.92	-0.78	0.5911	-2.38	-0.47	1.91	0.3257	-9.00	0.73	9.73	0.0001	
GODDARD	0.46	-3.18	-3.64	0.0027	-4.53	-1.87	2.66	0.1179	-7.29	-1.98	5.31	0.0067	
HILLSCRK	1.77	2.01	0.25	0.8878	-5.63	2.44	8.06	0.0012	-9.27	4.98	14.25	0.0001	
LAURHILL	0.00	-3.43	-3.43	0.0208	-4.26	-3.13	1.13	0.5997	-8.31	-0.25	8.07	0.0017	
LITTBUFF	1.48	-2.52	-4.00	0.0220	-6.96	0.96	7.91	0.0003	-7.84	-0.53	7.31	0.0032	
SLOCUM	1.77	3.78	2.01	0.2680	-2.72	2.84	5.55	0.0079	-7.98	2.82	10.80	0.0001	
VALLFORG	2.37	-2.36	-4.73	0.0022	-3.81	0.06	3.87	0.0495	-5.86	-9.40	-3.54	0.1166	
LITTPINE	-0.01	-1.40	-1.39	0.4219	-2.23	-4.12	-1.89	0.4014	-4.70	3.58	8.28	0.0008	
PSUNADP	-0.53	0.04	0.56	0.7413	-5.54	-1.52	4.02	0.0251	-7.12	-2.53	4.60	0.0199	
KANE	-0.13	-1.37	-1.24	0.4134	-2.20	-0.73	1.47	0.4015	-5.01	-2.06	2.94	0.1165	
LEADRIDG	-0.89	1.37	2.26	0.2400	-3.47	-1.38	2.10	0.2959	-5.93	-2.22	3.71	0.0852	
MILFORD	0.85	-0.57	-1.42	0.4283	-4.74	0.27	5.00	0.0033	-5.74	-3.39	2.35	0.2181	
----- potassium -----					----- sodium -----					----- chloride -----			
CROOKCRK	0.66	4.94	4.28	0.1918	-1.68	6.93	8.61	0.0019	1.76	-6.46	-8.22	0.0001	
GODDARD	2.04	10.08	8.04	0.0131	-2.36	5.99	8.34	0.0005	0.01	0.95	0.94	0.5165	
HILLSCRK	5.15	10.64	5.48	0.1341	-0.30	7.96	8.26	0.0019	-1.40	1.71	3.11	0.0398	
LAURHILL	4.30	6.55	2.25	0.5282	-1.08	3.76	4.84	0.0768	-0.80	-2.38	-1.58	0.2597	
LITTBUFF	4.27	5.29	1.02	0.7877	-1.87	0.43	2.30	0.3868	-0.39	-2.99	-2.59	0.0982	
SLOCUM	2.55	10.00	7.45	0.0398	-1.78	5.94	7.72	0.0018	0.17	1.52	1.35	0.3746	
VALLFORG	4.55	6.55	2.00	0.5510	-0.28	-10.06	-9.77	0.0002	0.48	-10.14	-10.62	0.0001	
LITTPINE	2.44	13.71	11.26	0.0087	2.22	11.22	9.00	0.0134	0.89	3.15	2.26	0.2319	
PSUNADP	-3.10	-0.19	2.91	0.2781	-3.49	-7.56	-4.07	0.1003	-2.81	-1.96	0.85	0.5586	
KANE	-0.38	-2.30	-1.92	0.4842	-1.53	-7.43	-5.90	0.0039	-1.70	-3.51	-1.82	0.1618	
LEADRIDG	-5.43	-3.97	1.46	0.5996	-3.20	-6.66	-3.46	0.1341	-1.41	-3.26	-1.85	0.2454	
MILFORD	-6.75	-0.78	5.97	0.0259	-0.53	-5.80	-5.27	0.0139	-2.55	-4.16	-1.61	0.3732	

Table 4. Changes in trends of ionic wet deposition in Pennsylvania before (1983-94) and after (1995-2004) implementation of Phase I emission reductions.

site	1983-94 trend (%/yr)	1995-2004 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2004 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2004 trend (%/yr)	Change in trends (%/yr)	p	
----- hydrogen ion -----					----- sulfate -----					----- nitrate -----			
CROOKCRK	-0.50	-4.20	-3.70	0.0077	0.27	-0.87	-1.14	0.3878	-0.24	-2.55	-2.31	0.1167	
GODDARD	-3.43	-1.68	1.76	0.2590	-2.11	-0.61	1.49	0.3102	-2.98	-2.61	0.37	0.7862	
HILLSCRK	-1.62	0.95	2.57	0.1276	-2.14	3.89	6.03	0.0004	-2.46	1.57	4.03	0.0179	
LAURHILL	-1.45	-7.65	-6.20	0.0001	-0.37	-5.76	-5.39	0.0010	-1.56	-6.94	-5.38	0.0002	
LITTBUFF	-4.05	-1.29	2.77	0.0856	-1.85	0.89	2.74	0.0782	-3.03	-2.26	0.76	0.5750	
SLOCUM	-1.46	1.78	3.24	0.0264	-0.48	5.50	5.98	0.0003	-1.10	2.62	3.72	0.0105	
VALLFORG	-2.52	-1.70	0.82	0.6520	-1.93	-0.83	1.10	0.5306	-3.00	-0.88	2.12	0.2223	
LITTPINE	1.39	-5.88	-7.26	0.0001	1.66	-1.17	-2.83	0.0531	0.28	-4.06	-4.34	0.0032	
PSUNADP	-0.41	0.20	0.61	0.7077	-0.23	1.02	1.25	0.4412	-0.35	-0.46	-0.11	0.9438	
KANE	-1.43	-0.73	0.69	0.6265	-1.95	0.71	2.66	0.0636	-1.06	-1.05	0.00	0.9970	
LEADRIDG	-1.34	0.08	1.42	0.3300	-1.88	1.79	3.67	0.0148	-1.37	-0.52	0.85	0.5169	
MILFORD	-0.40	-2.24	-1.84	0.3458	-0.83	-1.15	-0.32	0.8483	-0.09	-1.85	-1.76	0.2411	
----- ammonium -----					----- calcium -----					----- magnesium -----			
CROOKCRK	1.22	0.87	-0.36	0.8337	-1.98	1.32	3.30	0.1388	-8.39	2.53	10.92	0.0001	
GODDARD	-0.32	-0.86	-0.54	0.7484	-3.99	0.49	4.48	0.0177	-7.57	0.38	7.96	0.0003	
HILLSCRK	0.55	4.57	4.02	0.0493	-6.76	5.00	11.76	0.0001	-10.34	7.58	17.92	0.0001	
LAURHILL	0.58	-5.51	-6.08	0.0013	-3.71	-5.21	-1.51	0.4696	-8.55	-2.38	6.17	0.0128	
LITTBUFF	0.86	-1.11	-1.97	0.2337	-6.97	2.42	9.39	0.0005	-7.90	0.92	8.82	0.0041	
SLOCUM	1.85	7.98	6.13	0.0028	-2.58	6.99	9.58	0.0001	-7.91	6.99	14.90	0.0001	
VALLFORG	1.71	-1.93	-3.64	0.0562	-4.29	0.50	4.79	0.0535	-6.00	-8.99	-2.99	0.2971	
LITTPINE	1.86	1.46	-0.40	0.8114	-0.39	-1.34	-0.95	0.6830	-3.99	6.59	10.58	0.0003	
PSUNADP	0.88	1.83	0.95	0.5893	-3.28	0.20	3.48	0.0674	-5.03	-0.72	4.31	0.0396	
KANE	-0.61	0.68	1.30	0.4315	-2.71	1.36	4.07	0.0150	-5.42	0.02	5.44	0.0040	
LEADRIDG	-0.71	3.36	4.07	0.0142	-3.31	0.62	3.93	0.0271	-6.12	-0.26	5.86	0.0031	
MILFORD	2.40	0.53	-1.87	0.3194	-3.27	1.42	4.69	0.0097	-5.09	-2.24	2.85	0.2203	
----- potassium -----					----- sodium -----					----- chloride -----			
CROOKCRK	0.97	6.85	5.89	0.0788	-0.97	8.83	9.80	0.0015	3.15	-4.78	-7.93	0.0001	
GODDARD	1.72	12.78	11.06	0.0023	-2.10	8.52	10.61	0.0004	-0.26	3.38	3.64	0.0808	
HILLSCRK	3.92	13.46	9.53	0.0193	-1.50	10.65	12.15	0.0004	-1.26	4.25	5.51	0.0148	
LAURHILL	2.91	4.23	1.32	0.7235	-0.52	1.53	2.05	0.4715	-0.23	-4.48	-4.25	0.0174	
LITTBUFF	5.27	6.82	1.54	0.7074	-2.23	1.89	4.12	0.1877	-0.68	-1.59	-0.91	0.6088	
SLOCUM	2.62	14.46	11.84	0.0046	-1.69	10.23	11.93	0.0001	0.22	5.64	5.41	0.0056	
VALLFORG	4.72	7.06	2.35	0.5231	-0.40	-9.66	-9.25	0.0040	0.35	-9.74	-10.09	0.0004	
LITTPINE	4.00	17.24	13.24	0.0092	4.08	14.44	10.37	0.0165	2.73	6.14	3.41	0.1547	
PSUNADP	-1.00	1.69	2.69	0.3725	-1.33	-5.89	-4.56	0.1111	-0.63	-0.16	0.47	0.8006	
KANE	-2.45	-0.24	2.21	0.4283	-3.07	-5.49	-2.42	0.3023	-2.23	-1.46	0.77	0.6410	
LEADRIDG	-5.83	-2.03	3.79	0.1547	-3.04	-4.75	-1.70	0.5071	-1.51	-1.28	0.23	0.9057	
MILFORD	-5.56	0.34	5.90	0.0431	0.28	-4.69	-4.97	0.0515	-0.66	-3.04	-2.37	0.2927	

affected sources and climatic variability, particularly the amount and seasonal distribution of precipitation across the state.

**Nitrate** - Like sulfate, mean annual nitrate concentrations have decreased across Pennsylvania since 1995 (Table 5, Figure 8); however, the reductions are statistically significant ( $p < 0.05$ ) at only seven of the long-term monitoring sites (Kane, Hills Creek, Leading Ridge, Penn State, Valley Forge, Slocum, and Milford). The largest statistically significant reduction in mean annual nitrate concentrations (0.400 mg/L) occurred at the Milford site in eastern Pennsylvania. The smallest significant reduction (0.284 mg/L) was measured at the Valley Forge site. With the exception of the Kane site in western Pennsylvania, decreases in mean annual nitrate concentrations since 1995 were larger in the eastern (0.344 mg/L) and central (0.291 mg/L) portions of the state than in the western region (0.215 mg/L). The reductions in concentrations also appear to be larger across the northern tier counties than in the southern half of Pennsylvania.

Although decreasing nitrate concentrations patterns are evident at all sites for both growing and dormant seasons (Table 5), the largest and most statistically significant seasonal reductions occurred during the growing season. The statewide growing season mean concentration was 0.404 mg/L lower the past 10 years than during the previous 13-year pre-CAAA period. At eight sites (Kane, Hills Creek, Leading Ridge, Little Pine, Penn State, Valley Forge, Milford, and Slocum), the reductions are significant ( $p < 0.05$ ). With the exception of Little Pine, these are the same sites that exhibit statistically significant reductions in mean annual nitrate concentrations. The largest significant ( $p < 0.05$ ) reductions during the growing season were measured at the Penn State and Leading Ridge sites (0.569 mg/L) in central Pennsylvania and the Milford site (0.568 mg/L) in Pike County. The smallest significant reduction (0.360 mg/L) was measured at the Slocum site. The smallest overall reduction (0.222 mg/L) was measured at Laurel Hill State Park. Reductions in growing season nitrate concentrations since 1995 were greater in central (0.456 mg/L) and eastern (0.441 mg/L) Pennsylvania and lowest in the western third (0.314 mg/L) of the state (Table 5).

