

**Reductions in Acidic Wet Deposition in Pennsylvania Following
Implementation of the Clean Air Act Amendments of 1990:
1995-2006**

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Reductions in Acidic Wet Deposition in Pennsylvania Following Implementation of the Clean Air Act Amendments of 1990: 1995-2006

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.

Chemical analyses from the initial couple of years of operation of the NADP 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 weekly 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 high nitrate and sulfate concentrations were attributed to sulfur dioxide (SO₂) and nitrogen oxides (NO_x) 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 with respect to major emissions sources in the Ohio River Valley, the preliminary indication that precipitation in Pennsylvania was more acidic than most, if not all, regions of the 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 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 Environmental 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

Pennsylvania Atmospheric Deposition Monitoring Network

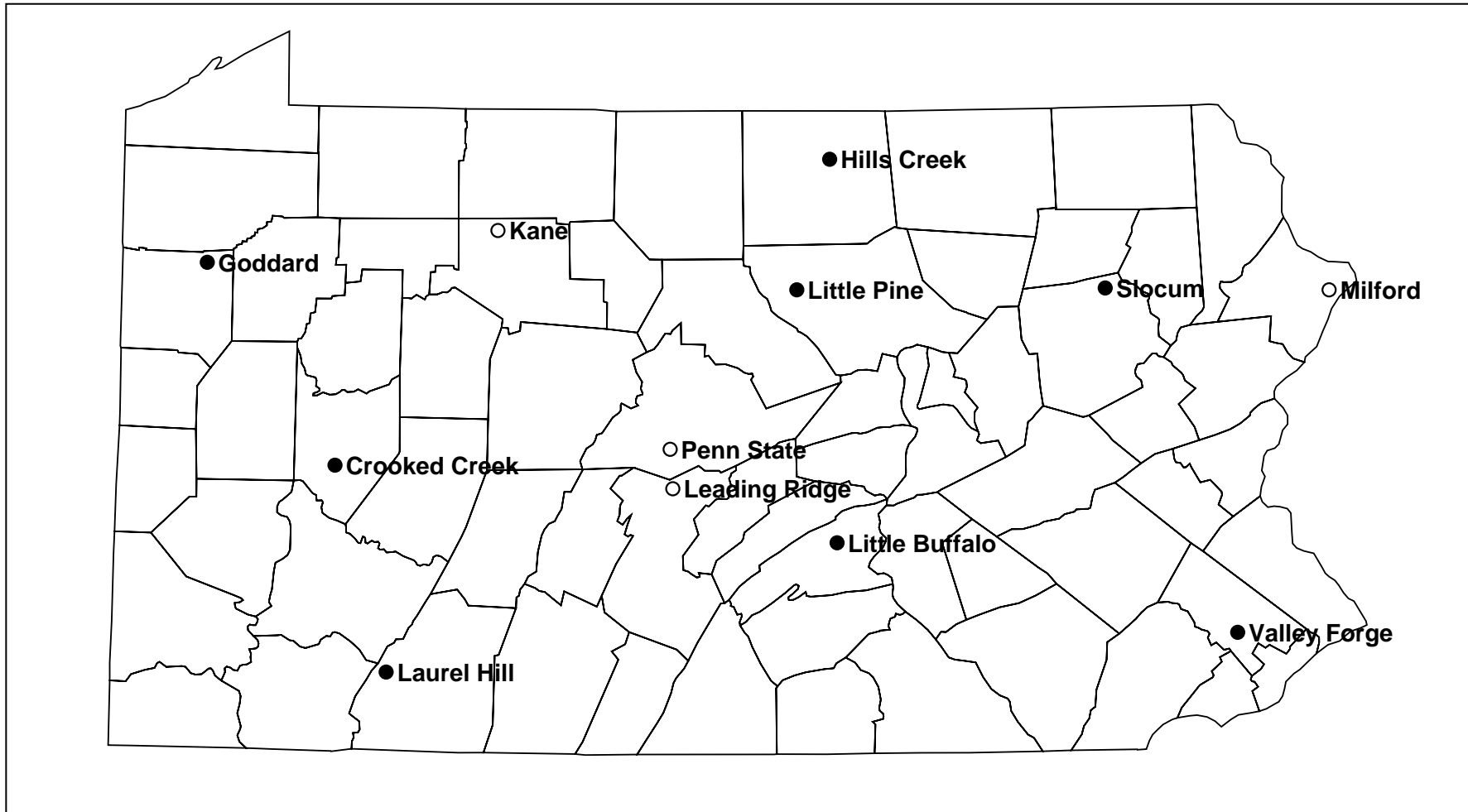


Figure 1. Locations of long-term sites in the Pennsylvania Atmospheric Deposition Monitoring Network. Sites marked with an empty circle are part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN).

(Frances Slocum 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 the 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. (2006) 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 (SO₂) and nitrogen oxides (NO_x) emissions. Phase I of the SO₂ reduction program was implemented on 1 January 1995. On that date additional limitations were imposed on SO₂ emissions at 110 electric utility plants (263 units) in 21 states of which 17 are located east of the Mississippi River (P. L. 101-549, Table A). Phase II of the SO₂ 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. In 2006, the SO₂ Phase II requirements applied to 1213 facilities and 3,484 operating units in the United States (EPA, 2007).

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, 2007). 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 9.4 million tons and averaged 10.4 million tons. In 2006, emissions from Title IV affected sources (3484 electric generating units) measured 9.4 million tons, a decrease of 0.8

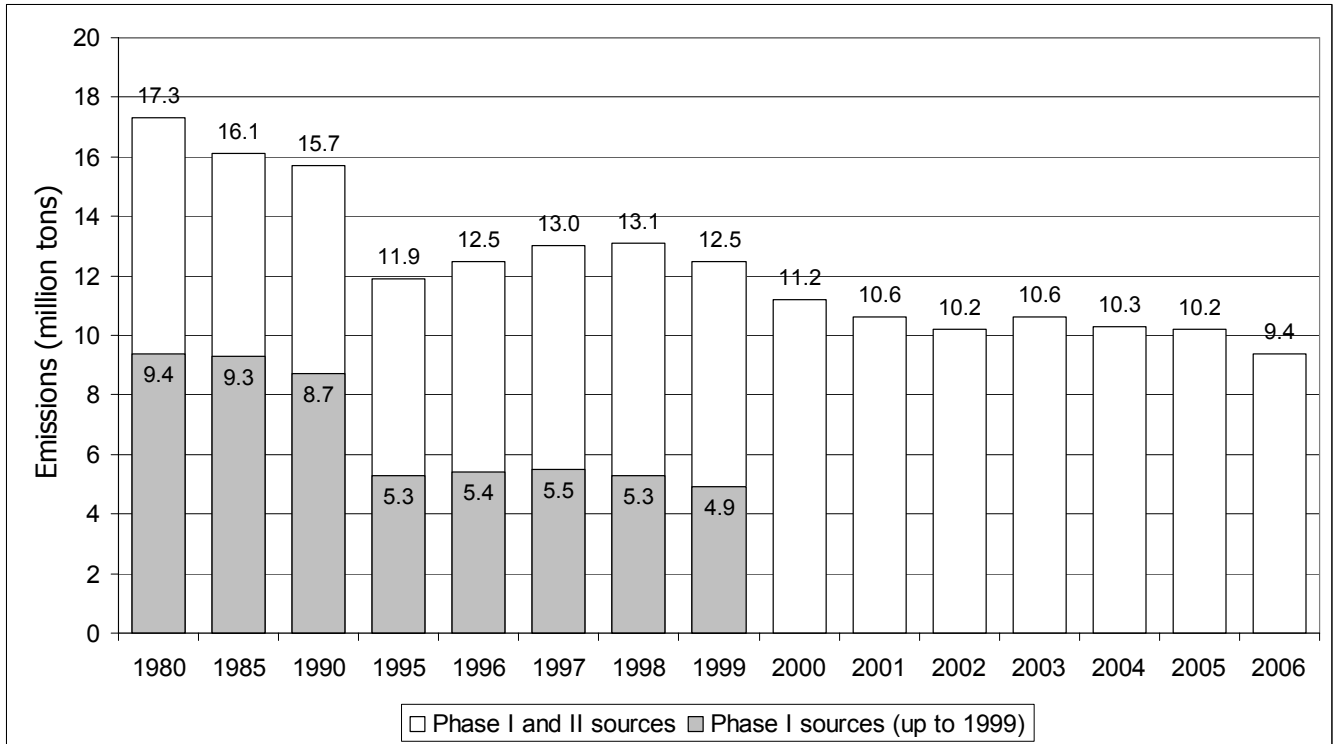


Figure 2. Sulfur dioxide emissions for 1980, 1985, 1990 and 1995 through 2006 from Title IV affected sources of the Clean Air Act Amendments of 1990 (EPA, 2007).

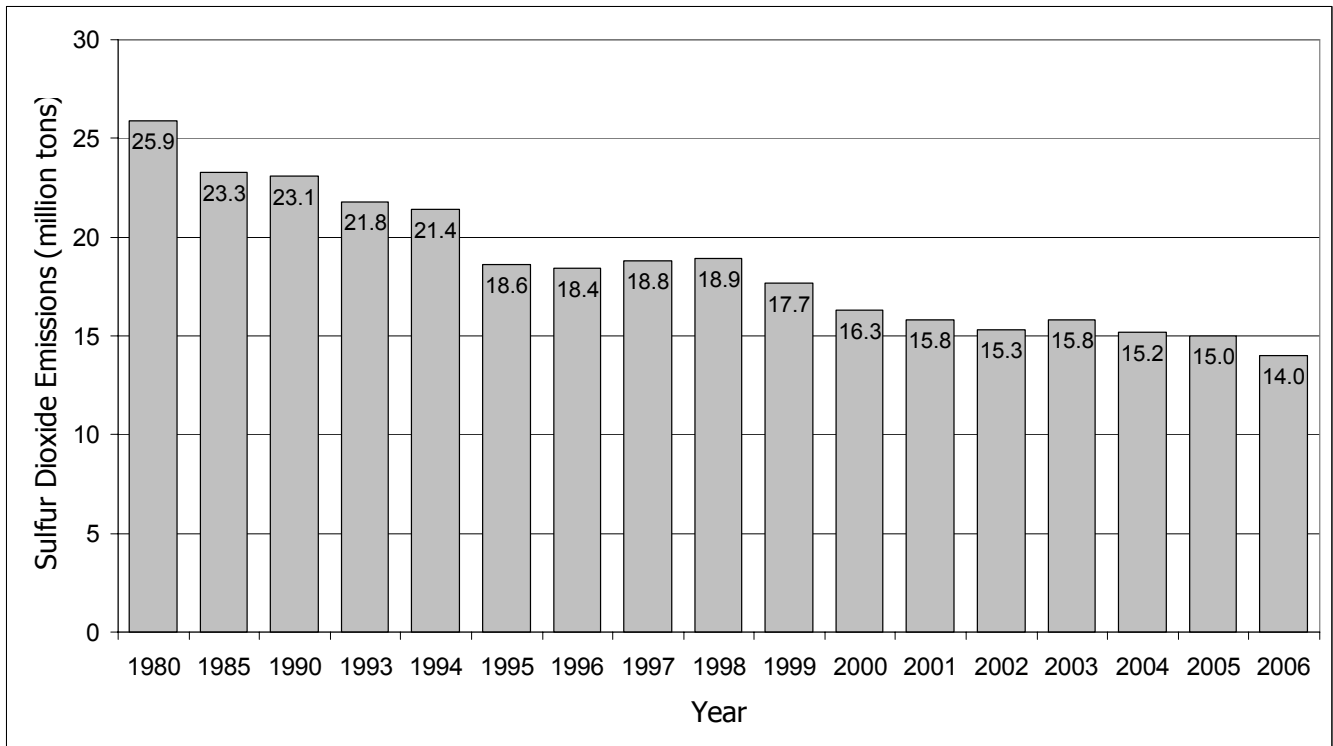


Figure 3. Sulfur dioxide emissions trend from all point and area sources in the United States (EPA, 2007). Emissions estimates for 2005 and 2006 are preliminary .

million tons over 2005 emissions (Figure 2). Reduced energy demand, decreased oil use because of fuel prices, and early Clean Air Interstate Rule (CAIR) compliance all appear to be factors in the decline in sulfur dioxide emissions in 2006 (EPA, 2007). The average annual reduction in sulfur emissions from all Title IV sources since 1995 has been 4.4 million tons (28.0%) when compared to 1990 emissions (Figure 2). Sulfur dioxide emissions in 2006 represent a decrease of more than 40% when compared to 1990 levels and marked the first time emissions fell below 10 million tons under the acid rain control program. Sulfur dioxide emissions in 2006 from Title IV affected sources also marked the first time that emissions were below the emission cap of 9.5 million tons required under Title IV of the CAAA (EPA, 2007).

Total SO₂ emissions from all point and area sources in the United States totaled 23.1 million tons in 1990 (Figure 3). In 1995, total SO₂ emissions dropped to 18.6 million tons. From 1995 through 1999, SO₂ emissions averaged 18.5 million tons. In 2006, preliminary estimates for total SO₂ emissions were 14.0 million tons, 9.1 million tons (39%) below 1990 levels and 1.0 million ton below the 2005 preliminary estimate of 15 million tons (EPA, 2007). Most of the decrease in total SO₂ emissions from 1995 through 1999 and from 2000 through 2006 resulted from implementation of Phase I and Phase II, respectively, of Title IV of the CAAA.

Many of the SO₂ emissions sources targeted by Phase I and Phase II of the CAAA are located in Pennsylvania, Ohio, West Virginia, Kentucky, Indiana, and Maryland. Nitrogen oxides (NO_x) and SO₂ emissions within these states likely have a direct impact on precipitation chemistry in Pennsylvania. Annual SO₂ emissions from affected units in these states for 1990 and from 1995 through 2006 are shown in Table 1. Sulfur dioxide emissions from within these states in 2006 totaled 3.8 million tons, a reduction of 45.8% from 1990 levels. The average percent reduction in emissions since 1995 was 36.7%. Sulfur dioxide emissions from Pennsylvania units affected by Phases I and II totaled 0.89 million tons in 2006, 0.32 million tons below 1990 levels and 0.09 million tons below 2005 levels. Since 1995, SO₂ emissions from Phase I and Phase II affected units in Pennsylvania averaged 0.98 million tons, a 19.0% reduction over 1990 emissions. Percentage reductions in SO₂ emissions since 1995 averaged 44.9% in Ohio, 41.3% in West Virginia, 36.9% in Kentucky, 41.5% in Indiana, and 6.0% in Maryland (Table 1).

