

**Reductions in Acidic Wet Deposition Following Implementation of the
Clean Air Act Amendments of 1990: 1995-2003**

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Reductions in Acidic Wet Deposition Following Implementation of the Clean Air Act Amendments of 1990: 1995-2003

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 eastern United States, including one site located on the Allegheny National Forest near Kane, Pennsylvania (Lamb and Bowersox, 2000). The original and continuing goal of this program is to provide data on temporal trends and the geographic distribution of the wet deposition of acidic compounds, nutrients, and base cations. Data from the initial couple of years of operation of this network indicated that precipitation over the Mid-Atlantic and Northeast regions of the United States, especially eastern Ohio and western Pennsylvania, was very acidic. The pH of precipitation samples collected in this region was frequently below 4.0, while annual sulfate and nitrate concentrations averaged above 3.5 mg/L and 2.0 mg/L, respectively. The very high acidity and nitrate and sulfate concentrations were attributed to sulfur dioxide (SO₂) and nitrogen oxides (NO_x) emissions, the principle precursors of acid rain, from sources located within the region and in upwind Midwestern states, particularly states along the Ohio River Valley.

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

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

Pennsylvania Atmospheric Deposition Monitoring Network

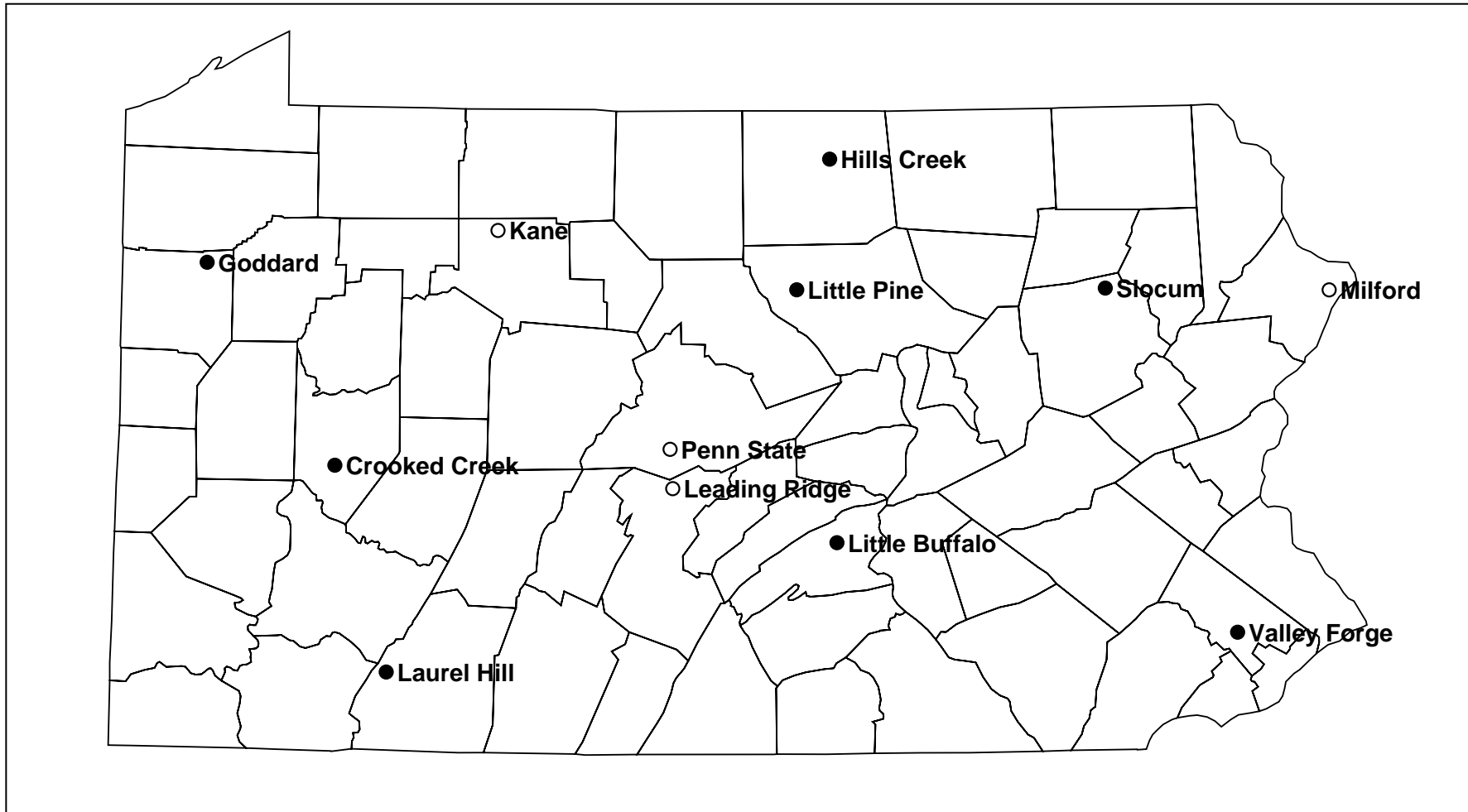


Figure 1. Locations of long-term sites in the Pennsylvania Atmospheric Deposition Monitoring Network. Sites marked with an empty circle are part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN).