Dormant season nitrate concentrations since 1995 have also been lower than the pre-CAAA reference period; however, the reductions are relatively small and significant ( $p < 0.05$ ) at only the Milford (0.310 mg/L), Slocum (0.405 mg/L), and Hills Creek (0.291 mg/L) sites. Despite the lack of statistically significant reductions at most sites, the central (0.154 mg/L) and eastern (0.306 mg/L) regional means were significantly lower as was the statewide mean reduction of 0.176 mg/L. On a regional basis, changes in dormant season nitrate concentrations since 1995 have been much greater in eastern Pennsylvania than in either the central or western portions of the state (Table 5).

Annual wet nitrate deposition since 1995 has decreased throughout the state (Table 5, Figure 9). Significant ( $p < 0.05$ ) reductions in mean annual nitrate deposition were measured at Kane (5.57 kg/ha), Hills Creek (3.58 kg/ha), Leading Ridge (3.82 kg/ha), Milford (4.87 kg/ha) and Slocum (4.45 kg/ha). Except for Leading Ridge, all of these sites are located in the northern tier counties of the state. Decreases in mean annual nitrate deposition are significant ( $p < 0.05$ ) for all three regions, with the greatest regional reductions occurring in the eastern (4.11 kg/ha) and western



Table 5. Comparison of mean annual and seasonal nitrate ion concentrations and depositions at 12 atmospheric deposition monitoring stations in Pennsylvania before (1983-1994) and after (1995-2004) implementation of the Clean Air Act Amendments, Title IV (CAAA).

Site/Region	Nitrate Ion Concentrations (mg/L)								
	Annual			Growing Season			Dormant Season		
	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference
LAURHILL	1.846	1.720	-0.125	1.949	1.727	-0.222	1.780	1.737	-0.043
GODDARD	2.076	1.888	-0.188	2.188	1.896	-0.291	1.987	1.924	-0.064
CROOKCRK	2.141	1.904	-0.237	2.374	2.016	-0.358	1.899	1.791	-0.108
KANE	1.899	1.590	-0.309*	1.958	1.574	-0.384*	1.850	1.640	-0.210
<b>Western Region</b>	1.990	1.775	-0.215*	2.117	1.803	-0.314*	1.879	1.773	-0.106
LITTBUFF	2.011	1.836	-0.174	2.214	1.915	-0.299	1.877	1.759	-0.118
HILLSCRK	1.851	1.474	-0.377*	1.967	1.504	-0.463*	1.748	1.457	-0.291*
LEADRIDG	2.001	1.677	-0.324*	2.228	1.659	-0.569*	1.828	1.717	-0.110
LITTPINE	2.059	1.836	-0.223	2.185	1.802	-0.383*	1.973	1.904	-0.069
PSUNADP	1.877	1.526	-0.351*	2.135	1.566	-0.569*	1.672	1.500	-0.171
<b>Central Region</b>	1.961	1.670	-0.291*	2.145	1.689	-0.456*	1.822	1.668	-0.154*
VALLFORG	1.718	1.434	-0.284*	1.926	1.530	-0.396*	1.541	1.339	-0.203
MILFORD	1.784	1.384	-0.400*	1.987	1.419	-0.568*	1.666	1.356	-0.310*
SLOCUM	1.954	1.605	-0.349*	2.033	1.674	-0.360*	1.935	1.530	-0.405*
<b>Eastern Region</b>	1.818	1.474	-0.344*	1.982	1.541	-0.441*	1.714	1.408	-0.306*
<b>Statewide</b>	1.935	1.656	-0.278*	2.094	1.690	-0.404*	1.814	1.638	-0.176*

Site/Region	Nitrate Ion Wet Depositions (kg/ha)								
	Annual			Growing Season			Dormant Season		
	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference
LAURHILL	24.615	22.649	-1.966	12.286	11.302	-0.984	12.331	11.347	-0.984
GODDARD	23.435	20.562	-2.873	13.679	11.270	-2.409	9.757	9.295	-0.463
CROOKCRK	22.874	20.705	-2.169	13.327	11.790	-1.537	9.548	8.912	-0.636
KANE	24.014	18.443	-5.571*	12.856	9.605	-3.251*	11.163	8.839	-2.323*
<b>Western Region</b>	23.735	20.590	-3.145*	13.037	10.992	-2.045*	10.700	9.598	-1.102*
LITTBUFF	21.713	20.892	-0.821	12.072	11.718	-0.354	9.640	9.173	-0.467
HILLSCRK	17.346	13.763	-3.583*	10.417	8.005	-2.412*	6.927	5.759	-1.168
LEADRIDG	21.583	17.766	-3.816*	12.128	9.705	-2.423*	9.454	8.060	-1.394*
LITTPINE	21.586	19.298	-2.287	12.310	10.247	-2.063*	9.278	9.050	-0.228
PSUNADP	18.890	17.552	-1.338	11.065	10.097	-0.968	7.824	7.456	-0.368
<b>Central Region</b>	20.246	17.854	-2.392*	11.605	9.954	-1.650*	8.641	7.900	-0.742*
VALLFORG	20.248	17.230	-3.018	11.501	9.708	-1.793	8.745	7.521	-1.224
MILFORD	21.339	16.470	-4.869*	12.387	9.039	-3.349*	8.953	7.432	-1.521*
SLOCUM	21.565	17.119	-4.446*	12.579	9.875	-2.704*	8.989	7.244	-1.745*
<b>Eastern Region</b>	21.051	16.940	-4.111*	12.156	9.541	-2.615*	8.896	7.399	-1.497*
<b>Statewide</b>	21.639	18.537	-3.102*	12.233	10.197	-2.036*	9.407	8.341	-1.066*

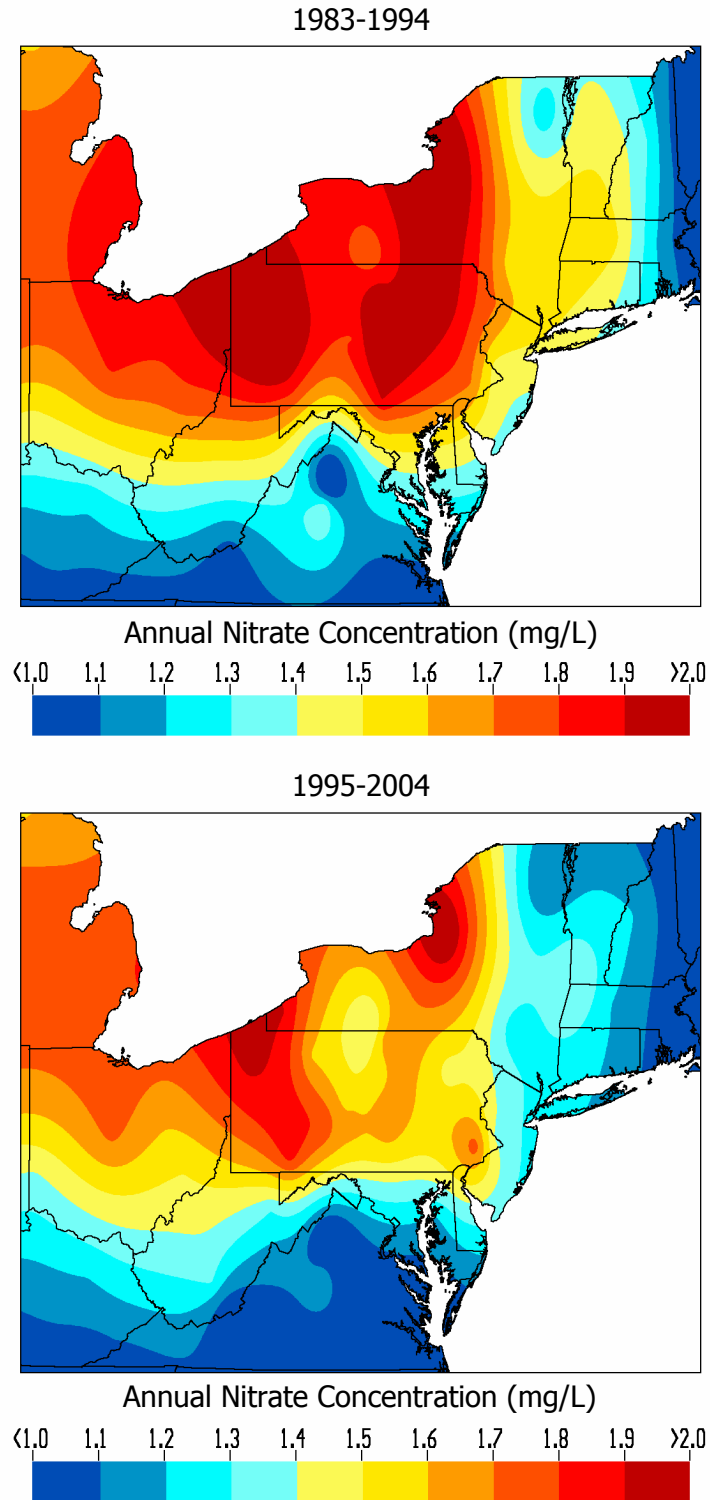


Figure 8. Mean annual nitrate concentrations across Pennsylvania and neighboring states before (1983-1994) and after (1995-2004) implementation of Title IV of the Clean Air Act Amendments of 1990.