Title IV of the CAAA also specifies a two-part strategy to reduce nitrogen oxides (NO_x) emissions (Krolewski and Mingst, 2000). The first stage of this program was implemented 1 January 1996; the second phase began 1 January 2000. In 2006, the Phase II NO_x requirements applied to 982 operating coal-fired operating units that were equal to or greater than 25 megawatts and burned coal between 1990 and 1995 (EPA, 2007). Actual NO_x 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 2006 (Phase II), NO_x emissions averaged 3.74 million tons, 1.66 million tons below 1995 levels and 1.06 million tons below 1999 emissions. Nitrogen oxides emissions from all Title IV affected sources in 2006 were 3.1 million tons, 0.2 million tons lower than 2005 emissions and 2.4 million tons lower than 1990 levels (Figure 4). The reductions in NO_x emissions were primarily from high temperature combustion sources, such as those that occur in coal-fired electric plants and automobiles (EPA, 2007).

Table 1. Sulfur dioxide (SO₂) and nitrogen oxides (NO_x) emissions (1000 tons) from all Phase I and Phase II affected sources in PA, OH, WV, KY, IN, and MD since implementation of Title IV of the Clean Air Act Amendments of 1990. Phase I SO₂ reductions were implemented 1 January 1995; Phase II was implemented 1 January 2000. Phase I NO_x reductions were implemented on 1 January 1996; Phase II was implemented 1 January 2000 (from EPA, 2007).

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	4452.0
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
2005	985.5	1085.5	467.1	502.1	870.8	281.8	4192.8
2006	894.2	962.1	454.2	427.6	821.0	276.3	3835.4
Mean 1995-2006	982.6	1219.5	568.7	571.1	876.9	265.6	4484.5
Average % Reduction ¹	19.0	44.9	41.3	36.9	41.5	6.0	36.7
<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	177.6	266.8	172.3	164.1	224.3	60.3	1065.4
2005	171.0	254.4	159.5	165.6	208.0	60.2	1018.7
2006	171.2	238.6	151.7	171.8	202.7	53.7	989.7
Mean 1996-2006	205.6	384.0	233.8	246.5	298.0	85.4	1453.3
Average % Reduction ²	22.2	27.4	15.5	33.9	16.0	12.7	23.3
% Reduction ³	35.3	54.9	45.2	53.9	42.9	45.1	47.8

¹Average % reduction in SO₂ emissions from 1995-2006 relative to 1990 emissions.

²Average percent reduction in NO_x emissions from 1996-2006 relative to 1995 emissions.

³Percent reduction in 2006 NO_x emissions relative to 1995 emissions.

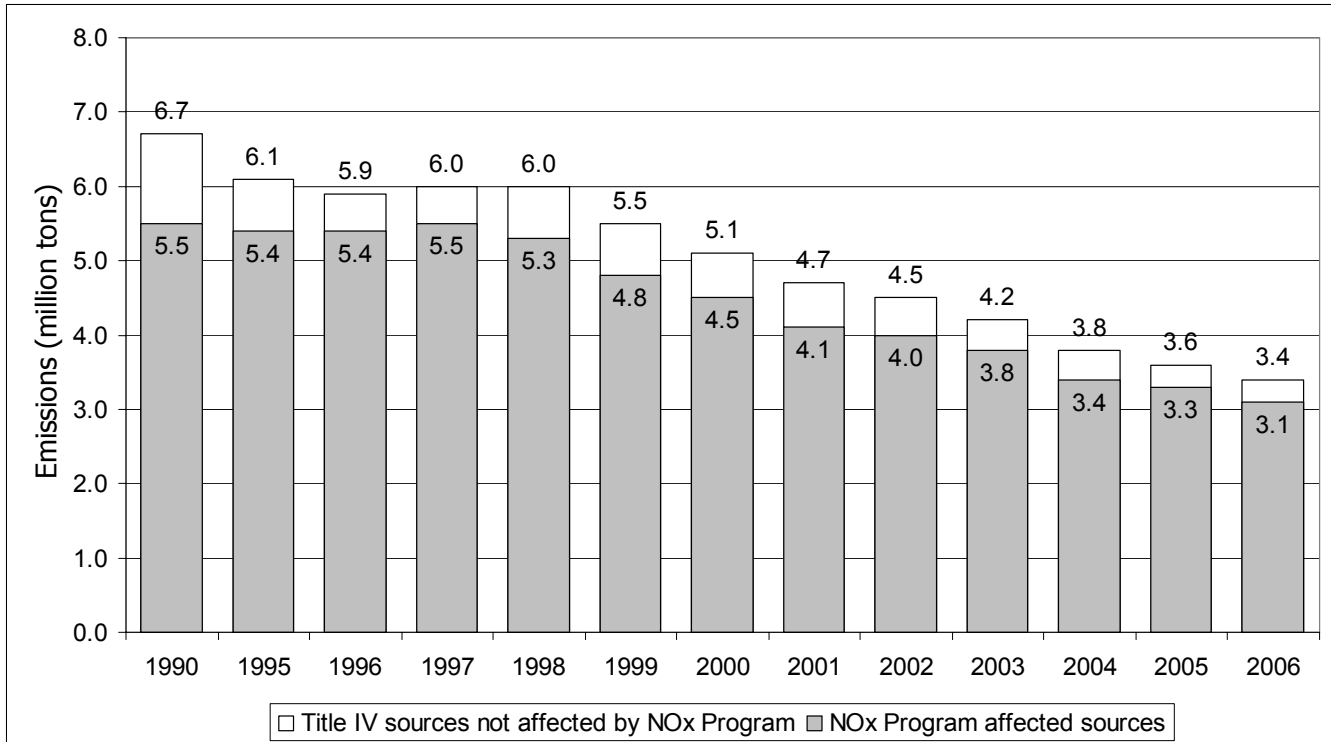


Figure 4. Nitrogen oxides emissions for 1990 and 1995 through 2006 from Title IV affected sources of the Clean Air Act Amendments of 1990 (EPA, 2007) .

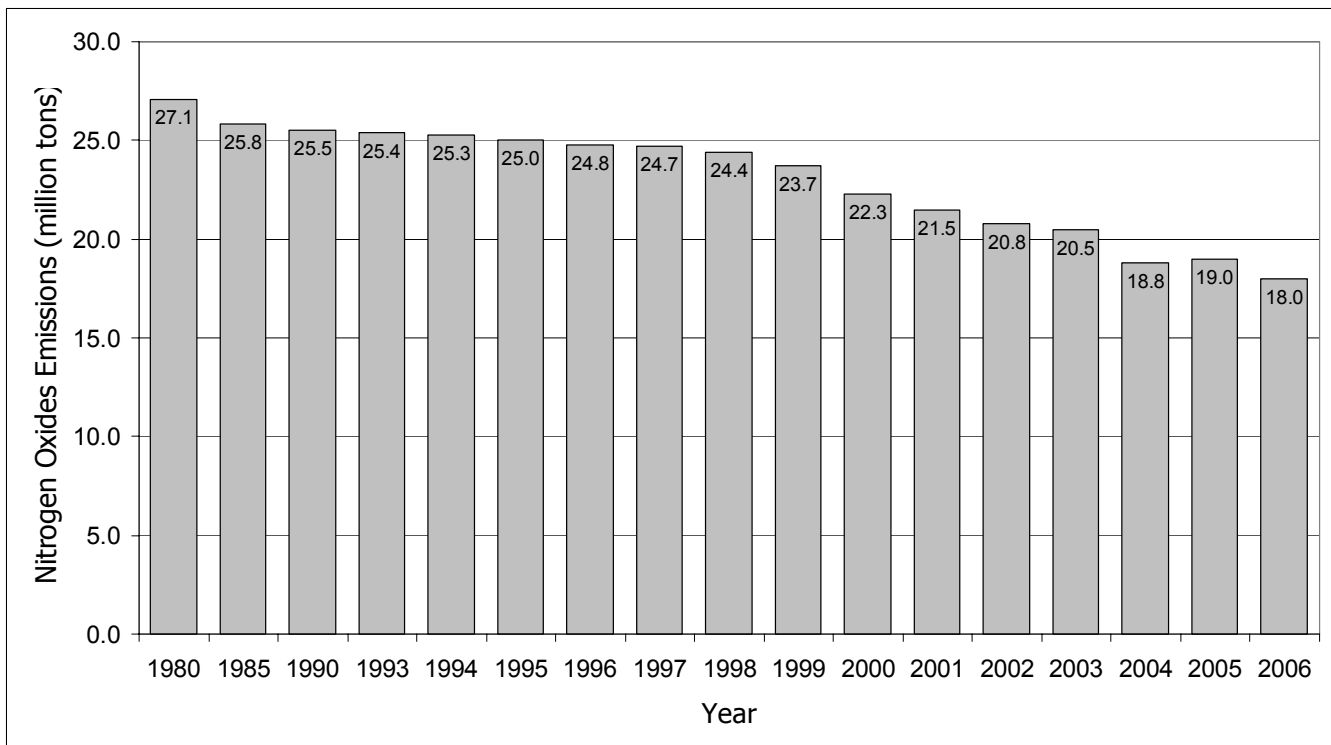


Figure 5. Nitrogen oxides emissions trend from all point and area sources in the United States (EPA, 2007). Emission estimates for 2005 and 2006 are preliminary .

Nitrogen oxides emissions reductions in Pennsylvania and in selected upwind states are listed in Table 1. The average percent reduction in NO_x emissions in PA, OH, MD, WV, KY, and IN from 1996 through 2006 relative to 1995 emissions was 23.3% (range 15.5% to 33.9%); the percent reduction in 2006 NO_x emissions averaged 47.8% (range 35.3% to 54.9%). The largest overall reductions in NO_x emissions occurred in Kentucky and Ohio. The substantial decrease in 2003 emissions relative to previous years reflects changes since implementation of Phase II controls, as well as other emissions control programs aimed at reducing ozone levels. In Pennsylvania, the average reduction in NO_x emissions since 1996 was 22.2% (48,900 tons). Nitrogen oxides emissions at all Title IV affected sources in PA in 2006 were 93,400 tons lower than in 1995 and the lowest reported since implementation of Title IV controls (Table 1).

Nitrogen oxides emissions from all sources in the United States for 1980, 1985, 1990, and 1993 through 2006 are shown in Figure 5. Clearly, NO_x emissions in 1995 from all Title IV affected sources represented a relatively small percentage (approximately 24%) of total NO_x emissions from all sources (Figure 4 vs. Figure 5). Likewise, reductions in NO_x emissions from Title IV sources from 1996 to 1999 (0.60 million tons) represented a very small percentage reduction when compared to total NO_x emissions from all sources over this period. Since 2000, NO_x emissions from all Title IV sources declined from 4.8 million tons in 1999 to 3.1 million tons in 2006 (Figure 4). Preliminary nitrogen oxides emissions from all sources (except fire) for 2006 were estimated at 18.0 million tons, 6.8 million tons below 1996 emissions (EPA, 2007a). The greater reduction in total NO_x emissions relative to reductions from Title IV sources represents a decrease in NO_x emissions from other non-Title IV sources, primarily mobile sources. Consequently, the mix of emissions and sources and their relative importance have changed since 1990 and even 1995 with on-road and non-road sources accounting for a larger percentage of all NO_x emissions. Changes in the relative contribution of emission sources in a region likely influence the distribution and magnitude of reductions in nitrate concentrations in precipitation across that region.

Methods

Evaluation of the effects of changes in time series data, such as the sharp reduction in SO₂ 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 (1995-2006), 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 (H⁺, SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Ca²⁺, Mg²⁺, 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, 1988). 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 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 2006 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 2006 (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

Sulfate Concentrations - Sulfate concentrations in precipitation (Figure 6, Table 2) have decreased substantially across Pennsylvania since 1995. Statistically significant ($p < 0.05$) reductions in mean annual sulfate concentrations were evident at all long-term monitoring sites and range from 0.619 mg/L at Laurel Hill State Park in Somerset County to 0.924 mg/L at Hills Creek State Park in Tioga County. The average reduction was slightly greater in central Pennsylvania (0.834 mg/L) than in either the eastern (0.823 mg/L) or western (0.809 mg/L) regions of the state. The overall average reduction in mean annual sulfate concentrations across the state since 1995 was 0.823 mg/L, a 28.1% decrease when compared to the pre-CAAA mean (Table 2).

The largest seasonal reductions in sulfate concentrations occurred during the growing season (Table 2). Average growing season reductions ranged from 0.971 mg/L at Slocum State Park in Luzerne County to 1.593 mg/L at the Leading Ridge NADP/NTN site in Huntingdon County, with all long-term monitoring sites exhibiting statistically significant ($p < 0.05$) decreasing trends. As with annual concentration means, the mean growing season reduction in central Pennsylvania (1.340 mg/L) was slightly larger than in the western (1.265 mg/L) and eastern (1.090 mg/L) regions of the state (Table 2). The overall average growing season reduction in sulfate concentrations since 1995 was 1.251 mg/L, a 32.7% decrease when compared to the pre-CAAA mean (Table 2).

Mean dormant season sulfate concentrations also decreased since 1995 (Table 2), although the reductions were smaller than observed during the growing season. Reductions in mean dormant season sulfate concentrations ranged from 0.251 mg/L at Laurel Hill State Park to 0.637 mg/L at Slocum State Park. Reductions in mean dormant season concentrations were significant ($p < 0.05$) at all sites (Table 2). However, unlike growing season concentrations, reductions in mean dormant season sulfate concentrations were greater in eastern Pennsylvania (0.566 mg/L) than in either the central (0.382 mg/L) or western (0.335 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 magnitude of the decline in dormant season sulfate concentrations since 1995. This spatial pattern was not evident during the growing season.

Wet Sulfate Deposition - As would be expected given the large reductions in sulfate concentrations since 1995, wet sulfate deposition has also decreased across the state (Table 2, Figure 7). On an annual basis, reductions in sulfate deposition at each of the long-term monitoring sites ranged from 13.04 kg/ha at the Kane NADP/NTN site in Elk County to 5.79 kg/ha at the Penn State NADP/NTN site in Centre County. The average statewide reduction in sulfate deposition since 1995 was 8.82 kg/ha. The smallest regional reduction in wet deposition occurred in central Pennsylvania (7.74 kg/ha) despite the fact that reductions in sulfate concentrations (Table 2) were actually greater in central Pennsylvania than in any other region of the state. Reductions in central Pennsylvania were approximately 2.0 kg/ha less than those in western Pennsylvania (9.78 kg/ha) and 1.4 kg/ha less than those in the eastern portion of the state (9.12 kg/ha).