Lycoming (Little Pine State Park), Perry (Little Buffalo State Park), Luzerne (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, Northeast 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. (2004) which can be viewed over the internet at <http://www.dep.state.pa.us>. Precipitation chemistry data and wet deposition estimates for all DEP sites for all years of operation are available at this web address. Network design and operation of all NADP/NTN sites in Pennsylvania and all other locations in the United States are also available over the internet at <http://nadp/sws.uiuc.edu>. Concentration measurements and wet deposition estimates for all NADP/NTN sites are also accessible at this web address.

Emission 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 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.

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, 2004b). 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 reduction programs prior to the mandatory date of 1 January 2000. This was also the case in 1994-1995 for some Phase I affected sources. Since 2000, annual sulfur dioxide emissions from all Title IV affected sources ranged from 11.2 million tons to 10.2 million tons and averaged 10.65 million tons. In 2003, emissions from Title IV affected sources measured 10.6 million tons, an increase of 0.4 million tons over 2002 emissions (Figure 2). This increase was attributed to an increase in the combustion of coal as utilities sought to reduce costs by switching from oil or gas to lower cost coal as their primary source of energy

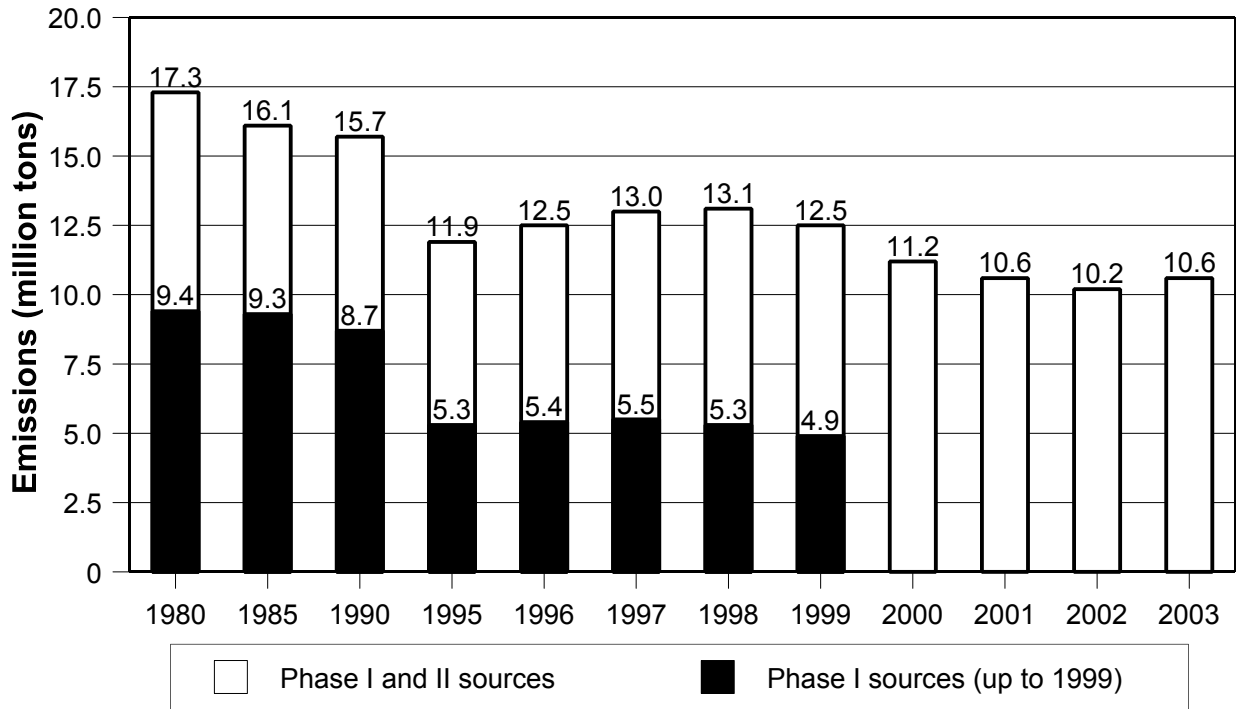


Figure 2. Sulfur dioxide emissions from Title IV affected sources of the Clean Air Act Amendments of 1990 for 1980, 1985, 1990, and 1995 through 2003 (EPA, 2004b).