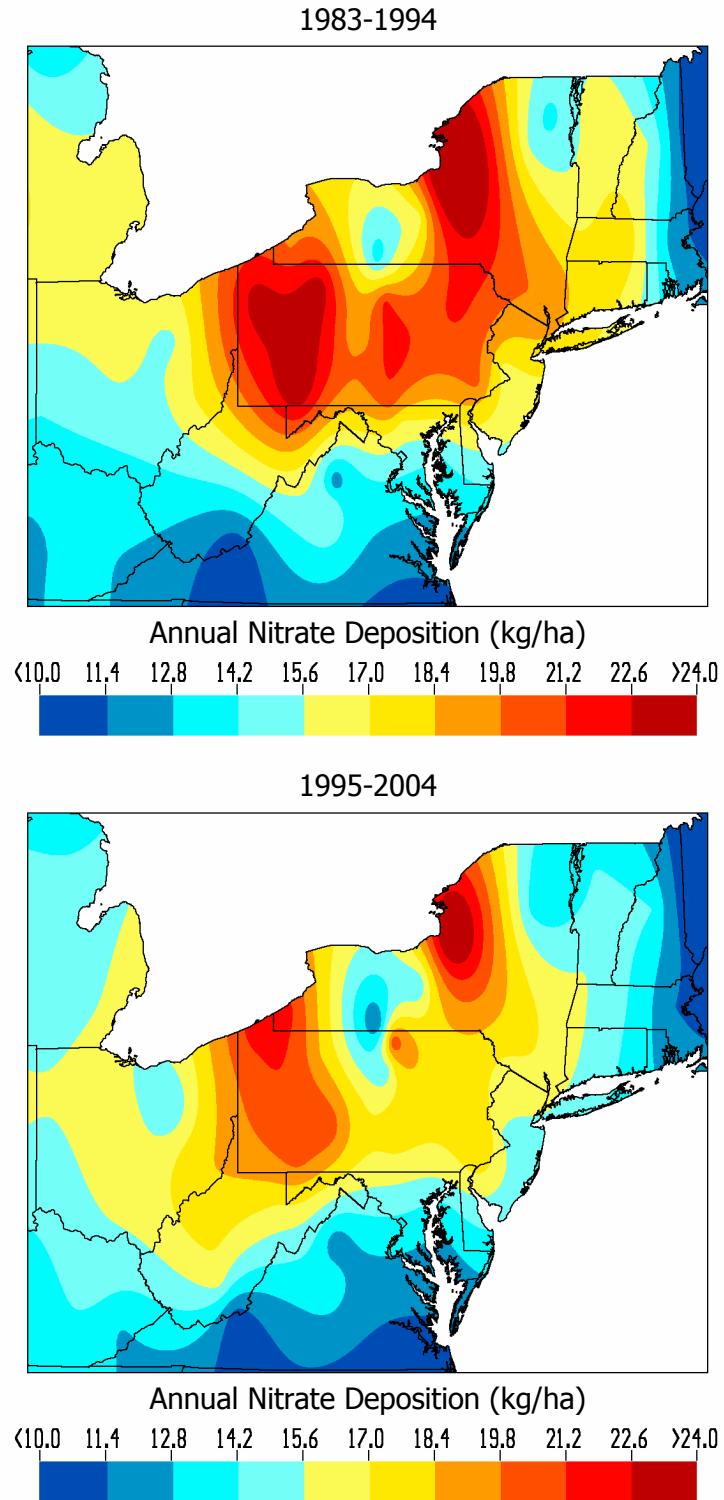


Figure 9. Mean annual nitrate deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2004) implementation of Title IV of the Clean Air Act Amendments of 1990.

(3.15 kg/ha) regions and the state; the reduction in wet nitrate deposition in central Pennsylvania averaged 2.39 kg/ha since 1995 (Table 5).

Like nitrate concentrations, the majority of the decrease in annual nitrate deposition since 1995 occurred during the growing season (Table 5). With two exceptions, significant reductions in mean growing season deposition were measured at each of the sites that reported significantly lower growing season concentrations. The two exceptions include the Penn State and Valley Forge sites where the decrease in growing season nitrate concentrations were significant ( $p < 0.05$ ), although wet deposition levels at these sites were not significantly different from pre-CAAA levels. The largest growing season reduction was measured at the Milford site (3.35 kg/ha); the smallest significant reduction (2.06 kg/ha) was observed at Little Pine. The overall average statewide reduction in growing season nitrate deposition since 1995 was 2.04 kg/ha, which was statistically significant ( $p < 0.05$ ). Significant reductions in growing season deposition were also reported for the western (2.05 kg/ha), central (1.65 kg/ha), and eastern (2.62 kg/ha) regions of Pennsylvania (Table 5).

Dormant season nitrate depositions since 1995 were also lower than the pre-CAAA reference period (Table 5). However, the reductions were much smaller when compared to the growing season and averaged around 1.0 kg/ha. Despite the fact that only four sites (Kane, Leading Ridge, Milford, and Slocum) recorded significantly ( $p < 0.05$ ) lower dormant season nitrate deposition since 1995, the statewide decrease (1.07 kg/ha) as well as the western (1.10 kg/ha), central (0.74 kg/ha) and eastern (1.50 kg/ha) regional mean reductions were significant ( $p < 0.05$ ). The largest reductions in dormant season nitrate deposition occurred at the Kane site (2.32 kg/ha). With the exception of the Leading Ridge site, all of the sites with significant decreasing trends in dormant season nitrate deposition are located in the northern tier counties of the state.

Deviations in pre- and post-CAAA nitrate concentrations and depositions (Table 5) at individual sites and across summary periods reflect to some extent differences in precipitation volumes between pre- and post-CAAA summary periods. Changes in regional nitrate concentrations have been consistently greater in eastern Pennsylvania and decreased to their lowest levels in western Pennsylvania. Regional changes in wet nitrate deposition were also greater in eastern Pennsylvania; however, the smallest changes occurred in central Pennsylvania despite the fact that concentrations changes were greater. This regional inconsistency between changes in pre- and post-CAAA concentrations and depositions results from differences in precipitation volumes between pre- and post-CAAA periods. As indicated earlier, the average annual precipitation across Pennsylvania was nearly the same during both the pre- and post-CAAA periods. This was also the case for the statewide seasonal mean volumes. However, on a regional basis, growing season precipitation during the post-CAAA period in central Pennsylvania was much lower than the pre-CAAA mean, even though precipitation in western and eastern portions of the state were similar for both summary periods. The lower precipitation volumes during the growing season in central Pennsylvania influenced both concentration and deposition levels in this region and contributed to the inconsistency between concentration and deposition reductions between pre- and post-CAAA periods. Regional differences in emission reductions may also be important, although such an analysis is beyond the scope of this report.

Year to year reductions in nitrate concentrations and wet deposition during the post-CAAA period relative to the pre-CAAA reference period are not as variable as was evident for sulfate concentrations and wet depositions (Tables 3 and 4, respectively). The reason for this is that the average annual decrease in nitrate concentrations and depositions over the 10-year post-CAAA period are largely the result of a more consistent and gradual decrease in NO<sub>x</sub> emissions starting around 1996 (Figures 4 and 5) as opposed to the step-function changes that occurred with SO<sub>2</sub> emissions reductions in 1995 and again in 1999-2000. Pre- and post-CAAA trend analyses indicate decreasing patterns in nitrate concentrations at all sites prior to 1995 and that this pattern continued at all sites during the post-CAAA period, with all but three sites (Hills Creek, Valley Forge, and Penn State) exhibiting even greater reductions in nitrate concentrations since 1995 (Table 3). Pre-CAAA nitrate deposition trends were also decreasing at all sites except Little Pine. Post-CAAA analyses indicate that the pre-CAAA decreasing patterns continued during the post-CAAA period, with five sites (Crooked Creek Lake, Laurel Hill, Slocum, Penn State and Milford) exhibiting even greater reductions. Pre- and post-CAAA trend analyses also indicate that the increasing nitrate deposition pattern at Little Pine prior to 1995 was reversed and that nitrate deposition at this site has declined significantly over the past 10 years (Table 4). In contrast, an increasing post-CAAA nitrate deposition trend is evident at Slocum, a statistically significant change from the decreasing pattern that was evident at this site from 1983-1994. Why this pattern occurred at Slocum is unclear but may be related to precipitation patterns between summary periods and/or local emissions.

Although both sulfate and nitrate concentrations and depositions have decreased across the state since 1995, the magnitude of annual, seasonal, and regional reductions for these anions are not the same. For example, decreases in nitrate concentrations, regardless of season, were consistently smallest in western Pennsylvania and generally largest in the eastern region (Table 5). In contrast, no such consistent pattern was evident for sulfate concentrations (Table 2); the smallest dormant season sulfate concentration changes were reported in western Pennsylvania while the smallest drop in growing season sulfate concentrations was observed in eastern Pennsylvania. Since variations in precipitation, would affect both anion concentrations similarly, the seasonal and regional differences between sulfate and nitrate are likely due to seasonal and regional differences in emissions and emissions reduction patterns. The fact that observed changes in wet deposition patterns across the state since 1995 are much more consistent than the concentration patterns tend to support this observation. Reductions in wet nitrate deposition were consistently smallest in the center region and highest in eastern Pennsylvania (Table 5). Reductions in wet sulfate depositions were also consistently smallest in central Pennsylvania; however, the largest seasonal reductions varied with the largest growing season drops occurring in the western region and the largest dormant season reductions occurring in the eastern portion of the state (Table 2).

**Hydrogen Ion (pH)** - The pH of precipitation in Pennsylvania since 1995 has increased (become less acidic, pH higher) throughout the Commonwealth (Table 6, Figure 10). The average increase in mean annual pH at each site relative to the pre-CAAA reference period is statistically significant ( $p < 0.05$ ). The greatest increase in mean annual pH was measured at the Leading Ridge site (0.18 unit); the smallest increase was measured at Laurel Hill State Park (0.11 unit) located in western Pennsylvania. The increase in mean annual pH across the state was 0.15 pH

Table 6. Comparison of mean annual and seasonal pH and hydrogen ion depositions at 12 atmospheric deposition monitoring stations in Pennsylvania before (1983-1994) and after (1995-2004) implementation of the Clean Air Act Amendments, Title IV (CAAA).

Site/Region	pH								
	Annual			Growing Season			Dormant Season		
	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference
LAURHILL	4.156	4.266	0.110*	4.060	4.189	0.129*	4.266	4.360	0.094*
GODDARD	4.148	4.296	0.149*	4.091	4.258	0.167*	4.226	4.347	0.121*
CROOKCRK	4.078	4.195	0.117*	3.995	4.123	0.128*	4.193	4.297	0.104*
KANE	4.162	4.326	0.164*	4.077	4.274	0.197*	4.272	4.394	0.122*
<b>Western Region</b>	4.136	4.271	0.135*	4.056	4.211	0.155*	4.239	4.349	0.110*
LITTBUFF	4.164	4.313	0.150*	4.082	4.261	0.178*	4.262	4.386	0.125*
HILLSCRK	4.184	4.354	0.170*	4.101	4.285	0.184*	4.320	4.472	0.152*
LEADRIDG	4.147	4.325	0.178*	4.042	4.280	0.238*	4.277	4.390	0.113*
LITTPINE	4.135	4.255	0.120*	4.052	4.200	0.148*	4.253	4.330	0.077*
PSUNADP	4.179	4.337	0.158*	4.095	4.273	0.177*	4.286	4.437	0.151*
<b>Central Region</b>	4.161	4.317	0.155*	4.074	4.260	0.186*	4.280	4.403	0.123*
VALLFORG	4.248	4.409	0.161*	4.172	4.355	0.182*	4.345	4.482	0.137*
MILFORD	4.222	4.391	0.169*	4.148	4.344	0.195*	4.316	4.454	0.137*
SLOCUM	4.191	4.341	0.151*	4.129	4.277	0.148*	4.277	4.439	0.162*
<b>Eastern Region</b>	4.220	4.381	0.160*	4.150	4.325	0.175*	4.313	4.458	0.146*
<b>Statewide</b>	4.168	4.318	0.150*	4.087	4.260	0.173*	4.274	4.399	0.125*

Site/Region	Hydrogen Ion Wet Depositions (kg/ha)								
	Annual			Growing Season			Dormant Season		
	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference
LAURHILL	0.947	0.726	-0.221*	0.561	0.437	-0.124*	0.387	0.292	-0.095*
GODDARD	0.820	0.567	-0.253*	0.516	0.342	-0.174*	0.303	0.223	-0.080*
CROOKCRK	0.908	0.710	-0.198*	0.577	0.454	-0.123*	0.330	0.258	-0.072*
KANE	0.902	0.556	-0.346*	0.569	0.337	-0.232*	0.329	0.221	-0.108*
<b>Western Region</b>	0.894	0.640	-0.254*	0.556	0.393	-0.163*	0.337	0.249	-0.089*
LITTBUFF	0.757	0.566	-0.191*	0.469	0.348	-0.121*	0.288	0.216	-0.072*
HILLSCRK	0.623	0.423	-0.200*	0.430	0.286	-0.144*	0.192	0.136	-0.056*
LEADRIDG	0.788	0.508	-0.280*	0.505	0.315	-0.190*	0.282	0.196	-0.086*
LITTPINE	0.780	0.594	-0.186*	0.513	0.370	-0.143*	0.268	0.226	-0.042*
PSUNADP	0.678	0.543	-0.135*	0.429	0.358	-0.071	0.247	0.186	-0.061*
<b>Central Region</b>	0.726	0.527	-0.199*	0.470	0.335	-0.134*	0.256	0.192	-0.064*
VALLFORG	0.678	0.483	-0.195*	0.414	0.292	-0.122*	0.264	0.191	-0.073*
MILFORD	0.733	0.491	-0.242*	0.457	0.298	-0.159*	0.275	0.198	-0.077*
SLOCUM	0.731	0.497	-0.234*	0.470	0.320	-0.150*	0.260	0.176	-0.084*
<b>Eastern Region</b>	0.714	0.490	-0.224*	0.447	0.303	-0.144*	0.266	0.188	-0.078*
<b>Statewide</b>	0.780	0.555	-0.225*	0.493	0.346	-0.147*	0.286	0.210	-0.076*