Table 2. Comparison of mean annual and seasonal sulfate ion concentrations and wet depositions at 12 atmospheric deposition monitoring stations in Pennsylvania before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

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	2.324	-0.619*	4.022	2.946	-1.075*	1.977	1.726	-0.251*
Goddard	3.179	2.352	-0.827*	3.957	2.719	-1.238*	2.211	1.926	-0.285*
Crookcrk	3.558	2.674	-0.884*	4.746	3.348	-1.398*	2.242	1.915	-0.327*
Kane	3.032	2.126	-0.905*	3.909	2.559	-1.350*	2.118	1.640	-0.478*
Western Region	3.178	2.369	-0.809*	4.158	2.893	-1.265*	2.137	1.802	-0.335*
Littbuff	2.917	2.170	-0.748*	3.889	2.640	-1.250*	1.982	1.638	-0.344*
Hillscrk	2.793	1.869	-0.924*	3.659	2.338	-1.321*	1.690	1.232	-0.458*
Leadridg	3.036	2.131	-0.905*	4.165	2.572	-1.593*	1.978	1.602	-0.377*
Littpine	2.965	2.230	-0.735*	3.894	2.727	-1.166*	1.951	1.662	-0.289*
PSUNADP	2.935	2.071	-0.864*	3.915	2.544	-1.371*	1.939	1.486	-0.453*
Central Region	2.928	2.094	-0.834*	3.904	2.564	-1.340*	1.906	1.524	-0.382*
Vallforg	2.576	1.817	-0.759*	3.227	2.154	-1.073*	1.919	1.444	-0.474*
Milford	2.397	1.523	-0.873*	3.052	1.827	-1.225*	1.762	1.176	-0.585*
Slocum	2.797	1.960	-0.838*	3.504	2.533	-0.971*	1.968	1.331	-0.637*
Eastern Region	2.590	1.767	-0.823*	3.261	2.172	-1.090*	1.883	1.317	-0.566*
Statewide	2.927	2.104	-0.823*	3.827	2.576	-1.251*	1.979	1.565	-0.414*

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	30.491	-8.642*	25.335	19.209	-6.126*	13.797	11.280	-2.517*
Goddard	35.841	26.402	-9.439*	24.701	17.168	-7.532*	11.142	9.233	-1.909*
Crookcrk	38.112	30.105	-8.007*	26.751	20.527	-6.224*	11.358	9.579	-1.778*
Kane	38.584	25.541	-13.043*	25.792	16.635	-9.158*	12.790	8.906	-3.884*
Western Region	37.917	28.135	-9.783*	25.645	18.385	-7.260*	12.272	9.750	-2.522*
Littbuff	31.324	24.699	-6.625*	21.045	16.108	-4.938*	10.278	8.592	-1.686
Hillscrk	26.186	17.966	-8.220*	19.372	13.053	-6.318*	6.813	4.911	-1.903*
Leadridg	32.865	22.418	-10.447*	22.624	14.898	-7.727*	10.238	7.521	-2.717*
Littpine	31.004	23.458	-7.547*	21.793	15.679	-6.114*	9.213	7.781	-1.432*
PSUNADP	29.401	23.610	-5.791*	20.380	16.243	-4.137*	9.019	7.367	-1.652*
Central Region	30.168	22.430	-7.738*	21.053	15.196	-5.857*	9.114	7.234	-1.880*
Vallforg	30.327	22.236	-8.092*	19.238	14.019	-5.219*	11.090	8.214	-2.876*
Milford	28.733	18.662	-10.071*	19.062	11.979	-7.083*	9.671	6.681	-2.990*
Slocum	30.880	21.677	-9.203*	21.517	15.184	-6.332*	9.363	6.492	-2.872*
Eastern Region	29.980	20.858	-9.122*	19.939	13.727	-6.212*	10.041	7.129	-2.912*
Statewide	32.758	23.939	-8.819*	22.332	15.892	-6.440*	10.426	8.046	-2.379*

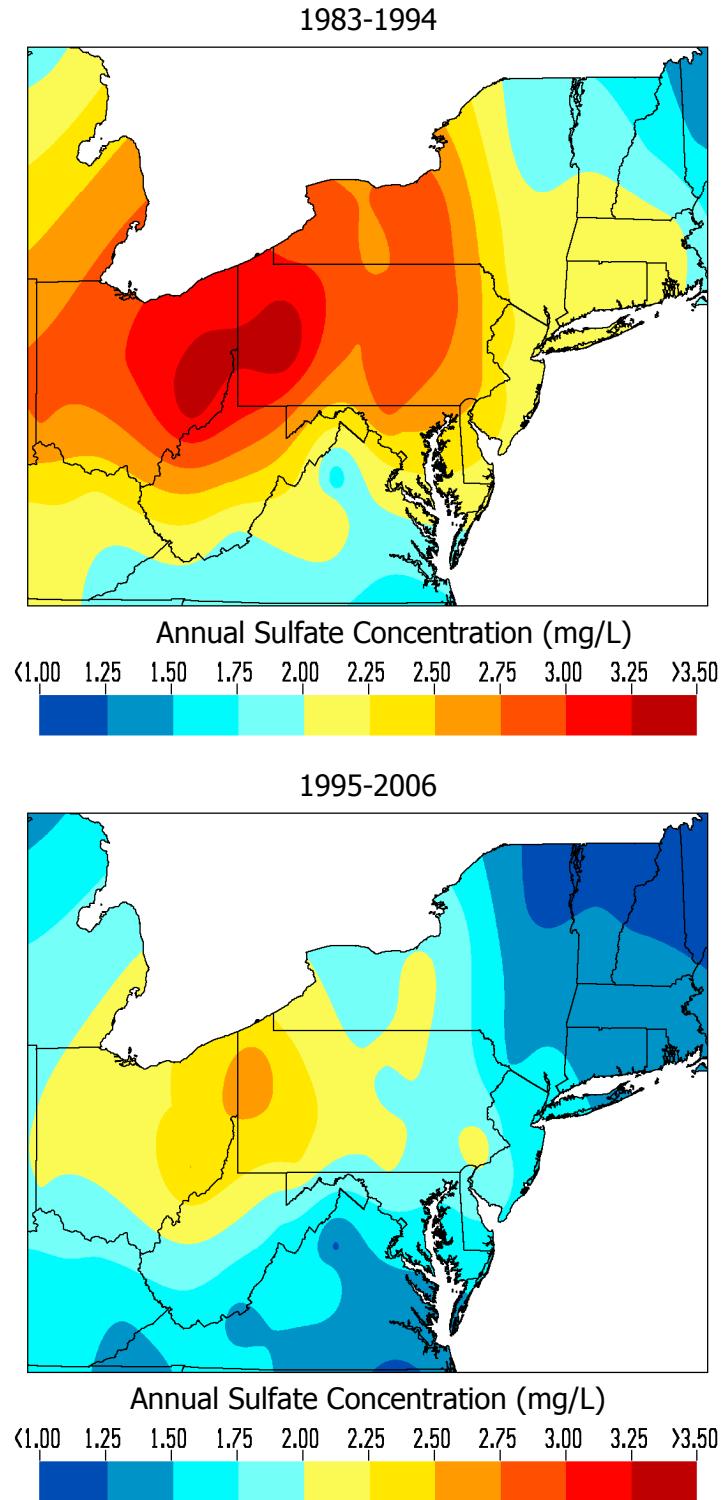


Figure 6. Mean annual sulfate concentrations across Pennsylvania and neighboring states before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

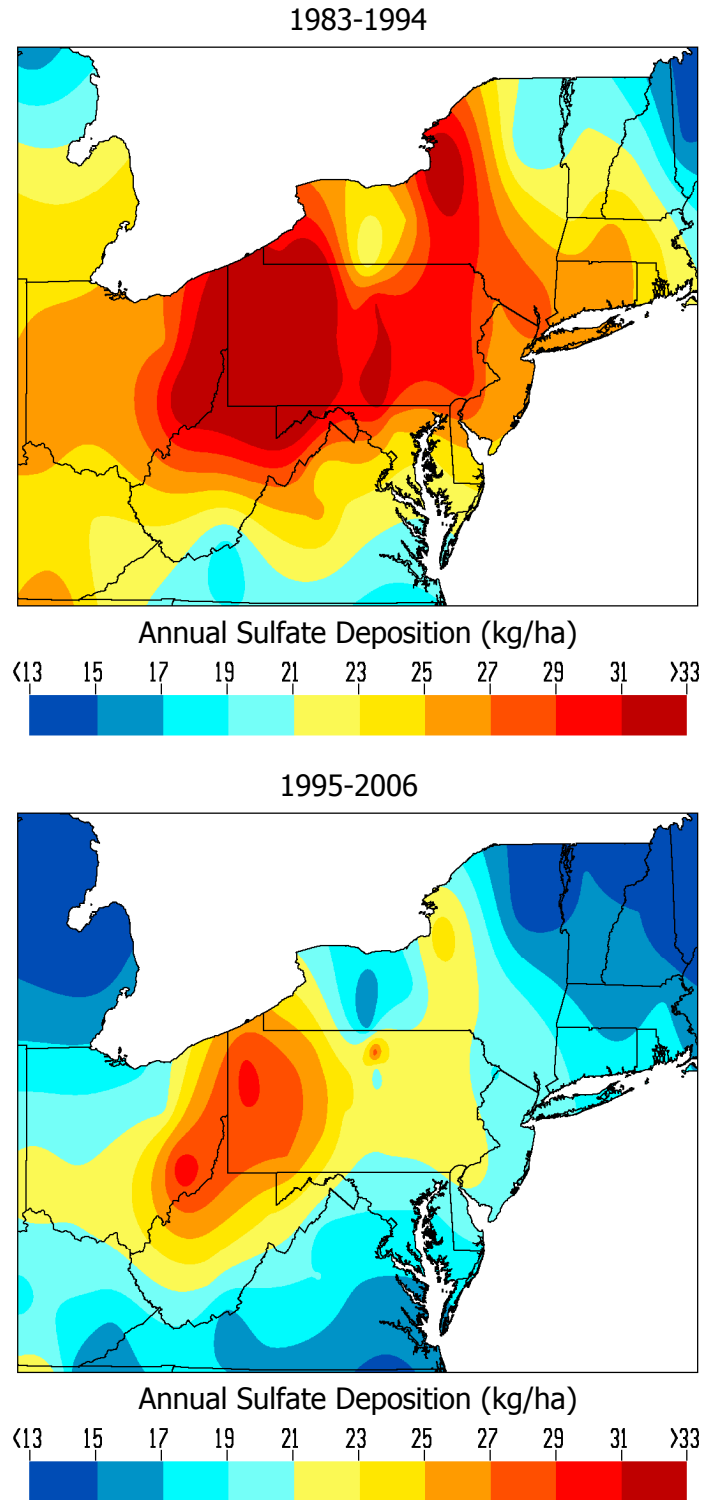


Figure 7. Mean annual sulfate wet deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

Reductions in wet sulfate deposition during the growing season were significant ($p < 0.05$) at all long-term network sites including the Penn State site which reported a statistically significant decline for the second consecutive year (Table 2). The largest decrease during the past 12 growing seasons (9.16 kg/ha) was measured at the Kane site; the smallest reduction (4.14 kg/ha) was measured at the Penn State site. The average statewide growing season reduction was 6.44 kg/ha. The smallest regional reduction in growing season sulfate deposition was measured in central Pennsylvania (5.86 kg/ha); the largest regional reduction (7.26 kg/ha) was observed in western Pennsylvania.

All sites also reported lower dormant season sulfate deposition since 1995 with an average post-CAAA statewide decrease of 2.38 kg/ha (Table 2). Statistically significant ($p < 0.05$) reductions were measured at Hills Creek (1.90 kg/ha), Kane (3.88 kg/ha), Laurel Hill (2.52 kg/ha), Leading Ridge (2.72 kg/ha), Milford (2.99 kg/ha), Penn State (1.65 kg/ha), Slocum (2.87 kg/ha), Little Pine (1.43 kg/ha), M.K. Goddard (1.91 kg/ha), Crooked Creek (1.78 kg/ha) and Valley Forge (2.88 kg/ha). A non-significant decrease of 1.69 kg/ha was measured at Little Buffalo State Park in Perry County. Interestingly, the greatest regional reduction in dormant season sulfate deposition occurred in eastern Pennsylvania (2.91 kg/ha) not western Pennsylvania (2.52 kg/ha) which had the largest reductions in annual and growing season depositions. Seasonal and regional reductions in wet deposition are also not consistent with sulfate concentration reduction patterns except in eastern Pennsylvania during the dormant season. The centre region, which recorded the largest annual and seasonal reductions in sulfate concentrations, had the smallest reductions in wet sulfate deposition. Changes in post-CAAA concentrations and wet deposition patterns were also out of sink in western Pennsylvania.

Sulfate Concentration and Wet Deposition Trends - Trend analyses of pre- and post-CAAA ionic concentrations are shown in Table 3. Clearly, sulfate concentrations at all sites during the pre-CAAA period were decreasing and these trends continued at most sites after 1995 when SO₂ emissions reductions mandated by Title IV of the CAAA were implemented. However, the magnitude, direction, and statistical significance of the post-CAAA trends are quite variable across Pennsylvania. At six of the long-term monitoring sites (Crooked Creek Lake, Laurel Hill, Little Pine, M.K. Goddard, Kane and Milford) post-CAAA sulfate concentration trends were greater than the trend observed at those sites during the pre-CAAA period. At four sites (Little Buffalo, Valley Forge, Penn State, and Leading Ridge) the decreasing pre-CAAA trend continued into the post-CAAA period although the rate of decline during the post-CAAA period was smaller than reported during the pre-CAAA period. Of the 10 sites exhibiting decreasing post-CAAA sulfate trends, the trends were statistically significant ($p < 0.05$) at only Crooked Creek Lake, Laurel Hill, and Little Pine. In addition, post-CAAA sulfate concentrations patterns at Hills Creek and Slocum actually increased when compared to the pre-CAAA trends, although the increasing patterns were not significant ($p < 0.05$).