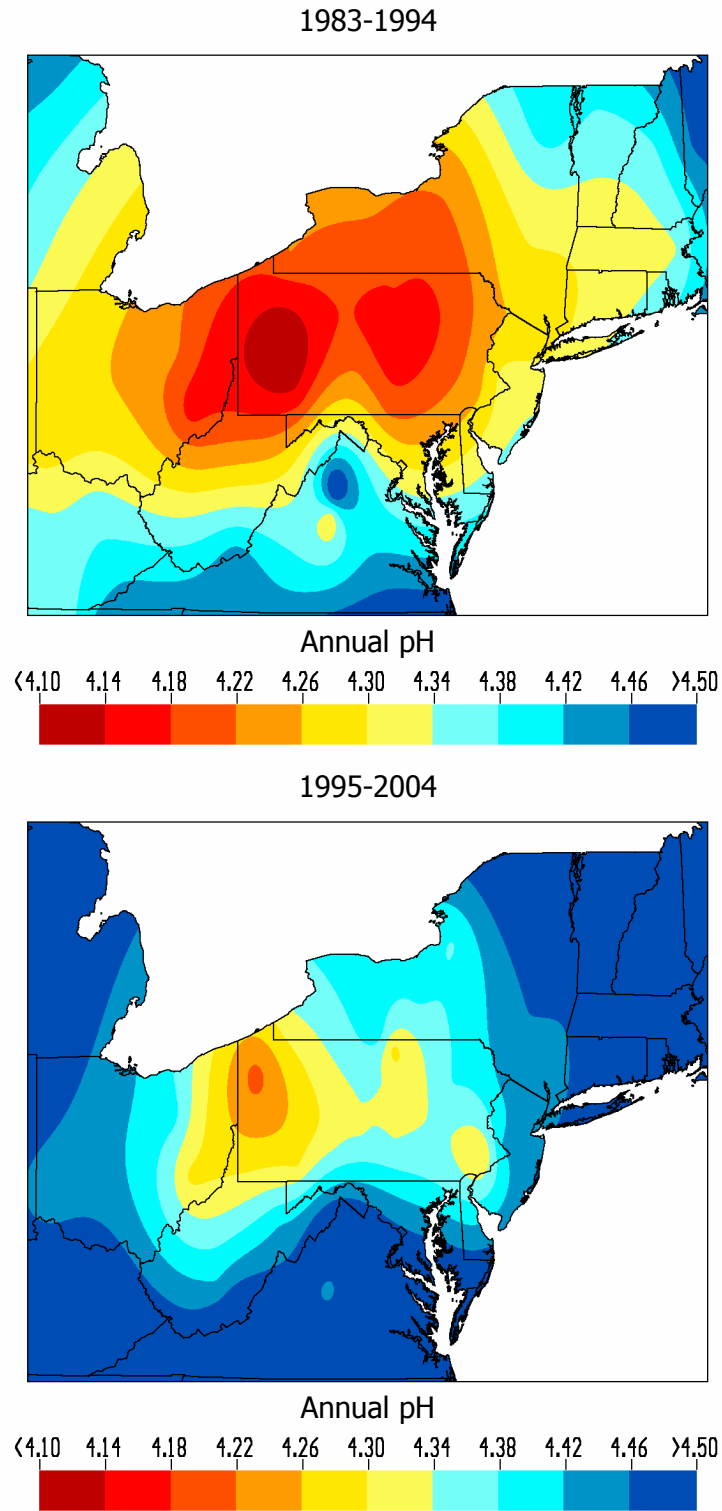


Figure 10. Mean annual pH across Pennsylvania and neighboring states before (1983-1994) and after (1995-2004) implementation of Title IV of the Clean Air Act Amendments of 1990.

unit. On a regional basis, the largest increase in pH was measured in eastern (0.16 unit) and central (0.15 unit) Pennsylvania; the increase in western Pennsylvania was 0.14 unit. The increase in pH across the state is fairly consistent with observed decreases in sulfate concentrations (Table 2) and to a lesser extent nitrate concentrations (Table 5), although fluctuations in ammonium and base cation concentrations exert some influence.

Growing season pH means since 1995 have also increased substantially when compared to the pre-CAAA means (Table 6). All of the increases are statistically significant ( $p < 0.05$ ). The statewide average increase in growing season pH since 1995 was 0.17 pH unit. The increase in mean growing season pH from 4.09 before 1995 to 4.26 after 1995 represents a decrease in  $H^+$  concentrations of nearly 33%. The largest increase in mean growing season pH (0.24 unit) was measured at the Leading Ridge site in Huntingdon County. This change represents a 42% reduction in  $H^+$  concentrations since 1995. Even the relatively small increase in pH at Crooked Creek Lake between the pre- and post-CAAA periods (3.99 versus 4.12) represents a reduction in  $H^+$  concentrations of 26%. Significantly ( $p < 0.05$ ) higher dormant season pH means were also evident at all long-term monitoring sites since 1995 (Table 6). The higher dormant season pH mean differences ranged from 0.16 unit at Slocum to 0.08 unit at Little Pine. The statewide increase in mean dormant season pH was 0.12 unit. Regional increases in post-CAAA dormant season mean pH values were about 0.03 to 0.06 unit lower than measured changes in post-CAAA growing season means. Although the smallest increases in growing and dormant season mean pH were observed in western Pennsylvania, the largest increases varied by season with the highest dormant season increase occurring in eastern Pennsylvania while the highest growing season pH increase was reported in the center region (Table 6). Regional differences between seasons are likely the result of regional and seasonal differences in measured reductions in nitrate (Table 5) and sulfate (Table 2) concentrations, both of which were largest in eastern Pennsylvania during the dormant season. It should also be noted that the increase in mean dormant season pH at Slocum was greater than the increase at this site during the growing season. This increase in pH at the Slocum site is consistent with a relatively large drop in nitrate concentrations at this Luzerne County site (Table 5).

Mean annual wet  $H^+$  deposition has decreased across the entire state with all sites reporting significant ( $p < 0.05$ ) drops since 1995 (Table 6, Figure 11). The largest decreases were measured at Kane (0.35 kg/ha) and Leading Ridge (0.28 kg/ha). The smallest annual decreases were measured at Penn State (0.14 kg/ha), Little Pine (0.19 kg/ha), and Little Buffalo (0.19 kg/ha) all of which are located in central Pennsylvania. On a regional basis, the decrease in annual  $H^+$  deposition was greater in western Pennsylvania (0.25 kg/ha) than either the central (0.20 kg/ha) or eastern (0.22 kg/ha) regions. The statewide mean reduction was 0.22 kg/ha (Table 6). It should be noted that the second largest drop in  $H^+$  deposition occurred in northern Huntingdon County (Leading Ridge), approximately 15 air miles south of the Penn State site in Centre County which recorded the smallest decrease in  $H^+$  deposition over the last 10 years. Difference in local land use patterns (forested versus agriculture/urban), emissions sources and climatic patterns are likely the reasons for the substantial differences over a relatively short distance.

Approximately 65% of the reduction in annual  $H^+$  deposition resulted from higher pH values (lower  $H^+$  concentrations) during the growing season (Table 6). Decreases in mean growing



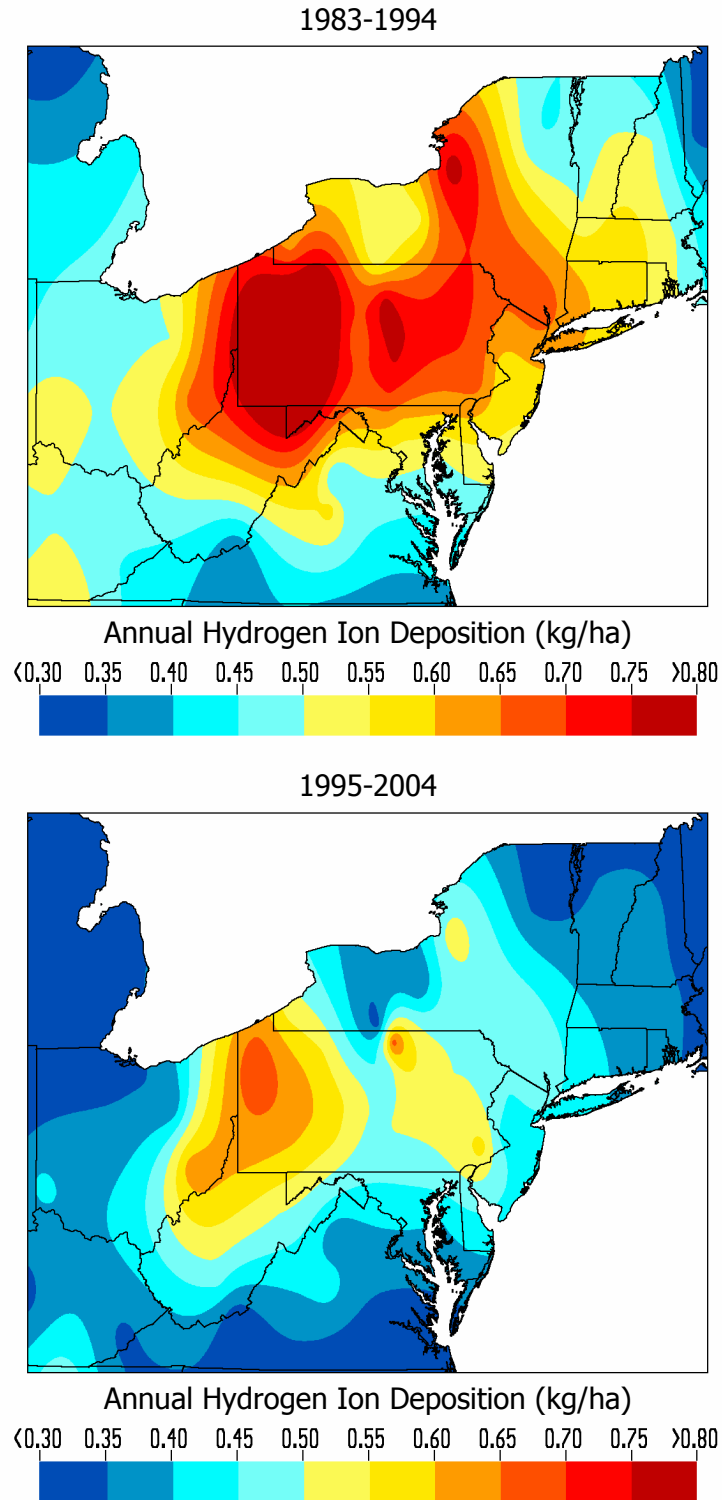


Figure 11. Mean annual hydrogen ion deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2004) implementation of Title IV of the Clean Air Act Amendments of 1990.

season  $H^+$  deposition since 1995 ranged from 0.23 kg/ha at Kane to 0.07 kg/ha at Penn State. All decreases in growing season  $H^+$  deposition since 1995 are significant ( $p < 0.05$ ) except for the Penn State site in Centre County. The statewide decrease in mean growing season  $H^+$  deposition is 0.15 kg/ha; the largest (0.16 kg/ha) and smallest (0.13 kg/ha) regional reductions were observed in western and eastern Pennsylvania, respectively.