Pre- and post-CAAA wet sulfate deposition trends (Table 4) are even more variable than the concentration patterns and reflect not only differences in sulfate concentrations but also differences in the spatial and temporal distribution of precipitation between pre- and post-CAAA periods. Pre-CAAA wet sulfate deposition patterns were decreasing at 10 long-term sites and increasing at two sites (Little Pine in Lycoming County and Crooked Creek Lake in Armstrong

Table 3. Changes in trends of ionic concentrations in precipitation in Pennsylvania before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

site	1983-94 trend (%/yr)	1995-2006 trend (%/yr)	change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2006 trend (%/yr)	change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2006 trend (%/yr)	change in trends (%/yr)	p	
----- hydrogen ion -----					----- sulfate -----					----- nitrate -----			
CROOKCRK	-1.86	-6.41	-4.55	0.0001	-1.09	-2.84	-1.75	0.0261	-1.64	-4.44	-2.80	0.0013	
GODDARD	-3.11	-3.99	-0.88	0.2190	-1.54	-2.03	-0.49	0.4519	-2.40	-4.14	-1.75	0.0127	
HILLSCRK	-0.91	-2.46	-1.55	0.0550	-0.96	0.56	1.52	0.1048	-1.28	-2.05	-0.77	0.3948	
LAURHILL	-2.06	-5.46	-3.40	0.0003	-0.96	-3.09	-2.13	0.0279	-2.16	-4.24	-2.08	0.0195	
LITTBUFF	-4.03	-3.51	0.52	0.5925	-1.80	-0.69	1.11	0.2416	-3.01	-3.23	-0.23	0.8182	
SLOCUM	-1.53	-3.71	-2.18	0.0313	-0.54	0.11	0.65	0.5424	-1.20	-1.61	-0.41	0.6845	
VALLFORG	-1.88	-3.52	-1.64	0.1003	-1.28	-0.90	0.38	0.7104	-2.42	-1.06	1.35	0.1888	
LITTPINE	-0.46	-7.42	-6.96	0.0001	-0.19	-3.11	-2.92	0.0175	-1.57	-5.32	-3.75	0.0027	
PSUNADP	-2.61	-1.98	0.63	0.4468	-2.43	-0.91	1.52	0.1148	-2.55	-2.84	-0.29	0.7713	
KANE	-1.66	-3.22	-1.56	0.0359	-1.44	-1.88	-0.44	0.5991	-0.59	-4.32	-3.73	0.0001	
LEADRIDG	-1.51	-2.39	-0.88	0.3131	-2.05	-0.53	1.52	0.1493	-1.55	-3.18	-1.63	0.1112	
MILFORD	-1.91	-4.28	-2.37	0.0275	-2.58	-3.12	-0.53	0.6371	-1.33	-4.44	-3.11	0.0038	
----- ammonium -----					----- calcium -----					----- magnesium -----			
CROOKCRK	-0.14	-1.26	-1.12	0.2809	-2.38	-0.90	1.48	0.2819	-9.00	-0.42	8.58	0.0001	
GODDARD	0.46	-2.28	-2.74	0.0025	-4.53	-0.89	3.64	0.0061	-7.29	-1.97	5.31	0.0004	
HILLSCRK	1.77	1.33	-0.44	0.7317	-5.63	2.27	7.90	0.0001	-9.27	3.54	12.81	0.0001	
LAURHILL	-0.00	-2.60	-2.60	0.0206	-4.26	-0.60	3.66	0.0287	-8.31	0.44	8.75	0.0001	
LITTBUFF	1.48	-1.36	-2.84	0.0291	-6.96	2.88	9.84	0.0001	-7.84	1.43	9.27	0.0001	
SLOCUM	1.77	3.16	1.39	0.3107	-2.72	3.41	6.13	0.0002	-7.98	3.24	11.22	0.0001	
VALLFORG	2.37	-0.69	-3.06	0.0150	-3.81	3.23	7.04	0.0001	-5.86	-4.13	1.74	0.3927	
LITTPINE	-0.01	-0.27	-0.26	0.8450	-2.23	-1.12	1.11	0.5203	-4.70	4.11	8.82	0.0001	
PSUNADP	-0.53	0.37	0.90	0.4817	-5.53	-0.29	5.25	0.0001	-7.12	-0.43	6.69	0.0001	
KANE	-0.13	-1.33	-1.21	0.2888	-2.20	-1.30	0.90	0.5123	-5.01	-2.67	2.33	0.1145	
LEADRIDG	-0.89	1.20	2.09	0.1337	-3.47	-0.18	3.29	0.0332	-5.93	-0.60	5.32	0.0020	
MILFORD	0.85	-1.73	-2.58	0.0850	-4.74	0.21	4.95	0.0005	-5.74	-1.56	4.18	0.0083	
----- potassium -----					----- sodium -----					----- chloride -----			
CROOKCRK	0.66	6.01	5.35	0.0232	-1.68	7.00	8.68	0.0001	1.76	-6.33	-8.09	0.0001	
GODDARD	2.04	9.05	7.01	0.0035	-2.36	6.59	8.95	0.0001	0.01	-0.55	-0.57	0.5984	
HILLSCRK	5.15	11.77	6.61	0.0125	-0.29	10.22	10.51	0.0001	-1.40	2.18	3.58	0.0055	
LAURHILL	4.30	8.42	4.12	0.1286	-1.07	7.00	8.06	0.0001	-0.80	-1.44	-0.64	0.5418	
LITTBUFF	4.27	6.54	2.27	0.4027	-1.87	3.68	5.55	0.0062	-0.39	-2.01	-1.61	0.1727	
SLOCUM	2.55	13.57	11.02	0.0001	-1.78	8.61	10.39	0.0001	0.17	1.73	1.56	0.2185	
VALLFORG	4.55	11.84	7.29	0.0129	-0.28	-2.28	-2.00	0.3844	0.48	-5.43	-5.91	0.0019	
LITTPINE	2.44	14.48	12.04	0.0001	2.20	12.83	10.63	0.0001	0.89	2.64	1.76	0.2355	
PSUNADP	-3.10	1.10	4.20	0.0404	-3.49	-4.77	-1.27	0.5065	-2.81	-1.53	1.28	0.2635	
KANE	-0.38	-0.85	-0.47	0.8261	-1.53	-5.86	-4.32	0.0060	-1.70	-3.94	-2.24	0.0261	
LEADRIDG	-5.43	-0.30	5.13	0.0231	-3.20	-4.71	-1.51	0.4000	-1.41	-2.59	-1.18	0.3430	
MILFORD	-6.75	1.37	8.11	0.0001	-0.53	-2.63	-2.10	0.2428	-2.55	-1.88	0.66	0.6549	

Table 4. Changes in trends of ionic wet depositions in Pennsylvania before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

site	1983-94 trend (%/yr)	1995-2006 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2006 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2006 trend (%/yr)	Change in trends (%/yr)	p	
----- hydrogen ion -----					----- sulfate -----					----- nitrate -----			
CROOKCRK	-0.50	-4.56	-3.99	0.0007	0.27	-0.92	-1.12	0.2946	-0.24	-2.55	-2.20	0.0473	
GODDARD	-3.43	-1.64	1.87	0.1558	-2.11	0.37	2.54	0.0378	-2.98	-1.79	1.27	0.2502	
HILLSCRK	-1.62	-0.18	1.46	0.2678	-2.14	2.91	5.08	0.0001	-2.46	0.24	2.72	0.0353	
LAURHILL	-1.45	-7.17	-5.62	0.0001	-0.37	-4.84	-4.40	0.0005	-1.56	-5.98	-4.32	0.0001	
LITTBUFF	-4.05	-2.69	1.44	0.2417	-1.85	0.16	2.05	0.0823	-3.03	-2.41	0.69	0.5093	
SLOCUM	-1.46	-0.38	1.16	0.3525	-0.48	3.57	4.12	0.0016	-1.10	1.79	3.00	0.0098	
VALLFORG	-2.52	-2.81	-0.22	0.8726	-1.93	-0.17	1.83	0.1842	-3.00	-0.33	2.75	0.0460	
LITTPINE	1.39	-5.80	-7.14	0.0001	1.66	-1.41	-3.03	0.0085	0.28	-3.67	-3.88	0.0008	
PSUNADP	-0.41	-1.71	-1.27	0.3222	-0.23	-0.65	-0.38	0.7670	-0.35	-2.58	-2.19	0.0894	
KANE	-1.43	-0.81	0.72	0.5390	-1.95	0.57	2.60	0.0309	-1.06	-1.93	-0.75	0.4633	
LEADRIDG	-1.34	-1.67	-0.28	0.8045	-1.88	0.21	2.13	0.0671	-1.37	-2.46	-1.05	0.3368	
MILFORD	-0.40	-2.21	-1.68	0.2402	-0.83	-1.03	-0.06	0.9601	-0.09	-2.37	-2.12	0.0709	
----- ammonium -----					----- calcium -----					----- magnesium -----			
CROOKCRK	1.22	0.69	-0.48	0.7100	-1.98	1.06	3.13	0.0525	-8.39	1.55	10.00	0.0001	
GODDARD	-0.32	0.11	0.50	0.6964	-3.99	1.54	5.66	0.0001	-7.57	0.43	8.11	0.0001	
HILLSCRK	0.55	3.70	3.17	0.0349	-6.76	4.67	11.45	0.0001	-10.34	5.94	16.30	0.0001	
LAURHILL	0.58	-4.36	-4.85	0.0008	-3.71	-2.41	1.36	0.3981	-8.55	-1.38	7.22	0.0001	
LITTBUFF	0.86	-0.52	-1.34	0.2933	-6.97	3.76	10.80	0.0001	-7.90	2.31	10.24	0.0001	
SLOCUM	1.85	6.72	4.96	0.0015	-2.58	6.98	9.70	0.0001	-7.91	6.80	14.78	0.0001	
VALLFORG	1.71	0.04	-1.60	0.2930	-4.29	4.00	8.45	0.0001	-6.00	-3.41	2.73	0.2632	
LITTPINE	1.86	1.47	-0.32	0.8045	-0.39	0.60	1.07	0.5380	-3.99	5.95	9.97	0.0001	
PSUNADP	0.88	0.64	-0.19	0.8970	-3.28	-0.02	3.29	0.0200	-5.03	-0.15	4.91	0.0024	
KANE	-0.61	1.13	1.86	0.1711	-2.71	1.16	3.95	0.0040	-5.42	-0.23	5.30	0.0004	
LEADRIDG	-0.71	1.94	2.70	0.0335	-3.31	0.55	3.90	0.0050	-6.12	0.11	6.26	0.0001	
MILFORD	2.40	0.40	-1.91	0.2046	-3.27	2.38	5.71	0.0001	-5.09	0.58	5.73	0.0022	
----- potassium -----					----- sodium -----					----- chloride -----			
CROOKCRK	0.97	8.11	7.17	0.0045	-0.97	9.11	10.13	0.0001	3.15	-4.47	-7.56	0.0001	
GODDARD	1.72	11.76	10.08	0.0003	-2.10	9.19	11.35	0.0001	-0.26	1.89	2.29	0.1335	
HILLSCRK	3.92	14.41	10.52	0.0005	-1.50	12.79	14.32	0.0001	-1.26	4.57	5.85	0.0017	
LAURHILL	2.91	6.45	3.55	0.2173	-0.52	5.06	5.62	0.0102	-0.23	-3.22	-2.90	0.0294	
LITTBUFF	5.27	7.47	2.21	0.4559	-2.23	4.57	6.83	0.0042	-0.68	-1.17	-0.45	0.7509	
SLOCUM	2.62	17.50	14.94	0.0001	-1.69	12.36	14.13	0.0001	0.22	5.25	5.10	0.0017	
VALLFORG	4.72	12.71	8.08	0.0117	-0.40	-1.56	-0.98	0.7140	0.35	-4.73	-4.91	0.0335	
LITTPINE	4.00	16.66	12.69	0.0006	4.08	14.80	10.74	0.0007	2.73	4.44	1.73	0.3655	
PSUNADP	-0.99	1.43	2.45	0.2865	-1.33	-4.51	-3.16	0.1459	-0.63	-1.27	-0.62	0.6747	
KANE	-2.45	1.63	4.15	0.0574	-3.07	-3.50	-0.40	0.8324	-2.23	-1.54	0.75	0.5714	
LEADRIDG	-5.83	0.43	6.30	0.0047	-3.04	-4.01	-0.94	0.6392	-1.51	-1.87	-0.33	0.8257	
MILFORD	-5.56	3.57	9.18	0.0001	0.28	-0.52	-0.77	0.7228	-0.66	0.23	0.94	0.6101	

County). Post-CAAA trend analyses indicate that the increasing patterns at Little Pine and Crooked Creek Lake were reversed, while the decreasing pre-CAAA patterns continued into the post-CAAA period at Laurel Hill, Valley Forge, Penn State, and Milford but were reversed at M. K. Goddard, Hills Creek, Little Buffalo, Slocum, Kane, and Leading Ridge. Laurel Hill was the only site where the decreasing pre-CAAA pattern continued into the post-CAAA period and was statistically significant ($p < 0.05$). At Hills Creek, Slocum, M. K. Goddard, and Kane the increasing post-CAAA trends were significant ($P < 0.05$) as well. The decreasing post-CAAA wet sulfate deposition trend at Little Pine was also significant. With four exceptions (M. K. Goddard, Little Buffalo, Leading Ridge, and Kane), wet sulfate deposition trends, since 1995, are generally consistent with the concentration trends. However, fluctuations in precipitation volumes between and within summary periods has been a strong, influencing factor on wet deposition trends and the reason for the increasing deposition patterns at four of the sites listed above while sulfate concentrations at these sites have decreased the past 12 years.

Nitrate Concentrations - 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 nine of the 12 long-term monitoring sites (Crooked Creek Lake, Kane, Hills Creek, Leading Ridge, Little Pine, Penn State, Valley Forge, Slocum, and Milford). The largest statistically significant reduction (0.476 mg/L) was measured at the Milford site in eastern Pennsylvania. The smallest significant reduction (0.275 mg/L) was measured at the Little Pine site in Lycoming County. Decreases in mean annual nitrate concentrations since 1995 were larger in eastern (0.394 mg/L) and central (0.349 mg/L) portions of the state than in the western region (0.289 mg/L). The reductions in nitrate concentrations also appear to be larger across the northern tier counties than in the southern half of Pennsylvania. The mean annual statewide reduction in nitrate concentrations since 1995 is 0.340 mg/L (Table 5).