Reductions in dormant season  $H^+$  depositions were much smaller than growing season reductions, but still statistically significant at all sites, including the Penn State NADP/NTN site (Table 6). The largest post-CAAA drop in dormant season deposition since 1995 was 0.11 kg/ha at Kane; the smallest decrease (0.04 kg/ha) was measured at the Little Pine site in Lycoming County. The average statewide dormant season reduction in  $H^+$  deposition since 1995 relative to the pre-CAAA reference period was 0.08 kg/ha (Table 6). Regional reductions in dormant season  $H^+$  deposition ranged from 0.06 kg/ha in central Pennsylvania to 0.09 kg/ha in the western third of the state.

The acidity (as measured by pH) of precipitation results from a balance between the acid anions (primarily sulfate and nitrate), the base cations (e.g., calcium, magnesium, etc.) and ammonium concentrations. Consequently, year to year variability in mean annual pH during pre- and post-CAAA years represents a balance between year to year fluctuations in all anion and cation concentrations in precipitation as well as year to year variability in the amount and distribution of precipitation. As a result, post-CAAA trends in  $H^+$  concentrations (Table 3) as well as year to year variability during summary periods tend to reflect the composite changes observed in acid anion and base cation concentrations as well as fluctuations in climatic conditions.

Prior to implementation of the CAAA,  $H^+$  concentrations were decreasing at all sites (Table 3). Since 1995, the decreasing patterns have continued at all sites with the rate of decline at 10 of the 12 sites greater during the post-CAAA period. At the two sites where the rate of decline during the post-CAAA period was smaller than the pre-CAAA period (Little Buffalo and Penn State), post-CAAA nitrate concentrations appear to be the primary reason for the decrease in  $H^+$  concentrations offset somewhat by changes in ammonium and/or base cation concentrations. Ammonium and base cation concentrations in precipitation act to neutralize some of the acidity resulting in a larger net decrease in  $H^+$  concentrations with increasing cation concentrations. Consequently, when evaluating changes in pH or  $H^+$  concentrations over time, changes in both cations and acid anions must be considered since the difference between the sum of these ions determines the change in pH resulting from reductions in emissions. For example, at Little Pine the rather large drop in  $H^+$  concentrations during the post-CAAA period was caused by substantial decreases in sulfate and nitrate concentrations as well as increasing base cation concentrations (Table 3). At Hills Creek, increasing ammonium concentrations were a contributing factor to the continued decline in  $H^+$  concentrations; sulfate and nitrate concentrations also continued to decline during the post-CAAA period by at a very modest rate.

Prior to implementation of the CAAA, wet  $H^+$  deposition was decreasing at all sites except Little Pine. Since 1995, wet  $H^+$  deposition at Little Pine has decreased as has deposition levels of at all other sites, except Slocum and Hills Creek state parks. The post-CAAA trend at Penn State and Leading Ridge NADP/NTN sites is also increasing, but ever so slightly. The increasing pattern

at Slocum is consistent with the increasing trends in sulfate, nitrate, and some cation concentrations at this site since 1995. The statistically significant decrease in  $H^+$  deposition at Little Pine during the post-CAAA period is consistent with statistically significant post-CAAA decreases in  $H^+$  and nitrate concentrations and to a lesser extent sulfate concentrations (Table 3).

A comparison of mean annual and seasonal ionic concentrations in precipitation and wet depositions before (1983-1994) and after (1995-2004) implementation of emissions control requirements under Title IV of the CAAA are listed in Table 7. The “p” values indicate the level of significance with all sites exhibiting very significant reductions in hydrogen, sulfate, and nitrate ion concentrations and wet depositions since 1995. Changes in post-CAAA base cations, ammonium, and chloride concentrations are much smaller and generally not statistically significant. However, their influence on the acidity of precipitation needs to be considered when evaluating the magnitude of spatial patterns and temporal trends in acid rain across Pennsylvania.

### **Summary and Recommendations**

The results presented in this report demonstrate clearly that implementation of Title IV of the Clean Air Act Amendments of 1990 in 1995 has resulted in lower sulfur dioxide emissions in Pennsylvania and upwind states (EPA, 2005b). The reductions in sulfur dioxide have subsequently lowered sulfate concentrations in precipitation throughout the state. The average statewide reduction in sulfate concentrations since 1995 was 0.775 mg/L, a reduction of 34% over the pre-CAAA mean. Concurrent with the drop in sulfate concentrations has been a significant statewide average reduction in wet sulfate deposition of 8.51 kg/ha (26%). Likewise, nitrate concentrations have also decreased across Pennsylvania, with significant drops occurring in most but not all regions of the state. Since 1996, the average statewide decrease in nitrate concentrations and wet deposition were 0.278 mg/L (14.4%) and 3.10 kg/ha (14.3%), respectively. The reductions in nitrate concentrations and wet deposition are a direct response to lower nitrogen oxides emissions in Pennsylvania and neighboring states, particularly from fuel combustion sources (EPA, 2005a). The net affect of the reductions in sulfate and nitrate concentrations in precipitation has been a dramatic and statistically significant ( $p < 0.05$ ) reduction in acid rain across the entire state. The mean annual statewide pH in 2004 based on the 12 long-term monitoring sites was 4.44, an increase of 0.27 pH unit when compared to the pre-CAAA (1983-1994) average pH of 4.17 at these sites. The 0.27 unit increase represents a decrease of hydrogen ion concentrations of approximately 46%. The average reduction in pH at the 12 long-term monitoring sites during the entire post-CAAA period (1995-2004) was 0.15 unit (pre-CAAA pH of 4.17 versus a post-CAAA pH of 4.32) which resulted in a 29% reduction in hydrogen ion concentrations in precipitation. Changes in base cation and ammonium concentrations have also influenced the post-CAAA acidity at some sites although their overall influence has been relatively small from a statewide prospective.

The changes in sulfate and nitrate concentrations over the past 23 years, particularly since 1995, are even more remarkable given that between 1970 and 2002 (the last year for which data are available), gross domestic products in the United States increased 164 percent, vehicle miles traveled increased 155 percent, energy production increased 42 percent, and the population increased 38 percent. At the same time, total emissions of six primary pollutants (nitrogen

Table 7. Comparison of mean annual and seasonal concentrations of precipitation and wet depositions before (1983-1994) and after (1995-2004) implementation of the Clean Air Act Amendment emission controls.

Site	Hydrogen Ion																	
	Annual						Growing Season						Dormant Season					
	pH			Deposition (kg/ha)			pH			Deposition (kg/ha)			pH			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	4.078	4.195	0.0005	0.908	0.710	0.0008	3.995	4.123	0.0016	0.577	0.454	0.0076	4.192	4.297	0.0007	0.330	0.258	0.0055
GODDARD	4.148	4.296	0.0001	0.820	0.567	0.0005	4.091	4.258	0.0001	0.516	0.342	0.0025	4.226	4.347	0.0006	0.303	0.223	0.0041
HI LLSCRK	4.184	4.354	0.0001	0.623	0.423	0.0001	4.101	4.285	0.0001	0.430	0.286	0.0001	4.320	4.472	0.0001	0.193	0.136	0.0016
KANE	4.162	4.326	0.0001	0.902	0.556	0.0001	4.077	4.274	0.0001	0.569	0.337	0.0003	4.272	4.394	0.0001	0.329	0.221	0.0001
LAURHILL	4.156	4.266	0.0007	0.947	0.726	0.0028	4.060	4.189	0.0032	0.561	0.437	0.0131	4.266	4.360	0.0022	0.387	0.292	0.0044
LEADRIDG	4.147	4.325	0.0001	0.787	0.508	0.0001	4.042	4.280	0.0001	0.505	0.315	0.0001	4.277	4.390	0.0023	0.282	0.196	0.0004
LI TTBUFF	4.164	4.313	0.0004	0.757	0.566	0.0060	4.082	4.261	0.0015	0.469	0.348	0.0113	4.262	4.386	0.0004	0.288	0.216	0.0225
LI TTPINE	4.135	4.255	0.0008	0.780	0.594	0.0002	4.052	4.200	0.0033	0.513	0.370	0.0003	4.253	4.330	0.0068	0.268	0.226	0.0351
MI LFORD	4.222	4.391	0.0001	0.733	0.491	0.0001	4.148	4.344	0.0001	0.457	0.298	0.0001	4.316	4.454	0.0007	0.275	0.198	0.0110
PSUNADP	4.179	4.337	0.0001	0.678	0.543	0.0122	4.095	4.272	0.0004	0.429	0.358	0.0973	4.286	4.437	0.0001	0.247	0.186	0.0037
SLOCUM	4.191	4.341	0.0001	0.731	0.497	0.0001	4.129	4.277	0.0014	0.470	0.320	0.0005	4.277	4.439	0.0009	0.260	0.176	0.0006
VALLFORG	4.248	4.409	0.0002	0.678	0.483	0.0005	4.172	4.355	0.0021	0.414	0.292	0.0026	4.345	4.482	0.0002	0.264	0.191	0.0205

Site	Sulfate																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	3.558	2.755	0.0001	38.112	30.228	0.0012	4.746	3.474	0.0001	26.751	20.567	0.0067	2.242	1.932	0.0290	11.358	9.661	0.0665
GODDARD	3.179	2.404	0.0001	35.841	26.452	0.0008	3.957	2.779	0.0001	24.701	16.952	0.0021	2.211	1.965	0.0332	11.143	9.500	0.0679
HI LLSCRK	2.793	1.880	0.0001	26.186	17.652	0.0001	3.659	2.353	0.0001	19.372	12.758	0.0001	1.690	1.236	0.0001	6.813	4.892	0.0068
KANE	3.032	2.173	0.0001	38.584	25.383	0.0001	3.909	2.618	0.0001	25.793	16.231	0.0001	2.118	1.689	0.0001	12.790	9.151	0.0001
LAURHILL	2.943	2.339	0.0001	39.133	30.866	0.0003	4.022	2.972	0.0001	25.335	19.547	0.0028	1.977	1.727	0.0171	13.798	11.316	0.0197
LEADRIDG	3.036	2.173	0.0001	32.865	23.178	0.0001	4.165	2.642	0.0001	22.624	15.607	0.0001	1.978	1.601	0.0051	10.238	7.570	0.0002
LI TTBUFF	2.917	2.244	0.0002	31.324	25.570	0.0031	3.889	2.750	0.0016	21.045	16.780	0.0020	1.982	1.674	0.0009	10.278	8.790	0.1728
LI TTPINE	2.965	2.260	0.0004	31.005	23.847	0.0003	3.894	2.792	0.0014	21.793	15.995	0.0004	1.951	1.645	0.0197	9.213	7.854	0.0579
MI LFORD	2.397	1.586	0.0001	28.733	18.943	0.0001	3.052	1.933	0.0001	19.063	12.358	0.0001	1.762	1.195	0.0003	9.671	6.583	0.0020
PSUNADP	2.935	2.123	0.0001	29.401	24.696	0.0205	3.915	2.632	0.0001	20.380	17.260	0.0497	1.939	1.480	0.0009	9.019	7.435	0.0196
SLOCUM	2.798	2.017	0.0001	30.880	21.646	0.0001	3.504	2.559	0.0010	21.517	15.188	0.0005	1.968	1.355	0.0011	9.363	6.458	0.0039
VALLFORG	2.576	1.869	0.0001	30.327	22.539	0.0002	3.227	2.222	0.0005	19.238	14.177	0.0006	1.919	1.476	0.0004	11.090	8.360	0.0399

Site	Nitrate																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	2.141	1.904	0.0916	22.874	20.705	0.1227	2.374	2.016	0.0464	13.327	11.790	0.1612	1.899	1.791	0.4059	9.548	8.912	0.3646
GODDARD	2.076	1.888	0.1745	23.435	20.562	0.0966	2.188	1.896	0.0799	13.679	11.270	0.0771	1.987	1.924	0.7227	9.758	9.295	0.3584
HI LLSCRK	1.851	1.474	0.0041	17.346	13.763	0.0033	1.967	1.504	0.0070	10.418	8.005	0.0021	1.748	1.457	0.0236	6.928	5.759	0.0670
KANE	1.899	1.590	0.0100	24.014	18.443	0.0003	1.958	1.574	0.0114	12.856	9.605	0.0013	1.850	1.640	0.0642	11.163	8.839	0.0032
LAURHILL	1.846	1.720	0.3107	24.615	22.649	0.3318	1.949	1.727	0.1212	12.286	11.302	0.3472	1.780	1.737	0.8774	12.331	11.347	0.4575
LEADRIDG	2.001	1.677	0.0035	21.583	17.766	0.0031	2.228	1.659	0.0003	12.128	9.705	0.0068	1.828	1.718	0.4215	9.454	8.060	0.0137
LI TTBUFF	2.011	1.836	0.1883	21.713	20.892	0.5971	2.214	1.915	0.1637	12.072	11.718	0.6171	1.877	1.759	0.4194	9.640	9.173	0.7757
LI TTPINE	2.059	1.836	0.0684	21.585	19.298	0.0767	2.185	1.802	0.0461	12.310	10.247	0.0288	1.973	1.904	0.6483	9.278	9.050	0.6490
MI LFORD	1.784	1.384	0.0004	21.339	16.470	0.0009	1.987	1.419	0.0008	12.388	9.039	0.0006	1.666	1.356	0.0441	8.953	7.432	0.0303
PSUNADP	1.877	1.526	0.0030	18.890	17.552	0.2054	2.135	1.566	0.0034	11.065	10.097	0.1921	1.672	1.500	0.1065	7.824	7.456	0.5071
SLOCUM	1.954	1.605	0.0159	21.565	17.119	0.0021	2.033	1.674	0.0220	12.579	9.875	0.0116	1.935	1.530	0.0633	8.989	7.244	0.0277
VALLFORG	1.718	1.434	0.0259	20.248	17.230	0.0500	1.926	1.530	0.0414	11.501	9.708	0.0767	1.541	1.339	0.1236	8.745	7.521	0.2525

Table 7 (continued).

Site	Ammonium																	
	Annual			Growing Season			Dormant Season											
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)								
Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	
CROOKCRK	0.325	0.329	0.8652	3.478	3.605	0.6067	0.402	0.375	0.2476	2.257	2.248	0.9218	0.243	0.275	0.2706	1.220	1.356	0.2547
GODDARD	0.379	0.391	0.6329	4.282	4.292	0.9912	0.454	0.436	0.6101	2.857	2.640	0.5210	0.290	0.343	0.0841	1.425	1.653	0.0831
HI LLSCRK	0.284	0.271	0.4273	2.667	2.560	0.5648	0.349	0.319	0.1662	1.875	1.735	0.4171	0.203	0.207	0.8844	0.789	0.824	0.8049
KANE	0.292	0.260	0.1036	3.694	3.051	0.0213	0.354	0.288	0.0369	2.317	1.793	0.0195	0.230	0.232	0.9305	1.376	1.259	0.3648
LAURHI LL	0.292	0.322	0.0562	3.908	4.255	0.2148	0.329	0.352	0.2418	2.082	2.354	0.2469	0.264	0.292	0.2303	1.825	1.901	0.5147
LEADRI DG	0.300	0.277	0.2661	3.233	2.947	0.1936	0.379	0.307	0.0288	2.056	1.813	0.1754	0.228	0.241	0.4803	1.178	1.133	0.5661
LI TTBUFF	0.375	0.417	0.0648	4.043	4.763	0.0455	0.466	0.481	0.7170	2.540	2.952	0.1336	0.301	0.347	0.0570	1.503	1.811	0.0165
LI TTPI NE	0.310	0.325	0.4537	3.254	3.453	0.5135	0.377	0.367	0.7451	2.135	2.135	0.9474	0.243	0.277	0.2045	1.122	1.317	0.0902
MI LFORD	0.213	0.207	0.7203	2.545	2.494	0.7496	0.277	0.247	0.2050	1.728	1.608	0.3943	0.152	0.160	0.5732	0.817	0.886	0.4537
PSUNADP	0.278	0.260	0.4283	2.776	3.007	0.4265	0.360	0.298	0.1101	1.866	1.947	0.7931	0.196	0.214	0.2564	0.911	1.060	0.0497
SLOCUM	0.302	0.322	0.4327	3.334	3.461	0.7210	0.368	0.398	0.4118	2.275	2.368	0.7704	0.231	0.230	0.9824	1.061	1.095	0.7660
VALLFORG	0.293	0.321	0.1728	3.435	3.889	0.1063	0.359	0.375	0.6407	2.138	2.403	0.1991	0.234	0.261	0.2179	1.298	1.484	0.1876

Site	Calcium																	
	Annual			Growing Season			Dormant Season											
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)								
Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	
CROOKCRK	0.175	0.157	0.2961	1.849	1.720	0.3673	0.206	0.171	0.1331	1.130	1.013	0.2414	0.142	0.143	0.9230	0.720	0.709	0.9459
GODDARD	0.181	0.159	0.2427	2.013	1.739	0.2035	0.209	0.168	0.1085	1.285	0.998	0.0842	0.150	0.154	0.8217	0.726	0.743	0.8414
HI LLSCRK	0.109	0.094	0.2652	1.017	0.891	0.3657	0.130	0.096	0.1278	0.675	0.515	0.1068	0.087	0.092	0.7381	0.343	0.377	0.6988
KANE	0.123	0.108	0.1531	1.551	1.251	0.0132	0.135	0.112	0.0958	0.879	0.674	0.0029	0.112	0.107	0.6874	0.673	0.577	0.2194
LAURHI LL	0.125	0.131	0.6039	1.659	1.717	0.7283	0.140	0.132	0.5771	0.880	0.862	0.8428	0.112	0.132	0.2129	0.777	0.858	0.4142
LEADRI DG	0.123	0.103	0.0524	1.317	1.100	0.0493	0.144	0.104	0.0029	0.783	0.606	0.0068	0.105	0.103	0.9408	0.537	0.494	0.4941
LI TTBUFF	0.138	0.107	0.0434	1.497	1.246	0.2217	0.154	0.121	0.0712	0.852	0.751	0.3418	0.129	0.093	0.1442	0.647	0.494	0.2489
LI TTPI NE	0.109	0.108	0.9352	1.140	1.162	0.9815	0.120	0.112	0.5460	0.671	0.647	0.6842	0.102	0.106	0.7563	0.468	0.514	0.6314
MI LFORD	0.092	0.072	0.0454	1.099	0.860	0.0386	0.096	0.071	0.0064	0.603	0.453	0.0064	0.092	0.074	0.2149	0.498	0.406	0.2431
PSUNADP	0.120	0.099	0.1264	1.194	1.145	0.7135	0.144	0.099	0.0049	0.768	0.645	0.2499	0.092	0.100	0.4794	0.424	0.502	0.1527
SLOCUM	0.107	0.091	0.0918	1.171	0.994	0.0812	0.121	0.098	0.1027	0.738	0.584	0.0449	0.093	0.085	0.4014	0.434	0.410	0.5723
VALLFORG	0.134	0.090	0.0018	1.577	1.104	0.0064	0.136	0.091	0.0048	0.807	0.596	0.0178	0.136	0.088	0.0278	0.768	0.509	0.0590

Site	Magnesium																	
	Annual			Growing Season			Dormant Season											
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)								
Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	
CROOKCRK	0.034	0.030	0.5195	0.358	0.330	0.6483	0.040	0.033	0.3417	0.219	0.195	0.5033	0.028	0.027	0.9273	0.138	0.134	0.9229
GODDARD	0.035	0.030	0.3251	0.392	0.322	0.2517	0.041	0.031	0.1501	0.257	0.183	0.1255	0.028	0.029	0.7493	0.136	0.140	0.7857
HI LLSCRK	0.028	0.019	0.0874	0.263	0.180	0.1126	0.034	0.020	0.0669	0.177	0.106	0.0587	0.021	0.018	0.4336	0.085	0.074	0.5721
KANE	0.023	0.016	0.0019	0.291	0.191	0.0004	0.025	0.018	0.0076	0.166	0.106	0.0010	0.021	0.016	0.0224	0.125	0.084	0.0039
LAURHI LL	0.026	0.023	0.3968	0.348	0.303	0.3107	0.030	0.023	0.1215	0.185	0.148	0.1055	0.023	0.024	0.9104	0.165	0.156	0.7891
LEADRI DG	0.025	0.017	0.0051	0.268	0.183	0.0062	0.029	0.018	0.0008	0.160	0.108	0.0031	0.021	0.016	0.0938	0.108	0.078	0.0586
LI TTBUFF	0.031	0.028	0.4729	0.351	0.321	0.7104	0.032	0.030	0.7452	0.182	0.191	0.8501	0.032	0.024	0.2410	0.169	0.129	0.3829
LI TTPI NE	0.023	0.022	0.7830	0.246	0.241	0.8724	0.025	0.023	0.4701	0.143	0.131	0.6638	0.022	0.023	0.6951	0.101	0.110	0.5539
MI LFORD	0.030	0.018	0.0063	0.358	0.216	0.0158	0.028	0.016	0.0037	0.172	0.107	0.0077	0.033	0.019	0.0152	0.185	0.110	0.0611
PSUNADP	0.021	0.015	0.0062	0.215	0.176	0.0913	0.025	0.016	0.0006	0.133	0.106	0.1100	0.018	0.014	0.1241	0.081	0.069	0.2562
SLOCUM	0.027	0.021	0.0882	0.303	0.224	0.0832	0.031	0.022	0.1181	0.188	0.131	0.0663	0.025	0.019	0.2036	0.116	0.092	0.2120
VALLFORG	0.057	0.040	0.0303	0.676	0.514	0.1238	0.053	0.040	0.1508	0.314	0.275	0.4231	0.062	0.040	0.0078	0.362	0.239	0.0833

Table 7 (continued).