Although decreasing nitrate concentration patterns were 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 0.492 mg/L lower the past 12 years than during the previous 12-year pre-CAAA period. And for the first time since implementation of the Title IV, the reductions were statistically significant ($p < 0.05$) at all sites, including the three sites (M. K. Goddard, Laurel Hill, and Little Buffalo) that did not 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 (0.666 mg/L) and Leading Ridge (0.669 mg/L) sites in central Pennsylvania and at the Milford site (0.676 mg/L) in Pike County. The smallest significant reduction (0.284 mg/L) was measured at Laurel Hill State Park in Somerset County. Reductions in growing season nitrate concentrations since 1995 were greater in central (0.549 mg/L) and eastern (0.511 mg/L) Pennsylvania and lowest in the western third (0.410 mg/L) of the state (Table 5).

Dormant season nitrate concentrations since 1995 were also lower than the pre-CAAA reference period; however, the reductions were generally small and significant ($p < 0.05$) at only the Kane (0.273 mg/L), Milford (0.353 mg/L), Slocum (0.417 mg/L), and Hills Creek (0.322 mg/L) sites, all of which are located in the northern tier counties of the state. Despite the lack of statistically significant reductions at most sites, the western, central, and eastern post-CAAA regional means

Table 5. Comparison of mean annual and seasonal nitrate ion concentrations and wet depositions at 12 atmospheric deposition monitoring stations in Pennsylvania before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

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	1.683	-0.163	1.949	1.665	-0.284*	1.780	1.722	-0.058
GODDARD	2.076	1.810	-0.266	2.188	1.802	-0.385*	1.987	1.872	-0.115
CROOKCRK	2.141	1.815	-0.326*	2.374	1.895	-0.479*	1.899	1.744	-0.155
KANE	1.899	1.496	-0.403*	1.958	1.465	-0.493*	1.850	1.576	-0.273*
Western Region	1.990	1.701	-0.289*	2.117	1.707	-0.410*	1.879	1.728	-0.151*
LITTBUFF	2.011	1.772	-0.239	2.214	1.814	-0.401*	1.877	1.732	-0.145
HILLSCRK	1.851	1.418	-0.433*	1.967	1.429	-0.538*	1.748	1.425	-0.322*
LEADRIDG	2.001	1.614	-0.387*	2.228	1.559	-0.669*	1.828	1.694	-0.134
LITTPINE	2.059	1.783	-0.275*	2.185	1.713	-0.472*	1.973	1.904	-0.069
PSUNADP	1.877	1.472	-0.405*	2.135	1.469	-0.666*	1.672	1.488	-0.184
Central Region	1.961	1.612	-0.349*	2.145	1.597	-0.549*	1.822	1.648	-0.174*
VALLFORG	1.718	1.391	-0.326*	1.926	1.464	-0.462*	1.541	1.318	-0.223
MILFORD	1.784	1.308	-0.476*	1.987	1.311	-0.676*	1.666	1.313	-0.353*
SLOCUM	1.954	1.575	-0.379*	2.033	1.638	-0.395*	1.935	1.518	-0.417*
Eastern Region	1.818	1.425	-0.394*	1.982	1.471	-0.511*	1.714	1.383	-0.331*
Statewide	1.935	1.595	-0.340*	2.094	1.602	-0.492*	1.814	1.609	-0.205*

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	22.059	-2.556	12.286	10.824	-1.462	12.331	11.236	-1.095
GODDARD	23.435	20.082	-3.353	13.679	11.084	-2.595	9.757	8.999	-0.758
CROOKCRK	22.874	20.131	-2.743*	13.327	11.424	-1.903	9.548	8.704	-0.844
KANE	24.014	17.834	-6.180*	12.856	9.301	-3.555*	11.163	8.534	-2.628*
Western Region	23.735	20.027	-3.708*	13.037	10.658	-2.379*	10.700	9.368	-1.331*
LITTBUFF	21.713	20.136	-1.577	12.072	11.078	-0.993	9.640	9.057	-0.583
HILLSCRK	17.346	13.512	-3.834*	10.417	7.789	-2.628*	6.927	5.723	-1.204
LEADRIDG	21.583	16.917	-4.666*	12.128	8.986	-3.142*	9.454	7.930	-1.524*
LITTPINE	21.586	18.691	-2.895*	12.310	9.773	-2.537*	9.278	8.917	-0.361
PSUNADP	18.890	16.612	-2.277	11.065	9.283	-1.782	7.824	7.330	-0.494
Central Region	20.246	17.174	-3.073*	11.605	9.382	-2.223*	8.641	7.792	-0.850*
VALLFORG	20.248	16.942	-3.307*	11.501	9.462	-2.039	8.745	7.480	-1.265
MILFORD	21.339	15.933	-5.406*	12.387	8.529	-3.858*	8.953	7.405	-1.548*
SLOCUM	21.565	17.198	-4.367*	12.579	9.783	-2.797*	8.989	7.415	-1.574*
Eastern Region	21.051	16.691	-4.360*	12.156	9.258	-2.898*	8.896	7.433	-1.462*
Statewide	21.639	18.004	-3.635*	12.233	9.776	-2.457*	9.407	8.228	-1.180*

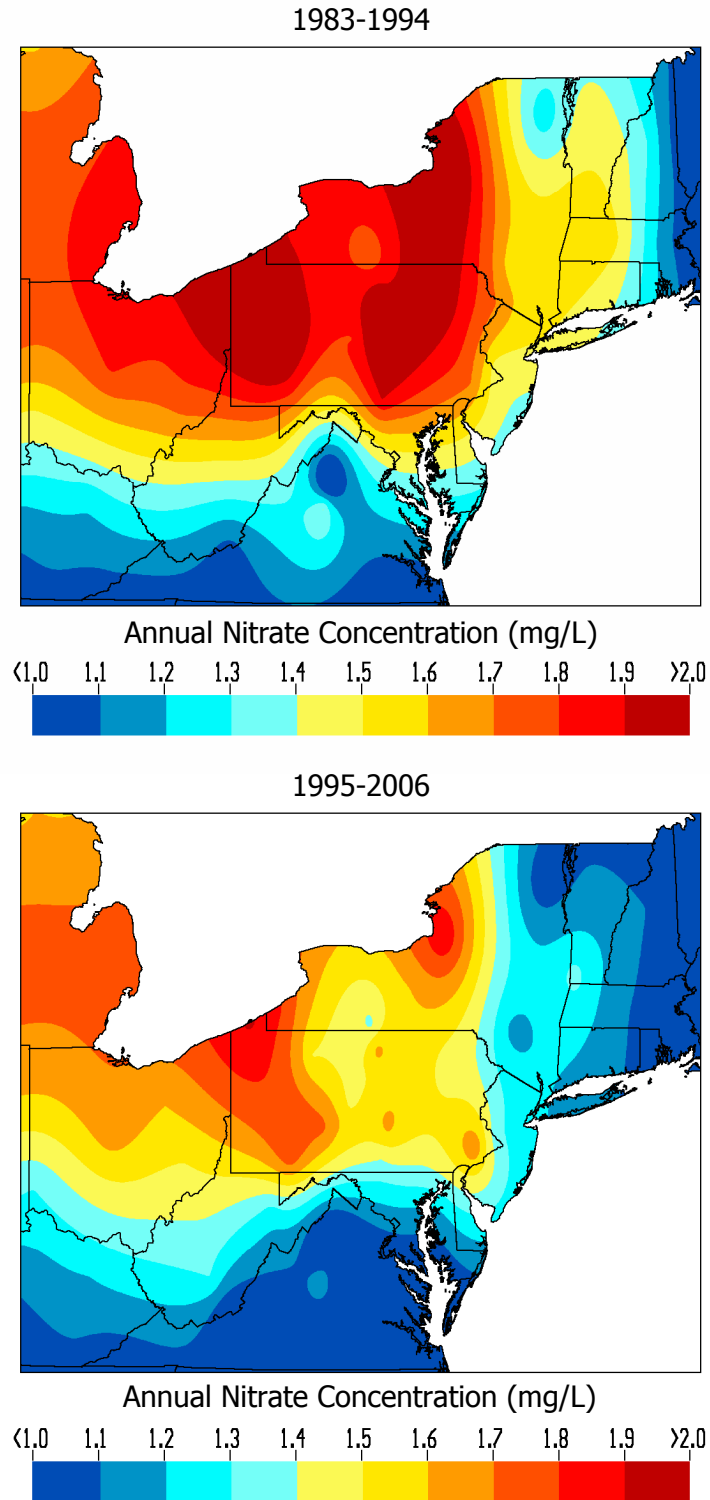


Figure 8. Mean annual nitrate concentrations across Pennsylvania and neighboring states before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

were significantly lower than the pre-CAAA means as was the statewide mean reduction of 0.205 mg/L. On a regional basis, changes in dormant season nitrate concentrations since 1995 were much greater in eastern Pennsylvania (0.331 mg/L) than in either the central (0.174 mg/L) or western (0.151 mg/L) portions of the state (Table 5).

Wet Nitrate Depositions - Annual wet nitrate deposition has decreased throughout the state since 1995 (Table 5, Figure 9). Significant ($p < 0.05$) reductions in mean annual wet nitrate deposition were measured at Crooked Creek Lake (2.74 kg/ha), Kane (6.18 kg/ha), Hills Creek (3.83 kg/ha), Leading Ridge (4.67 kg/ha), Little Pine (2.90 kg/ha), Valley Forge (3.31 kg/ha), Milford (5.41 kg/ha), and Slocum (4.37 kg/ha). Except for Leading Ridge, Crooked Creek Lake, and Valley Forge, all of these sites are located in the northern tier counties of the state. Decreases in mean annual nitrate deposition were significant ($p < 0.05$) for all three regions, with the greatest regional reductions occurring in eastern (4.36 kg/ha) and western (3.71 kg/ha) portions and the state; the reduction in central Pennsylvania averaged 3.07 kg/ha since 1995 (Table 5).

Like nitrate concentrations, the majority (68%) of the decrease in annual nitrate deposition since 1995 occurred during the growing season (Table 5). With two exceptions (Crooked Creek Lake and Valley Forge), significant reductions in mean growing season wet deposition were measured at each site that reported significantly lower annual wet nitrate deposition. Wet growing season depositions at Crooked Creek Lake and Valley Forge were sharply lower but not significantly ($p < 0.05$) different from pre-CAAA levels. The largest growing season reductions were measured at the Milford (3.86 kg/ha) and Kane (3.56 kg/ha) sites; the smallest significant reduction (2.54 kg/ha) was observed at Little Pine. The overall average statewide reduction in growing season nitrate deposition since 1995 was 2.46 kg/ha, which is statistically significant ($p < 0.05$). Significant reductions in regional growing season depositions were also observed in western (2.38 kg/ha), central (2.22 kg/ha), and eastern (2.90 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 growing season deposition. Despite the fact that only four sites (Kane, Leading Ridge, Milford, and Slocum) recorded significantly ($p < 0.05$) lower dormant season nitrate depositions since 1995, the statewide decrease (1.18 kg/ha) as well as the western (1.33 kg/ha), central (0.85 kg/ha) and eastern (1.46 kg/ha) regional mean reductions were significant ($p < 0.05$). The largest reduction in dormant season nitrate deposition occurred at the Kane site (2.63 kg/ha). With the exception of the Leading Ridge site, all of the sites with significantly lower dormant season nitrate deposition since 1995 are located in the northern tier counties of the state.

Nitrate Concentration and Wet Deposition Trends - Pre- and post-CAAA trend analyses indicate that nitrate concentrations were decreasing at all sites prior to 1995 and that these patterns continued at all sites during the post-CAAA period with all sites, except Valley Forge, exhibiting even greater reductions since 1995 (Table 3). At six sites (Crooked Creek Lake, M.K. Goddard, Laurel Hill, Little Pine, Kane, and Milford) the decreasing post-CAAA nitrate concentration trends are statistically significant ($p < 0.05$).

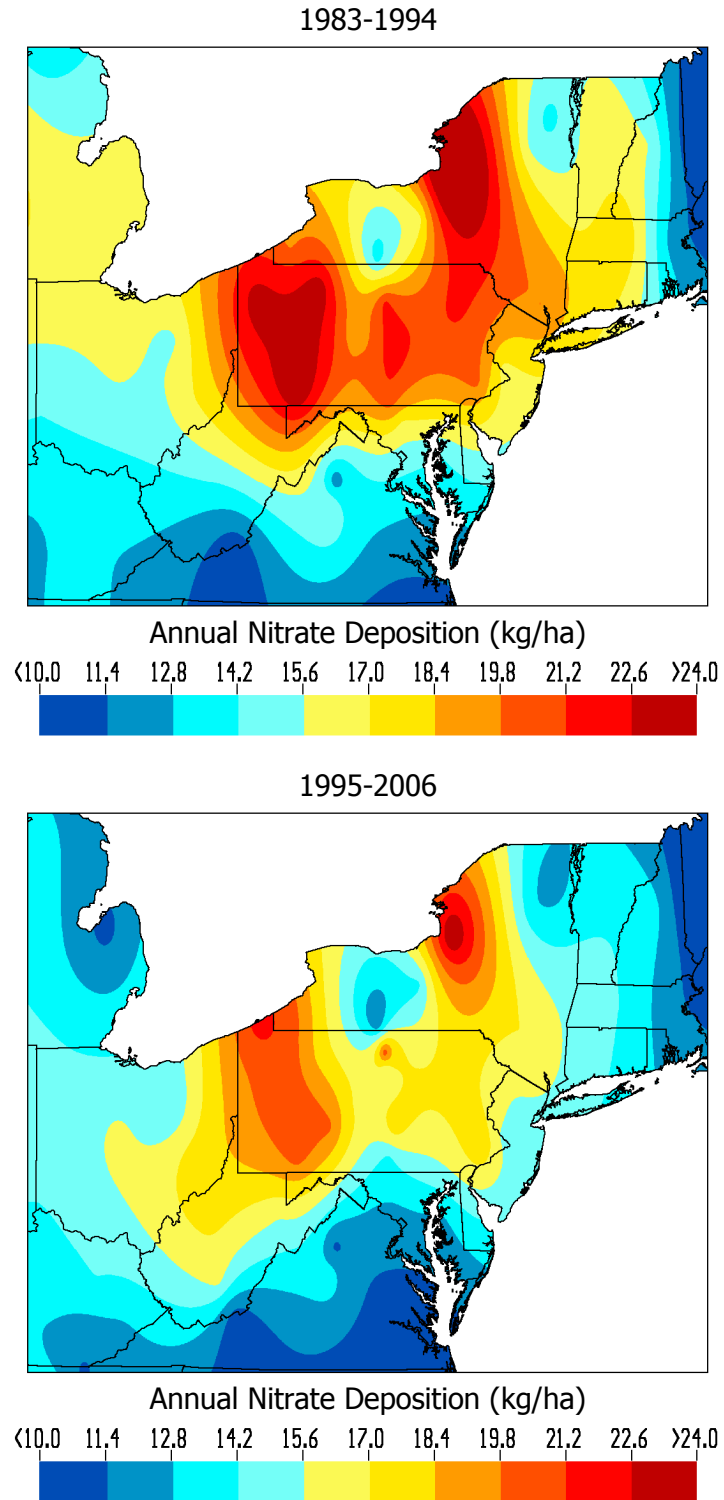


Figure 9. Mean annual nitrate wet deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

Pre-CAAA nitrate deposition trends were also decreasing at all sites except Little Pine (Table 4). Post-CAAA analyses indicate that the pre-CAAA decreasing pattern continued during the post-CAAA period at most sites, with six sites (Crooked Creek Lake, Laurel Hill, Penn State, Leading Ridge, Kane, and Milford) exhibiting even greater reductions, two of which (Crooked Creek Lake and Laurel Hill) are statistically significant ($p < 0.05$). 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 ($p < 0.05$) over the past 12 years (Table 4). In contrast, increasing post-CAAA nitrate deposition trends were evident at Slocum and Hills Creek, statistically significant changes from the decreasing pattern that were evident at these sites from 1983-1994.