Site	Potassium																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.038	0.049	0.1246	0.403	0.552	0.1196	0.046	0.054	0.4721	0.258	0.319	0.3055	0.029	0.046	0.0301	0.145	0.239	0.0406
GODDARD	0.034	0.045	0.0411	0.384	0.489	0.1257	0.036	0.040	0.5244	0.230	0.241	0.8091	0.031	0.050	0.0021	0.152	0.247	0.0077
HI LLS CRK	0.036	0.045	0.3343	0.332	0.436	0.2361	0.044	0.047	0.8164	0.219	0.260	0.5004	0.030	0.044	0.1038	0.113	0.176	0.0680
KANE	0.030	0.020	0.0461	0.379	0.228	0.0103	0.044	0.025	0.0331	0.285	0.146	0.0131	0.015	0.015	0.9414	0.094	0.083	0.5348
LAURHI LL	0.042	0.053	0.1630	0.572	0.706	0.2400	0.051	0.060	0.3943	0.326	0.389	0.3859	0.034	0.048	0.1287	0.246	0.317	0.2612
LEADRI DG	0.037	0.026	0.0744	0.399	0.276	0.0452	0.047	0.038	0.3426	0.259	0.211	0.3547	0.028	0.013	0.0068	0.142	0.063	0.0010
LI TTBUFF	0.038	0.067	0.0184	0.426	0.768	0.0227	0.046	0.079	0.0725	0.258	0.489	0.0404	0.033	0.052	0.0318	0.168	0.277	0.0344
LI TTPI NE	0.032	0.045	0.0909	0.344	0.494	0.1516	0.030	0.043	0.1338	0.170	0.271	0.1500	0.035	0.046	0.2821	0.174	0.224	0.3936
MI LFORD	0.022	0.018	0.0509	0.269	0.226	0.1455	0.027	0.023	0.3081	0.168	0.155	0.5921	0.018	0.013	0.0211	0.101	0.073	0.0493
PSUNADP	0.033	0.020	0.1805	0.330	0.240	0.3662	0.050	0.027	0.1059	0.271	0.185	0.3849	0.012	0.011	0.1758	0.058	0.054	0.5488
SLOCUM	0.046	0.049	0.7592	0.508	0.536	0.7570	0.055	0.054	0.9483	0.349	0.337	0.8897	0.035	0.042	0.4171	0.160	0.201	0.3287
VALLFORG	0.041	0.049	0.3399	0.477	0.612	0.2602	0.045	0.047	0.8433	0.271	0.314	0.5130	0.037	0.051	0.2045	0.205	0.297	0.1678
Site	Sodium																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.052	0.063	0.1024	0.560	0.711	0.0996	0.043	0.053	0.1492	0.242	0.325	0.1335	0.062	0.076	0.2185	0.316	0.387	0.2605
GODDARD	0.052	0.067	0.0159	0.583	0.736	0.0459	0.045	0.048	0.6754	0.264	0.304	0.5466	0.066	0.090	0.0198	0.322	0.433	0.0071
HI LLS CRK	0.043	0.052	0.1682	0.402	0.503	0.1283	0.041	0.044	0.7390	0.201	0.252	0.3128	0.052	0.062	0.2762	0.201	0.250	0.2033
KANE	0.053	0.037	0.0053	0.673	0.442	0.0019	0.044	0.031	0.0040	0.289	0.192	0.0048	0.064	0.046	0.0395	0.385	0.251	0.0119
LAURHI LL	0.049	0.064	0.0105	0.647	0.861	0.0317	0.033	0.055	0.0064	0.214	0.374	0.0119	0.062	0.074	0.1996	0.434	0.485	0.4355
LEADRI DG	0.070	0.048	0.0098	0.754	0.540	0.0245	0.056	0.037	0.0059	0.311	0.231	0.1058	0.088	0.063	0.1334	0.443	0.308	0.0476
LI TTBUFF	0.079	0.092	0.1113	0.869	1.065	0.1505	0.059	0.073	0.1673	0.347	0.466	0.1646	0.101	0.115	0.2694	0.524	0.599	0.3543
LI TTPI NE	0.053	0.065	0.0967	0.572	0.688	0.2325	0.038	0.058	0.0898	0.223	0.344	0.1178	0.072	0.071	0.9518	0.350	0.345	0.9485
MI LFORD	0.119	0.094	0.0930	1.416	1.163	0.1633	0.080	0.063	0.0811	0.520	0.407	0.1497	0.166	0.130	0.1857	0.897	0.758	0.3238
PSUNADP	0.059	0.043	0.0080	0.599	0.511	0.2253	0.048	0.032	0.0067	0.257	0.220	0.3954	0.072	0.058	0.0927	0.342	0.291	0.2992
SLOCUM	0.082	0.066	0.2544	0.890	0.723	0.2092	0.064	0.055	0.5920	0.388	0.344	0.7070	0.108	0.079	0.0740	0.502	0.378	0.0554
VALLFORG	0.195	0.161	0.1912	2.324	2.105	0.4376	0.108	0.114	0.7039	0.651	0.791	0.3554	0.286	0.216	0.0745	1.673	1.312	0.2013
Site	Chloride																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.287	0.292	0.8900	3.086	3.170	0.7336	0.285	0.244	0.3939	1.600	1.428	0.5887	0.294	0.347	0.1666	1.487	1.742	0.2120
GODDARD	0.188	0.199	0.5064	2.118	2.164	0.9100	0.177	0.178	0.9331	1.060	1.043	0.8310	0.212	0.234	0.2387	1.059	1.122	0.4772
HI LLS CRK	0.176	0.157	0.3547	1.650	1.474	0.3935	0.191	0.152	0.3066	0.971	0.818	0.3484	0.168	0.163	0.7677	0.680	0.657	0.7976
KANE	0.150	0.111	0.0001	1.911	1.300	0.0001	0.135	0.101	0.0001	0.899	0.629	0.0027	0.168	0.124	0.0004	1.012	0.671	0.0001
LAURHI LL	0.208	0.208	0.9659	2.800	2.755	0.9337	0.193	0.205	0.6008	1.236	1.372	0.4330	0.227	0.213	0.7747	1.565	1.384	0.5737
LEADRI DG	0.178	0.131	0.0008	1.910	1.426	0.0061	0.166	0.120	0.0005	0.917	0.733	0.0961	0.196	0.145	0.0471	0.996	0.693	0.0035
LI TTBUFF	0.236	0.247	0.4823	2.566	2.811	0.3010	0.226	0.218	0.7775	1.275	1.341	0.5997	0.254	0.283	0.2318	1.289	1.469	0.1724
LI TTPI NE	0.192	0.189	0.8326	2.046	1.999	0.8539	0.179	0.184	0.7762	1.024	1.064	0.7012	0.210	0.195	0.3485	1.023	0.937	0.5568
MI LFORD	0.239	0.185	0.0230	2.864	2.283	0.0677	0.192	0.139	0.0038	1.231	0.896	0.0253	0.304	0.240	0.1387	1.633	1.386	0.2405
PSUNADP	0.164	0.125	0.0002	1.658	1.465	0.1545	0.159	0.110	0.0004	0.841	0.732	0.2530	0.174	0.146	0.0422	0.816	0.731	0.2664
SLOCUM	0.212	0.184	0.1639	2.327	1.985	0.0873	0.199	0.183	0.5444	1.204	1.077	0.3205	0.238	0.190	0.0808	1.122	0.908	0.1052
VALLFORG	0.415	0.387	0.5756	4.883	4.993	0.7720	0.293	0.333	0.4904	1.778	2.259	0.3219	0.538	0.450	0.2120	3.103	2.736	0.3728

oxides, ozone, sulfur dioxide, particulate matter, carbon monoxide, and lead) decreased 48 percent (EPA, 2005a).

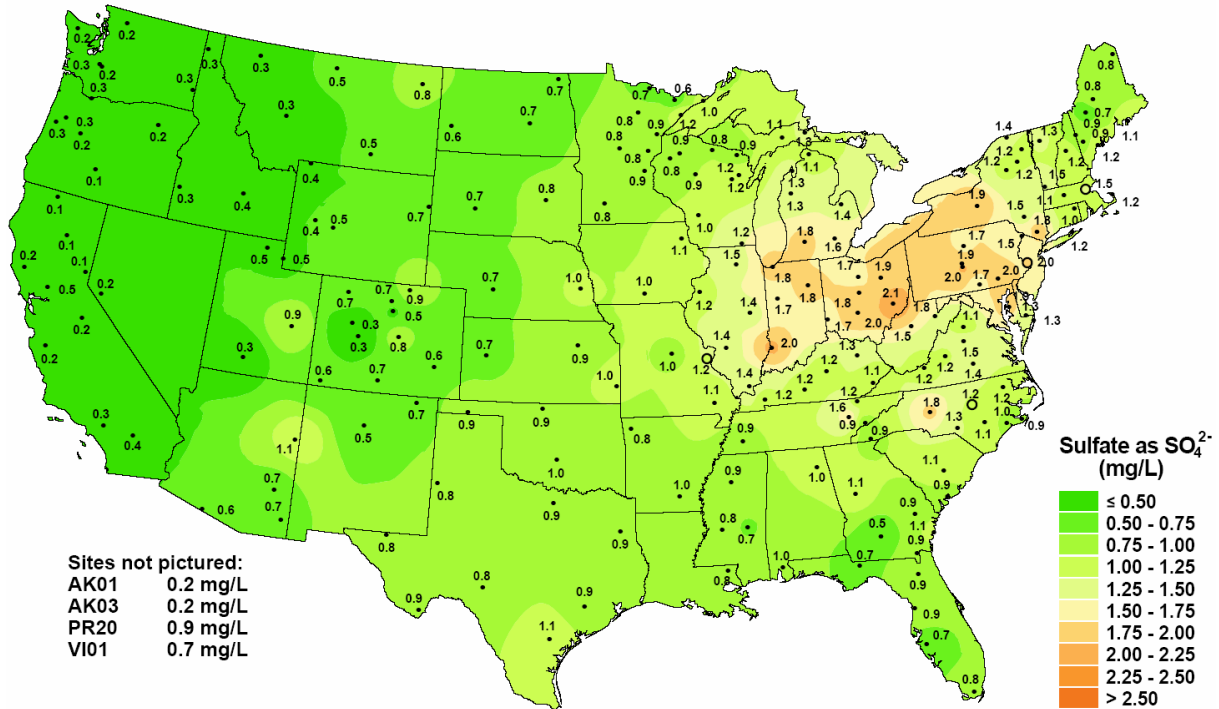
The observed reductions in sulfate and nitrate concentrations and wet depositions as well as acidity exhibit substantial seasonal differences. Although significant ( $p < 0.05$ ) reductions in seasonal sulfate concentrations and wet depositions have been evident throughout the state, the reductions were nearly three times greater during the growing season. For nitrate, all regions of the state have experienced decreasing growing and dormant season concentrations and wet depositions as well; however, the reductions are not significant ( $p < 0.05$ ) at all sites. The largest and most significant reductions occurred during the growing season and were generally twice as large as the measured reductions in dormant season concentrations and wet deposition. As one might expect, reductions in acidity and wet hydrogen ion depositions were also greatest during the growing season.

Regional patterns in post-CAAA reductions in sulfate and nitrate concentrations and wet depositions are also evident, although the reductions are not consistent across seasons or regions. This is particularly true for reductions in sulfate concentrations that tend to be greatest in central Pennsylvania during the growing season and annual period, but largest in the east during the dormant season. The largest reductions in annual and growing season wet sulfate depositions were measured in western Pennsylvania while the largest dormant season drop occurred in the eastern third of the state. Although regional and seasonal differences are evident for both sulfate concentrations and wet depositions, the magnitude of these differences are generally small between regions and seasons.