Hydrogen Ion Concentrations (as pH) - The pH of precipitation in Pennsylvania since 1995 has increased (become less acidic) throughout the Commonwealth (Table 6, Figure 10). The increases in mean annual pH at each site relative to the pre-CAAA reference period were statistically significant ($p < 0.05$). The greatest increases in mean annual pH were measured at the Leading Ridge and Milford NADP/NTN sites (0.19 and 0.20 unit, respectively); the smallest increase was measured at Laurel Hill State Park (0.13 unit) located in western Pennsylvania. The increase in mean annual pH across the state was 0.17 pH unit. On a regional basis, the largest increases in pH were measured in eastern (0.19 unit) and central (0.18 unit) Pennsylvania; the increase in western Pennsylvania was 0.16 unit. Increase in pH across the state are generally consistent with observed decreases in sulfate (Table 2) and nitrate (Table 5) concentrations; however, fluctuations in ammonium and some base cation concentrations have also exerted some influence on pH at some sites.

Growing season pH means since 1995 increased substantially when compared to the pre-CAAA means (Table 6). All of the increases were statistically significant ($p < 0.05$). The statewide average increase in growing season pH since 1995 was 0.20 pH unit. The increase in mean growing season pH from 4.09 before 1995 to 4.29 after 1995 represents a decrease in H^+ concentrations of nearly 37%. The largest increase in mean growing season pH (0.26 unit) was measured at the Leading Ridge site in Huntingdon County. This change represents a 45% reduction in H^+ concentrations since 1995. Even the relatively small increase in pH at Laurel Hill (0.15 unit) between the pre- and post-CAAA periods (4.06 versus 4.21) represents a reduction in H^+ concentrations of 29%.

Significantly ($p < 0.05$) higher dormant season pH means were also evident at all long-term monitoring sites since 1995 (Table 6). Increases in mean dormant season pH ranged from 0.09 unit at Little Pine to 0.18 unit at Slocum. The statewide increase in mean dormant season pH was 0.14 unit. Regional increases in post-CAAA dormant season pH values ranged from 0.04 to 0.08 unit lower than the measured changes in post-CAAA growing season means. Although the smallest increases in growing and dormant season pH means were generally 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 were likely the result of regional and seasonal differences in the relative change in nitrate (Table 5) and sulfate (Table 2) concentrations, both of which were largest in eastern Pennsylvania during the dormant season. It

Table 6. Comparison of mean annual and seasonal pH and hydrogen ion wet depositions at 12 atmospheric deposition monitoring stations in Pennsylvania before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

Site/Region	pH								
	Annual			Growing Season			Dormant Season		
	Pre-CAA Mean	Post-CAA Mean	Difference	Pre-CAA Mean	Post-CAA Mean	Difference	Pre-CAA Mean	Post-CAA Mean	Difference
LAURHILL	4.156	4.284	0.127*	4.060	4.210	0.150*	4.266	4.373	0.108*
GODDARD	4.148	4.320	0.172*	4.091	4.284	0.193*	4.226	4.365	0.140*
CROOKCRK	4.078	4.224	0.146*	3.995	4.159	0.163*	4.193	4.315	0.123*
KANE	4.162	4.342	0.180*	4.077	4.292	0.214*	4.272	4.409	0.137*
Western Region	4.136	4.292	0.156*	4.056	4.236	0.180*	4.239	4.366	0.127*
LITTBUFF	4.164	4.340	0.177*	4.082	4.294	0.211*	4.262	4.405	0.144*
HILLSCRK	4.184	4.371	0.186*	4.101	4.304	0.203*	4.320	4.485	0.164*
LEADRIDG	4.147	4.338	0.192*	4.042	4.296	0.255*	4.277	4.399	0.123*
LITTPINE	4.135	4.280	0.146*	4.052	4.236	0.184*	4.253	4.339	0.086*
PSUNADP	4.179	4.352	0.173*	4.095	4.293	0.198*	4.286	4.441	0.155*
Central Region	4.161	4.336	0.175*	4.074	4.285	0.211*	4.280	4.414	0.134*
VALLFORG	4.248	4.431	0.184*	4.172	4.379	0.207*	4.345	4.503	0.159*
MILFORD	4.222	4.421	0.198*	4.148	4.380	0.232*	4.316	4.476	0.159*
SLOCUM	4.191	4.370	0.180*	4.129	4.305	0.177*	4.277	4.459	0.182*
Eastern Region	4.220	4.408	0.187*	4.150	4.355	0.205*	4.313	4.479	0.167*
Statewide	4.168	4.339	0.172*	4.087	4.286	0.199*	4.274	4.414	0.140*
	Hydrogen Ion Wet Depositions (kg/ha)								
Site/Region	Annual			Growing Season			Dormant Season		
	Pre-CAA Mean	Post-CAA Mean	Difference	Pre-CAA Mean	Post-CAA Mean	Difference	Pre-CAA Mean	Post-CAA Mean	Difference
LAURHILL	0.947	0.697	-0.250*	0.561	0.414	-0.147*	0.387	0.284	-0.102*
GODDARD	0.820	0.549	-0.271*	0.516	0.334	-0.182*	0.303	0.213	-0.090*
CROOKCRK	0.908	0.684	-0.224*	0.577	0.437	-0.140*	0.330	0.248	-0.082*
KANE	0.902	0.553	-0.349*	0.569	0.339	-0.230*	0.329	0.215	-0.114*
Western Region	0.894	0.621	-0.274*	0.556	0.381	-0.175*	0.337	0.240	-0.097*
LITTBUFF	0.757	0.536	-0.221*	0.469	0.325	-0.144*	0.288	0.207	-0.081*
HILLSCRK	0.623	0.417	-0.207*	0.430	0.282	-0.148*	0.192	0.134	-0.058*
LEADRIDG	0.788	0.488	-0.300*	0.505	0.299	-0.206*	0.282	0.192	-0.090*
LITTPINE	0.780	0.563	-0.217*	0.513	0.346	-0.167*	0.268	0.219	-0.049*
PSUNADP	0.678	0.516	-0.162*	0.429	0.334	-0.095*	0.247	0.183	-0.064*
Central Region	0.726	0.504	-0.222*	0.470	0.317	-0.153*	0.256	0.187	-0.069*
VALLFORG	0.678	0.466	-0.213*	0.414	0.282	-0.132*	0.264	0.183	-0.081*
MILFORD	0.733	0.474	-0.258*	0.457	0.284	-0.172*	0.275	0.194	-0.081*
SLOCUM	0.731	0.479	-0.252*	0.470	0.305	-0.165*	0.260	0.173	-0.087*
Eastern Region	0.714	0.473	-0.241*	0.447	0.290	-0.157*	0.266	0.184	-0.083*
Statewide	0.780	0.535	-0.245*	0.493	0.332	-0.161*	0.286	0.204	-0.082*

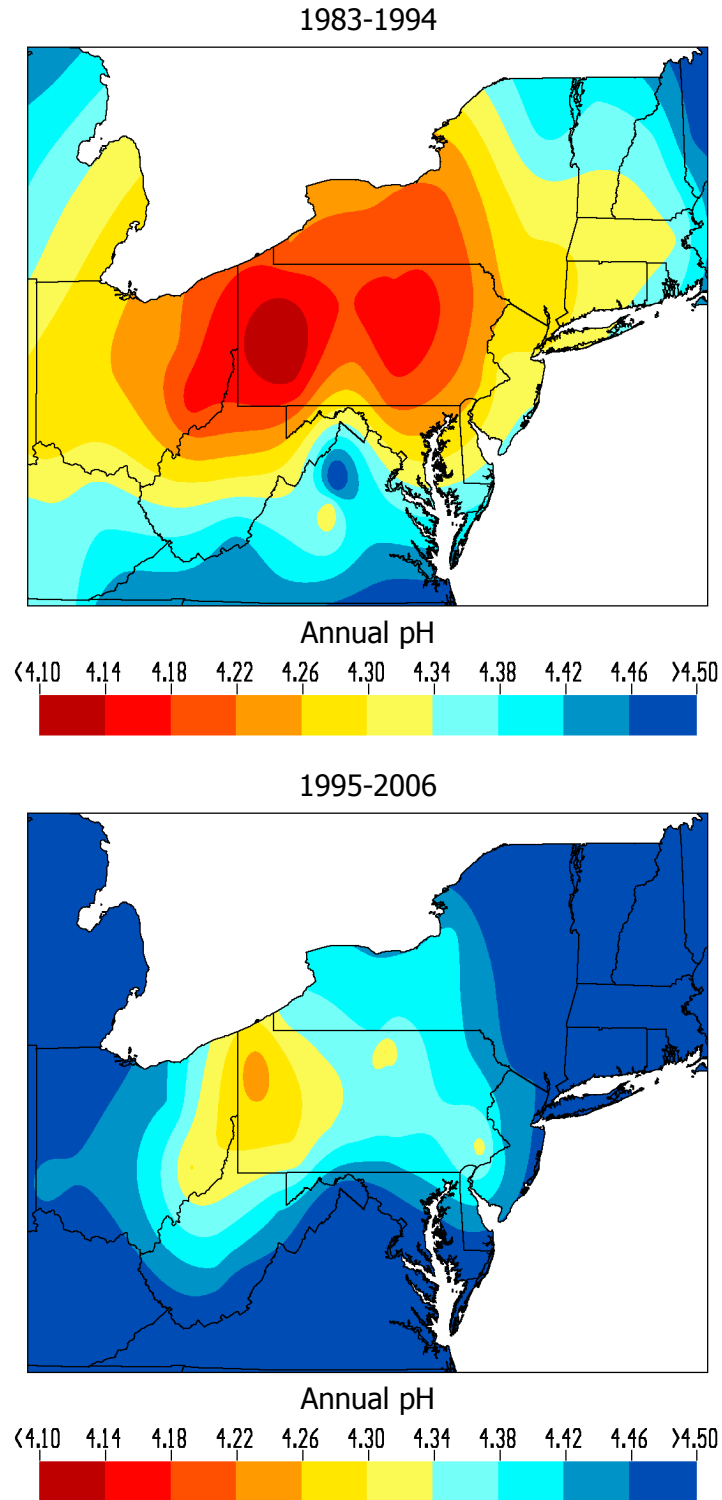


Figure 10. Mean annual pH across Pennsylvania and neighboring states before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

should also be noted that the increase in mean dormant season pH at Slocum was slightly larger than the increase at this site during the growing season. These seasonal increases in pH at Slocum are consistent with the measured seasonal changes in nitrate concentrations at this Luzerne County site (Table 5).

Wet Hydrogen Ion Deposition - Annual H⁺ wet deposition decreased across the entire state since 1995 with all sites reporting significant ($p < 0.05$) drops (Table 6, Figure 11). The largest decreases were measured at Kane (0.35 kg/ha) and Leading Ridge (0.30 kg/ha). The smallest annual decreases were measured at Penn State (0.16 kg/ha) and Valley Forge (0.21 kg/ha). On a regional basis, the decrease in annual H⁺ deposition was greater in western Pennsylvania (0.27 kg/ha) than either the central (0.22 kg/ha) or eastern (0.24 kg/ha) regions. The statewide mean reduction was 0.25 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 12 years. Difference in local land use patterns (forested versus agriculture/urban) and possibly emission sources and climatic patterns are likely the reasons for the substantial difference over a relatively short distance.

Approximately two-thirds of the reduction in annual H⁺ deposition resulted from higher pH values (lower H⁺ concentrations) during the growing season (Table 6). Decreases in growing season H⁺ deposition since 1995 ranged from 0.23 kg/ha at Kane to 0.09 kg/ha at Penn State. All decreases in growing season H⁺ deposition since 1995 were significant ($p < 0.05$). The statewide decrease in mean growing season H⁺ deposition was 0.16 kg/ha; the largest (0.17 kg/ha) and smallest (0.15 kg/ha) regional reductions were observed in western and central Pennsylvania, respectively.

Reductions in dormant season H⁺ depositions were much smaller than growing season reductions, but still statistically significant at all sites (Table 6). The largest post-CAAA drop in dormant season deposition was 0.11 kg/ha at Kane; the smallest decrease (0.05 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 ranged from 0.07 kg/ha in central Pennsylvania to 0.10 kg/ha in the western third of the state.

Hydrogen Ion Concentration and Wet Deposition Trends - Prior to implementation of the CAAA, H⁺ concentrations were decreasing at all sites across Pennsylvania (Table 3); since 1995, the decreasing patterns have continued at all sites, with the rate of decline at 10 of the 12 sites being greater during the post-CAAA period. At six of these sites (Crooked Creek Lake, Laurel Hill, Slocum, Little Pine, Kane and Milford) the post-CAAA trends are statistically ($p < 0.05$) significant. At the Little Buffalo and Penn State sites, the rate of decline during the past 12 years was smaller than observed before 1995 and not significant ($p < 0.05$).