On an annual basis, post-CAAA reductions in nitrate concentrations were lowest in the west and increased to the east. Reductions in growing season concentrations followed a similar pattern, although the differences between central and eastern Pennsylvania are relatively small. In contrast, reductions in dormant season nitrate concentrations were highest in eastern Pennsylvania and decreased to their lowest levels in western Pennsylvania. Reductions in wet nitrate deposition were consistently highest in eastern Pennsylvania and lowest in the center region regardless of season. Post-CAAA reductions in nitrate deposition appear to be greater across the northern tier counties than the southern tier counties of Pennsylvania. Differences in emissions, emission sources and emissions reductions as well as deviations in precipitation volumes from the pre-CAAA reference period are likely the reasons these spatial patterns.

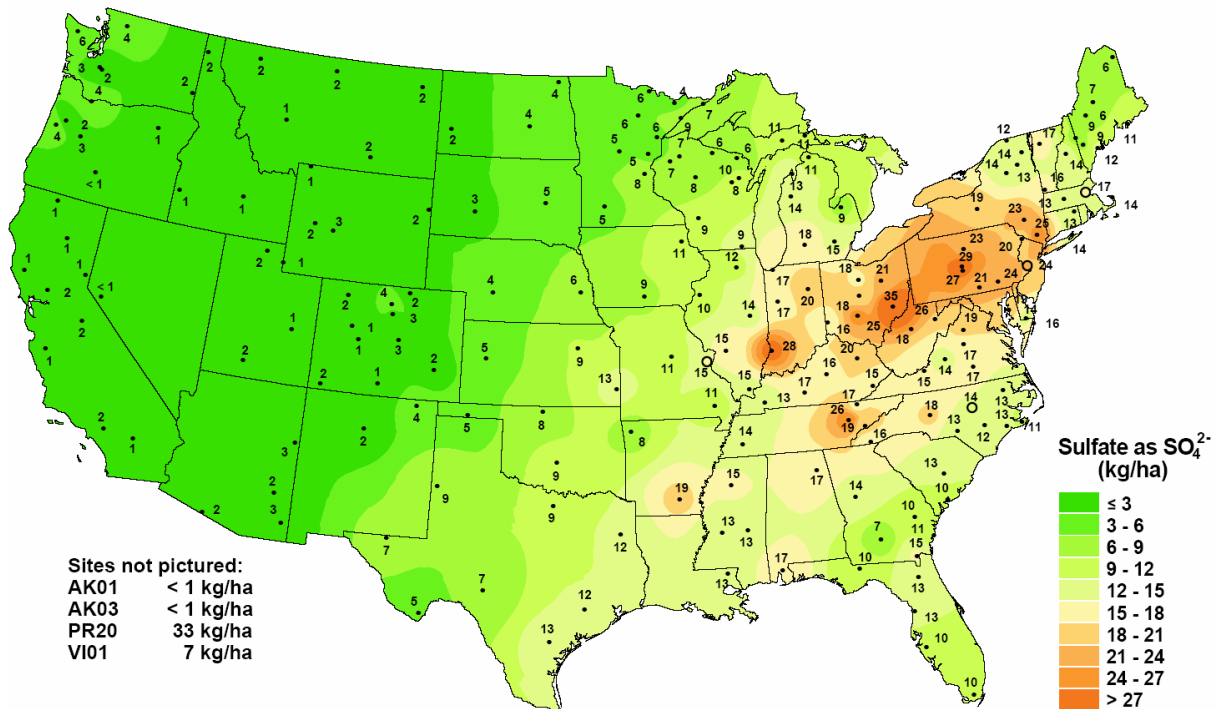
Despite the significant reductions in sulfate and nitrate concentrations in precipitation and its acidity as well as the reductions in wet deposition throughout the Commonwealth, Pennsylvania, particularly the western third of the state, still receives the most acidic precipitation of any region of North America. Sulfate and nitrate concentrations and wet depositions are also higher in Pennsylvania than most regions of North America (Figures 12 and 13). For a more detailed comparison of ionic concentrations and wet deposition measurements in Pennsylvania with the rest of the United States, readers are referred to the National Atmospheric Deposition Program 2004 Annual Summary (NADP, 2005) which can be viewed at <http://nadp.sws.uiuc.edu>.

## Sulfate ion concentration, 2004



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.sws.uiuc.edu>

## Sulfate ion wet deposition, 2004

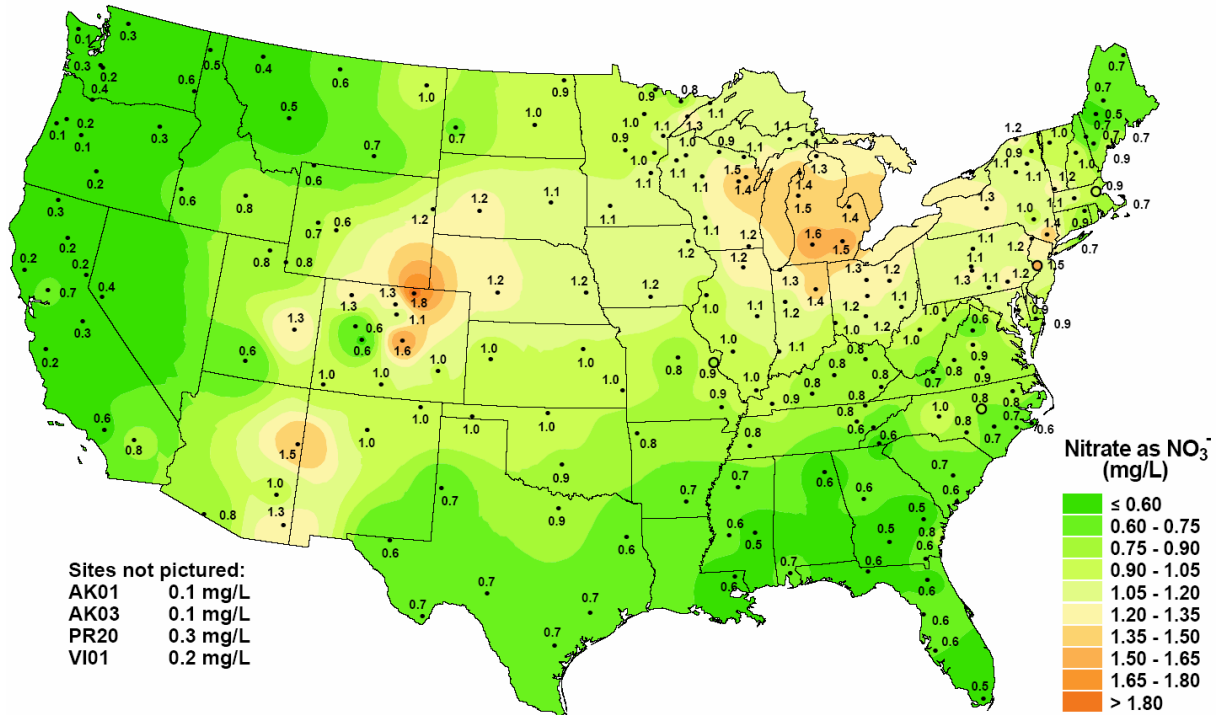


National Atmospheric Deposition Program/National Trends Network  
<http://nadp.sws.uiuc.edu>

Figure 12. Mean annual volume-weighted sulfate concentrations (mg/L) and estimated wet depositions (kg/ha) at National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites in the United States in 2004 that met NADP/NTN data completeness criteria.

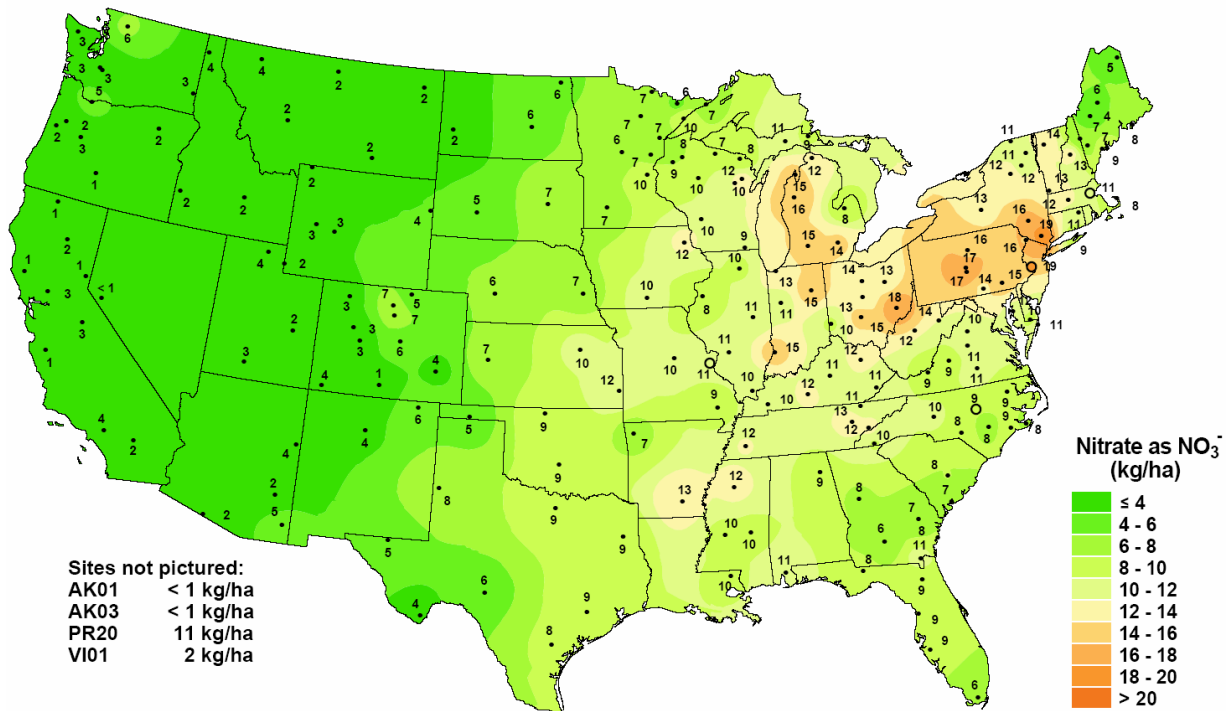


## Nitrate ion concentration, 2004



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.sws.uiuc.edu>

## Nitrate ion wet deposition, 2004



National Atmospheric Deposition Program/National Trends Network  
<http://nadp.sws.uiuc.edu>

Figure 13. Mean annual volume-weighted nitrate concentrations (mg/L) and estimated wet depositions (kg/ha) at National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites in the United States in 2004 that met NADP/NTN data completeness criteria..

Although significant progress has been made in reducing “acid rain” in Pennsylvania and across the Northeast and Mid-Atlantic regions, additional sulfur dioxide and nitrogen oxides emissions reductions will likely be necessary to provide adequate protection of all acid sensitive aquatic and terrestrial ecosystems and cultural and material resources in the Commonwealth, particularly in western Pennsylvania. Some of the year to year variability in post-CAAA reductions in wet acidic deposition can be attributed to above average precipitation. Since precipitation is an unmanageable parameter of climate, the only way to provide additional protection to the citizens of the Commonwealth and the environment is to reduce further sulfur dioxide and nitrogen oxides emissions in Pennsylvania and in upwind states. The expeditious implementation of a stringent national multi-pollutant strategy would not only reduce emissions and subsequently acidic deposition, but improve visibility as well. An assessment of source-receptor relationships should be undertaken to identify those sources that will provide the greatest opportunity for further reductions in acidic deposition in Pennsylvania. A detailed evaluation of spatial and temporal variations in precipitation and its influence on deposition patterns in the Commonwealth should also be undertaken. Such an analysis will provide valuable information to determine the level of emissions reductions that will be necessary to achieve adequate protection of the citizens of the Commonwealth and the environment.

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