Pre- and post-CAAA wet hydrogen ion wet deposition trends (Table 4) were more variable than the concentration patterns and reflect not only differences in hydrogen ion concentrations but also differences in the spatial and temporal distribution of precipitation between pre- and post-

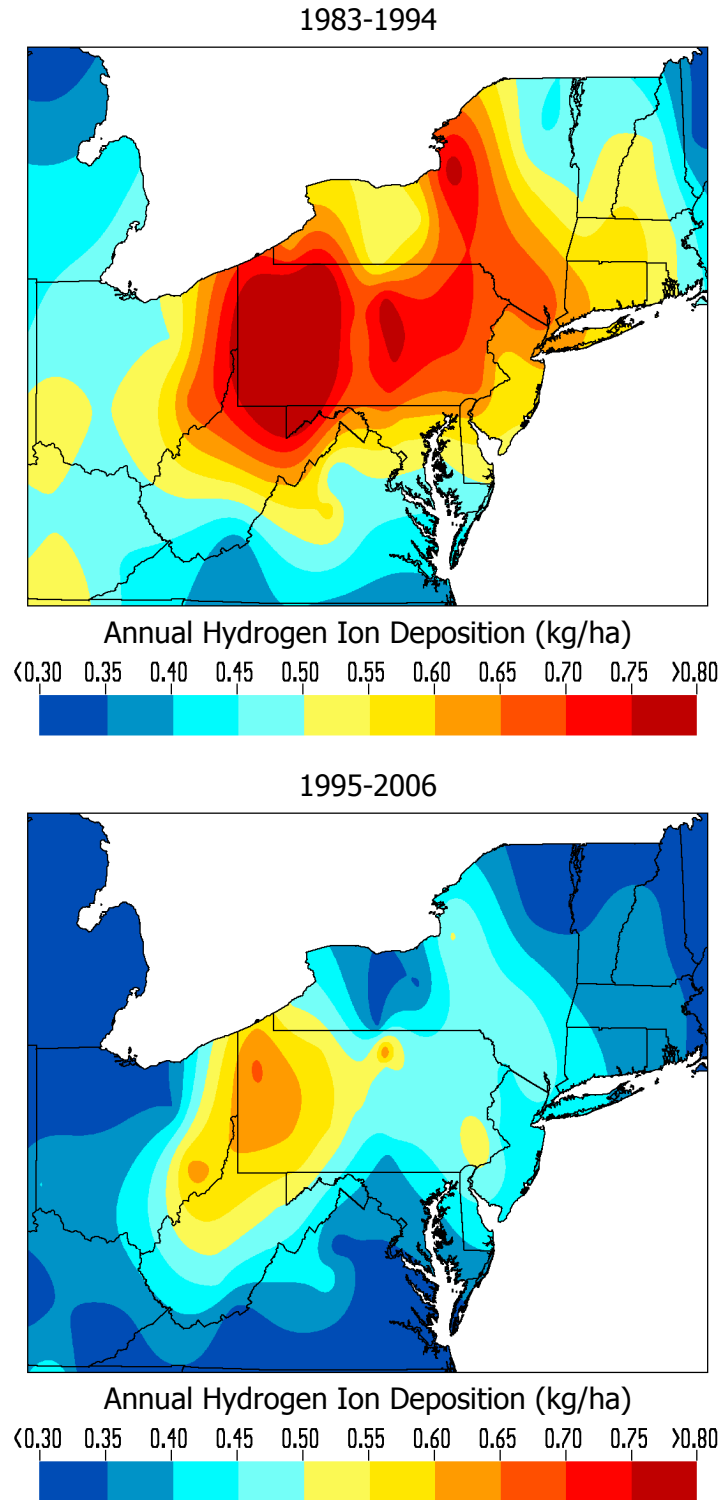


Figure 11. Mean annual hydrogen ion deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2006) implementation of Title IV of the Clean Air Act Amendments of 1990.

CAAA periods. Pre-CAAA wet hydrogen ion deposition patterns were decreasing at all sites but Little Pine. Post-CAAA trend analyses indicate that the increasing pattern at Little Pine was reversed after implementation of Title IV, while the decreasing pre-CAAA patterns continued into the post-CAAA period at the rest of the sites, with the post-CAAA decline being greater at Crooked Creek Lake, Laurel Hill, Valley Forge, Penn State, Milford, and Leading Ridge; however, Laurel Hill, Little Pine, and Crooked Creek Lake were the only sites where the decreasing post-CAAA wet deposition trends were statistically significant ($p < 0.05$).

Discussion

Sulfate and Nitrate Concentrations - Sulfate and nitrate concentrations in precipitation are a function of both natural and anthropogenic sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions within and upwind of the state and climatic conditions that support oxidation processes that convert SO_2 and NO_x to sulfate and nitrate ions that are then removed from the atmosphere during precipitation. Historically, sulfate and nitrate concentrations in Pennsylvania have been highest in western Pennsylvania and decreased across the state to their lowest levels in eastern Pennsylvania. This decreasing west to east gradient has been more pronounced and consistent for sulfate than nitrate concentrations and likely reflects differences in climatic patterns as well as differences in the levels of SO_2 and NO_x in the atmosphere in each region of the state. There have also been well defined seasonal patterns with the highest concentrations of nitrate and sulfate occurring during the growing season when higher temperatures and other climatic factors enhance the conversion of SO_2 and NO_x to sulfate or nitrate ions. Seasonal differences in the magnitude and sources of emissions impacting individual regions may also contribute to these seasonal patterns.

With implementation of Title IV of the CAAA, SO_2 and NO_x emissions were dramatically reduced as illustrated in Figures 2-5. The reductions in emissions resulted in corresponding reductions in both sulfate and nitrate concentrations in precipitation across the entire state (Table 2 and 5). For sulfate, the largest growing season reductions occurred in central and western Pennsylvania (Table 2), while reductions in dormant season concentrations were greatest in eastern Pennsylvania and smallest in the western third of the state. Changes in regional nitrate concentrations have been consistently greater in eastern Pennsylvania, except during the growing season, and decreased to their lowest levels in western Pennsylvania. Reductions in growing season nitrate concentrations have been larger in central Pennsylvania and much larger at sites located in northern tier counties than those in the southern portion of the state. The reasons for these deviations in spatial and seasonal patterns for post-CAAA sulfate and nitrate concentration reductions is uncertain but is likely associated with seasonal differences in the conversion of SO_2 and NO_x to sulfate and nitrate ions as well as seasonal differences in emission reductions, emissions sources, and long-range transport processes affecting specific regions of the Commonwealth. Differences in climatic patterns, particularly the amount and distribution of precipitation, are also important, particularly at individual sites.

The importance of emission sources and seasonal differences in emissions rates can be illustrated by comparing the 2006 annual and seasonal sulfate concentration patterns across Pennsylvania and monthly SO_2 emissions in Pennsylvania and from upwind sources. In 2006, annual sulfate concentrations were higher across the entire state than they were in 2005 and generally higher

than in any year since 2002. The higher annual sulfate concentrations resulted almost entirely from higher dormant season concentrations, especially in central Pennsylvania. Three sites in this region, Hills Creek (Tioga County), Leading Ridge (Huntingdon County), and Little Pine (Lycoming County) recorded their highest dormant season concentrations since implementation of Title IV controls on sulfur dioxide emissions. At Leading Ridge, sulfate concentrations in 2006 were 42% higher than in 2005 (1.885 mg/L versus 1.327 mg/L) and the highest measured at this site since 1991 (2.108 mg/L). The impact across the region was so pronounced that the dormant season mean for 2006 (1.766 mg/L) was the highest since 1992. In contrast, 2006 growing season sulfate concentrations were near their lowest levels in western Pennsylvania and generally higher than in 2005 in central and eastern regions of the state, but still well within the range of values reported since 1995. The higher sulfate concentrations occurred despite a significant drop in SO₂ emissions in 2006 in Pennsylvania and upwind states (Figures 2 and 3, Table 1). The decrease from all Title IV sources of 0.8 million tons of emissions represents one of the largest annual declines in annual SO₂ emissions since 2000 when a drop of 1.3 million tons was reported with implementation of Phase II controls. Annual SO₂ emissions from Pennsylvania sources, as well as those in neighboring states, declined by more than 357,000 tons in 2006 (Table 1) indicating that the higher sulfate concentrations were likely due to either long-range emission sources, seasonal differences in emissions, and/or climatic influence. Since the 2006 nitrate concentrations were only slightly higher in 2006 than 2005 and well within the range of values reported since 1995, the higher sulfate concentrations were most likely due to emissions patterns, not climatic variability, since changes in climate would affect but sulfate and nitrate concentrations similarly.

Differences in facility-level SO₂ emissions between 2005 and 2006 from all Title IV affected sources in upwind states (IL, IN, TN, KY, OH, PA, WV, MD, MI, MO, VA) most likely to have the greatest influence on sulfate concentrations in precipitation in Pennsylvania are shown in Table 7. Even though each of the above states reported lower annual SO₂ emissions in 2006 over 2005 levels (EPA, 2007), reductions in emissions were not uniform across seasons, nor were they uniform across all facilities. In fact, in some states such as TN, IN, WV, MD and MO, SO₂ emissions were higher in some months in 2006 (relative to 2005), especially during January through April. Even in those states where 2006 emissions were below 2005 levels during the dormant season (January through April and November and December), some facilities in those states had substantially higher emissions in 2006 than 2005. In Pennsylvania for example, dormant season emissions in 2006 were higher than 2005 at Elrama (1162 tons), Montour (1108 tons), Portland (1203 tons), Seward (850 tons), and Shawville (723 tons), even though total dormant season SO₂ emission in 2006 were 54,541 tons lower than in 2005 (Table 7). Depending on the location of these utilities and similar facilities in upwind states with respect to deposition monitoring sites in Pennsylvania, emissions from these sources may have a direct impact on sulfate concentrations and wet deposition patterns across the state.

Differences in spatial and temporal distributions of precipitation also influence ionic concentrations. Annual and seasonal precipitation patterns and volumes in 2006 were much different than those in 2005. Although annual precipitation was generally higher in 2006 than in 2005 by two to four inches, seasonal distributions were very different. Regional growing season precipitation in 2006 averaged from seven inches (central Pennsylvania) to 13.5 inches (western Pennsylvania) above 2005 volumes, and was nearly 10 inches higher in 2006 than in 2005 across

Table 7. Differences in dormant season (Jan-Apr and Nov-Dec) and growing season (May-Oct) sulfur dioxide emissions (tons) between 2005 and 2006 for Pennsylvania and selected upwind states (EPA, 2007). A negative value indicates that sulfur dioxide emissions in 2006 were higher than reported in 2005.

Month	PA	OH	TN	KY	IL	IN	WV	VA	MD	MI	MO
Jan	14728.5	27928.3	-2726.8	-4271.8	4248.1	5807.9	1048.6	4021.9	2308.9	3629.6	5938.6
Feb	9362.5	7200.9	-2586.2	1464.5	-2473.1	-1456.3	-4803.0	4237.9	-2215.4	639.7	-1575.8
Mar	17044.0	23824.9	-1661.5	9030.7	168.0	-4390.4	-2602.9	2495.1	-3116.2	-1994.2	-5110.3
Apr	5892.2	3445.8	-1260.2	8684.4	4383.0	-1364.1	5391.9	2910.3	-1925.7	172.2	-1753.5
Nov	2458.7	920.2	1457.7	4748.3	766.3	2489.7	2946.3	-2151.2	948.9	2901.2	3850.1
Dec	5055.0	16430.1	5043.9	14980.8	9205.0	12473.3	4283.7	4550.3	3987.3	3546.1	7533.4
Cold Period	54540.9	79750.1	-1733.2	34636.9	16297.3	13560.1	6264.6	16064.3	-12.3	8894.7	8882.4
May	957.4	-3682.3	1267.3	979.9	1041.2	-4344.0	-2601.3	-685.8	-5002.9	-5908.1	-10911.0
June	6716.8	12165.0	274.7	5103.7	7173.6	3810.2	1491.7	2923.2	1769.8	3464.3	5234.1
July	6560.0	4882.0	-490.9	5569.8	6162.1	4413.3	-1279.1	3471.2	1465.8	-148.7	1317.1
Aug	6609.0	1797.6	1212.0	8752.3	5817.9	5207.4	528.5	3445.3	2089.8	1411.3	3501.1
Sept	15576.5	19753.2	3110.0	12398.9	9036.4	19097.4	7184.6	7239.4	6001.6	2974.1	8975.8
Oct	354.4	8677.4	2835.3	7373.6	763.7	8074.0	1335.0	3347.6	-829.3	4555.9	3726.7
Warm Period	36774.0	43593.0	8208.5	40178.3	29994.8	36258.2	6659.5	19740.9	5494.9	6348.8	11843.7

the entire state. In contrast, 2006 statewide dormant season precipitation was 8 inches below 2005 levels with the largest deficits occurring in western (9 inches) and central (7 inches) Pennsylvania. Such differences can exert substantial influence on annual and seasonal concentration and wet deposition patterns across the state as well as comparisons of 2006 ionic concentration and wet deposition patterns with patterns measured in 2005 and other years. However, as previously noted, annual and seasonal nitrate concentrations in 2006 were not substantially different from 2005, even during the dormant season, which suggests that precipitation differences were not the driving force behind the differences in sulfate concentrations. To illustrate this point, nitrate concentrations were approximately 11% higher in central Pennsylvania during the 2006 dormant season than they were in 2005. The higher concentrations were likely the result of below average precipitation during the 2006 dormant season because concentrations are generally inversely related to precipitation volumes. In contrast, the 2006 mean dormant season sulfate concentrations in central Pennsylvania were 43% higher than in 2005. Obviously, below average precipitation was a contributing factor to the substantially higher sulfate concentrations in 2006; however, if precipitation was the main driving force behind the lower sulfate concentrations, nitrate concentrations should have been similarly affected, but were not. The only other contributing factor would be emissions, as discussed above.

Wet Sulfate and Nitrate Depositions - Wet sulfate and nitrate deposition are the product of the weekly concentration of each ion multiplied by and the amount of precipitation recorded for the weekly sampling period. Consequently, discrepancies between changes in ionic concentrations and wet depositions patterns and statistical significance at individual sites and across regions are largely the result of variability in the timing, amount, and distribution of precipitation at a site or across a region or summary period. For example, significantly lower dormant season sulfate concentrations were evident at all sites since 1995 (Table 2); however, the reduction in wet deposition at the Little Buffalo site (1.69 kg/ha) was not significant ($p < 0.05$). Mean annual precipitation at Little Buffalo during the post-CAAA period was very similar to the pre-CAAA mean. However, on a seasonal basis, precipitation has fluctuated widely with the dormant season average during the post-CAAA period being nearly five inches below the pre-CAAA mean while growing season precipitation was nearly two inches higher. The lower post-CAAA dormant season precipitation volumes resulted in a smaller reduction in wet sulfate deposition at Little Pine compare to other central Pennsylvania sites.

Variability in time series data also affects the sensitivity of the statistical method used to determine whether an observed change was significant or not. As discussed in the results section, post-CAAA reductions in growing season nitrate concentrations were significant at all monitoring sites (Table 5); however, reductions in growing season wet nitrate depositions were not significant at six sites (Laurel Hill, M.K Goddard, Crooked Creek Lake, Little Pine, Penn State, and Valley Forge). This inconsistency between concentration and wet deposition trends is largely the result of highly variable precipitation patterns between pre- and post-CAAA periods. To illustrate, post-CAAA growing season precipitation has been above the pre-CAAA mean across the entire state with five of the wettest growing seasons on record being recorded during the past 12 years. During this same period, some of the driest growing seasons on record have also been reported. Such high variance in time series data over a relatively short period affects

the sensitivity of the statistical method used in this study to determine significance of change, particularly where one of the highly variable parameters (e.g., precipitation volume) is a major determinant of the parameter of interest. As a result, the lack of statistical significance as illustrated above should not be interpreted to mean that lower SO₂ and NO_x emissions have not reduced sulfate and nitrate concentrations and wet depositions, which they have. What the results suggest is that when evaluating differences in wet deposition between summary periods it is important that deviations in precipitation volumes between the periods be considered in quantifying the impact of emission reductions on wet deposition.

Post-CAAA Sulfate and Nitrate Trends - Yearly reductions in post-CAAA sulfate concentrations relative to pre-CAAA levels are highly variable (Table 2). Decreases in sulfate concentrations over the 12-year post-CAAA period resulted from an initial step-function decrease in SO₂ emissions in 1995 followed by another step-function decrease in 1999 through 2000, not a gradual decrease in emissions over the entire period. Fluctuations in annual SO₂ emissions since 1995 (Figures 2 and 3) resulted in fluctuations in annual sulfate concentrations. Compounding this relationship was year to year variability in climatic patterns, especially the amount, distribution, and timing of precipitation, that also influence ionic concentrations in precipitations. Consequently, for any given year, mean annual and seasonal sulfate concentrations at any site can be higher or lower than the reported long-term reduction summarized in Table 2 and depicted in Figure 6.

Year to year fluctuations also influence the ability of the statistical method used to detect significance in differences between pre- and post-CAAA summary periods. Consequently, the lack of statistical significance between pre- and post-CAAA sulfate concentration trends should not be interpreted to mean that Title IV has not had an impact on the sites where the decreasing post-CAAA concentrations are not significantly different from the pre-CAAA concentrations. In fact, post-CAAA sulfate concentration patterns across the state are fairly consistent with SO₂ emissions (Figures 2 and 3) and precipitation patterns. After the initial step-function reduction in 1995, SO₂ emissions from Title IV affected sources increased until 1998 and did not fall below 1995 levels until 2000. After 2000, SO₂ emissions declined to their lowest level in 2002 before increasing slightly in 2003. Emissions in 2005 were lower than 2003 levels but equal to 2002 reported emissions (Figure 2). Sulfur dioxide emissions in 2006 at all Title IV affected sites were at their lowest level since monitoring began (EPA, 2007). Increasing SO₂ emissions from 1995 to 1998 followed by a decreasing pattern from 1999 through 2002 has resulted in highly variable sulfate concentration patterns during the post-CAAA period at most sites (Table 3) which in turn affect post-CAAA trend statistics.

Year to year reductions in nitrate concentrations during the post-CAAA period relative to the pre-CAAA period were not as variable as they were for sulfate concentrations (Table 3). The reason for this is that the decrease in nitrate concentrations over the 12-year post-CAAA period were largely the result of a consistent and gradual decrease in NO_x emissions starting around 1996 (Figures 4 and 5) and continuing through 2006 as opposed to the step-function reductions that occurred with SO₂ emissions in 1995 and again in 1999-2000. As a result, nitrate concentrations have declined continuously since 1996 as reflected in the post-CAAA trend statistics.

Temporal and spatial patterns in post-CAAA sulfate and nitrate concentrations are also influenced by the fact that the impact of emissions and emissions reductions on sulfate and nitrate concentrations are not uniform across the state. Pre- and post-CAAA mean annual sulfate (Table 2) and nitrate (Table 5) concentrations are highly variable across Pennsylvania differing by more than 1.2 mg/L and 0.5 mg/L during both the pre- and post-CAAA periods for sulfates and nitrate, respectively.

Post-CAAA wet nitrate and sulfate deposition trends were even more variable than the concentration trends because of highly variable precipitation patterns. Despite the fact that the average yearly precipitation between the pre- and post-CAAA periods has been nearly identical (44.53 inches versus 45.22 inches) during the last 12 years annual precipitation was below the pre-CAAA mean by as much as 10.32 inches (2001) and above the pre-CAAA mean by as much as 18.68 inches. In fact, some of the post-CAAA years are some of the wettest years on record including 1996, 2003 and 2004 which averaged slightly more than 11 inches (55.77 inches versus 44.53 inches) above the pre-CAAA mean. Post-CAAA mean annual precipitation ranged from 32.44 inches to 63.21 inches, a swing of more than 30 inches over this 12-year period. Even larger differences in annual and seasonal precipitation were evident at individual sites. Such variability in precipitation influences yearly wet deposition levels as well as trend statistics. Consequently, post-CAAA trend results should not be interpreted to mean that wet sulfate and nitrate depositions have not changed as a result of the CAAA. Instead they were included to illustrate that wet sulfate and nitrate deposition trends have changed since 1995 and that sulfate and nitrate wet depositions since then have been highly variable, reflecting to some extent patterns in SO₂ and NO_x emissions from Title IV affected sources as well as climatic variability, particularly the amount and seasonal distribution of precipitation across the state.

Hydrogen Ion (H⁺) Concentrations - Free acidity (measured as pH) in precipitation results primarily from the balance between acid anions (primarily sulfate and nitrate), base cations (calcium, magnesium, potassium, sodium), and ammonium concentrations. Ammonium and base cation concentrations in precipitation act to neutralize acidity resulting in a larger net decrease in H⁺ concentrations with increasing cation concentrations and vice versa. Consequently, when evaluating changes in pH or H⁺ concentrations over time, changes in both cation and anion concentrations must be considered since the difference between their sums determines the net change in pH resulting from reductions in emissions. Conversely, year to year variability in mean annual H⁺ concentrations during pre- and post-CAAA years represents a balance between year to year fluctuations in all anion and cation concentrations in precipitation. This is true with respect to differences in observed trends during the pre-CAAA as well as the post-CAAA summary periods.

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 being greater during the post-CAAA period (Table 3). Net changes in cation and anion concentrations over the post-CAAA period and the impact on pH (H⁺) are summarized in Table 8. The three sites with the greatest decline in H⁺ concentrations since 1995 are Crooked Creek Lake (-40.57 µeq/L), Laurel Hill (-28.43 µeq/L), and Little Pine (-40.12 µeq/L). At all three sites, decreasing sulfate and nitrate concentrations were the primary reasons for the decrease in

H⁺ concentrations offset somewhat by small changes in base cation concentrations and ammonium. The influence that changes in cation concentrations can have on post-CAAA trends was most evident at Hills Creek and Valley Forge (Table 8). At Hills Creek, the decrease in H⁺ concentrations was dominated by higher cation concentrations, especially ammonium and sodium; the small decrease in nitrate concentrations at this site was partially offset by an increase in sulfate concentrations since 1995. Sulfate concentrations also increased slightly at Frances Slocum State Park since 1995 which were partially offset by a decrease in nitrate concentrations. However, the majority of the observed decrease in H⁺ concentrations at Slocum resulted from a 13.35 µeq/L increase in cation concentrations with sodium and ammonium accounting for nearly 70% of the increase.

Large drops in anion concentrations reported at M. K. Goddard (-23.90 µeq/L) and Milford (-22.09 µeq/L) were primarily responsible for the significant decline in H⁺ concentrations at these sites, although lower cation concentrations at both sites were a contributing factor. A decrease in nitrate concentrations at Little Buffalo was clearly responsible for the observed decrease in H⁺ concentrations at this site, although changes in some cation concentrations were evident they tended to offset one another resulting in a small net change which had little influence on the increase in pH at Little Buffalo. Decreasing nitrate concentrations also dominated the Penn State (-7.59 µeq/L), Kane (-11.82 µeq/L), and Leading Ridge (-9.27 µeq/L) sites (Table 8); however, unlike Little Buffalo, these sites also experienced fairly large drops in sulfate concentrations. At Penn State and Kane decreasing cation concentrations, namely ammonium and sodium, were partially responsible for the change in H⁺ concentrations as well. The relatively small impact at Leading Ridge resulted from a small increase in ammonium and a smaller drop in sulfate concentrations at this site that were not evident at the other sites.

Summary and Recommendations

The results presented in this report demonstrate clearly that implementation in 1995 of Title IV of the Clean Air Act Amendments of 1990 resulted in lower sulfur dioxide and nitrogen oxides emissions in Pennsylvania and upwind states (EPA, 2007). Reductions in sulfur dioxide subsequently lowered sulfate concentrations in precipitation throughout the state by 28%. Concurrent with the drop in sulfate concentrations has been a 27% reduction in wet sulfate deposition. Like sulfate, nitrate concentrations have also decreased across Pennsylvania with significant reductions occurring in all regions of the state but not at all sites. Since 1995, the average statewide decrease in nitrate concentrations and wet deposition were 16.1% and 15.8%, respectively. The reductions in nitrate concentrations and wet depositions were a direct response to lower nitrogen oxides emissions in Pennsylvania and neighboring states, particularly from fuel combustion sources (EPA, 2007). 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 2006 based on the 12 long-term monitoring sites was 4.46, an increase of 0.29 pH unit when compared to the pre-CAAA (1983-1994) average pH of 4.17. The 0.29 unit increase represents a decrease in H⁺ concentrations of approximately 49%. Although decreasing sulfate concentrations have contributed significantly to observed reductions in H⁺ concentrations at most sites in Pennsylvania, decreasing nitrate concentrations were in many areas, equally as important, and in some cases (e.g., Little Buffalo and Leading Ridge) more important than reductions in sulfate

concentrations. Likewise, post-CAAA fluctuations in cation concentrations, especially ammonium, have also impacted some sites positively, such as Hills Creek and Slocum, where higher cation concentrations have accounted for the largest portion of the observed reduction in H^+ concentrations, and negatively at some sites, such as M.K. Goddard and Milford, where lower base cations and/or ammonium have actually offset some of the decrease in H^+ concentrations that would have been expected with the observed decrease and acid anion concentrations at these sites.

Observed reductions in sulfate and nitrate concentrations in precipitation and wet depositions exhibit substantial seasonal and regional differences. Reductions in sulfate concentrations and deposition during the growing season were nearly three times greater than during the dormant season. For nitrate, all regions of the state experienced decreasing growing and dormant season concentrations and wet depositions; however, the reductions were not significant at all sites. The largest and most significant reductions occurred during the growing season and were generally twice as large as measured reductions in dormant season concentrations and wet depositions. 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 were also evident, although the reductions were not consistent across seasons or regions. This is particularly true for reductions in sulfate concentrations and wet deposition that tend to be greatest in central Pennsylvania during the growing season and annual period, but largest in the east during the dormant season. In contrast, post-CAAA reductions in annual and growing season nitrate concentrations were lowest in the west and increased to the east. The reverse is true for dormant season reductions which were highest in eastern Pennsylvania and decreased to their lowest levels in western Pennsylvania. Reductions in wet nitrate depositions were consistently highest in eastern Pennsylvania and lowest in the center region regardless of season. Post-CAAA reductions in nitrate deposition also appear to be greater across the northern tier counties than the southern tier counties of Pennsylvania. Differences in emission rates, emissions sources and emissions reductions as well as deviations in precipitation volumes from the pre-CAAA reference period are likely the reasons for these spatial patterns.

Annual sulfate concentrations in 2006 were higher across the entire state than they were in 2005 and higher in Tioga County than they have been since 2000. The higher annual sulfate concentrations resulted almost entirely from higher dormant season concentrations particularly in central Pennsylvania which reported the highest dormant season concentrations since implementation of Title IV controls and at some sites as far back as 1989. The impact across the region was so pronounced that the dormant season mean for 2006 was the highest since 1992. The higher concentrations were evident despite a significant drop of 0.8 million tons in sulfur dioxide emissions in 2006. Since 2006 nitrate concentrations were only slightly higher than in 2005, the higher sulfate concentrations were most likely due to emissions patterns and not climatic variability, despite the fact that annual sulfur dioxide emissions from Pennsylvania sources and those in neighboring states declined by more than 357,000 tons in 2006. A review of monthly facility-level emissions in Pennsylvania and selected upwind states showed that 2006 emissions at some facilities were above 2005 levels during some of the dormant season months.

Even in Pennsylvania where monthly emissions in 2006 were below 2005 levels for all summary periods, some facilities actually had higher dormant season emissions in 2006 than 2005. These results suggest that emissions from specific facilities in Pennsylvania and in upwind states may have had a more direct impact on Pennsylvania than in past years because of the tremendous reductions in both sulfur dioxide and nitrogen oxides that have occurred across the region since 1995. The results also suggest that future emission reduction programs may have to target specific facilities in order to provide maximum protection to specific regions of the Commonwealth rather than rely solely on the very successful Cap and Trade Program that was the centerpiece of Title IV.

Measured changes in sulfate and nitrate concentrations over the past 26 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%, vehicle miles traveled increased 155%, and the population increased 38%. At the same time, total emissions of six primary pollutants (nitrogen oxides, ozone, sulfur dioxide, particulate matter, carbon monoxide, and lead) decreased 48% (EPA, 2005). From 1990 through 2005 electricity generation increased 34% while NO_x and SO₂ emissions decreased 46% and 35%, respectively, from all Title IV affected sources (EPA, 2006).

Despite significant reductions in sulfate and nitrate concentrations in precipitation and subsequent reductions in wet deposition throughout the Commonwealth, Pennsylvania, particularly the western third of the state, still receives some of 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 as illustrated in 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 NADP/NTN 2006 Annual Summary (NADP, 2007) which can be viewed at <http://nadp.sws.uiuc.edu>.

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 be necessary if adequate protection of all acid sensitive aquatic and terrestrial ecosystems and cultural and material resources in the Commonwealth are to be protected. Since precipitation is an unmanageable parameter of climate, the only way to provide additional protection 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. Furthermore, understanding how emissions and climate interact is essential in designing future emissions reduction strategies that will merge, as close as possible, our desires to provide maximum protection to our environment with what we can actually achieve while maintaining the quality of life for the citizens of Pennsylvania.

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