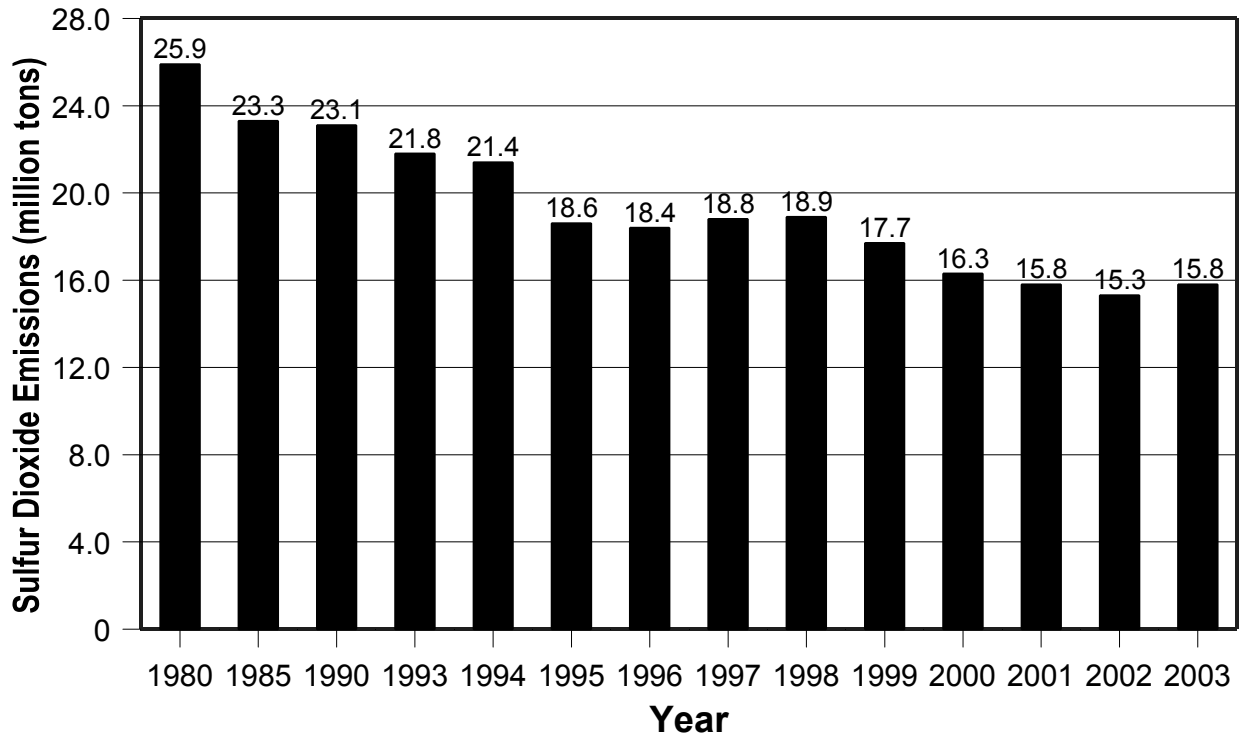


Figure 3. Sulfur dioxide emissions trend from all point and area sources in the United States (EPA, 2004a). Emission estimates for 2003 are preliminary.

(EPA, 2004b). The average annual reduction in sulfur emissions from all Title IV sources since 1995 has been 4.0 million tons (25.5%) when compared to 1990 emission levels (Figure 2).

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 (Figure 3). In 2003, SO₂ emissions totaled 15.8 million tons, 7.3 million tons below 1990 levels but 0.5 million tons over 2002 levels of 15.3 million tons. The decrease in total SO₂ emissions from 1995 through 1999 and from 2000 through 2003 resulted from implementation of Phase I and Phase II, respectively, of Title IV of the CAAA. The increase in 2003 over 2002 levels was largely due to fuel switching at Title IV affected sources as discussed above. (Note: sulfur dioxide emissions from all point and area sources as well as from Title IV affected sources are continuously evaluated by EPA and updated annually. As a result, SO₂ as well as NO_x emissions discussed in this report may differ slightly from emissions reported in previous reports).

Many of the SO₂ emission sources targeted by Phase I and Phase II of the CAAA are located in Pennsylvania, Ohio, West Virginia, Kentucky, Indiana, and Maryland. Sulfur dioxides and NO_x emissions within these states are likely to have a direct impact on precipitation chemistry in Pennsylvania. Annual SO₂ emissions from affected units in these states for 1990 and from 1995 through 2003 (EPA, 2004b) are shown in Table 1. Sulfur dioxide emissions from within these states in 2003 totaled 4.3 million tons, a reduction of 39.5% from 1990 levels. The average percent reduction in emissions from these sources since 1995 was 34.8%. Sulfur dioxide emissions at Pennsylvania units affected by Phase I and II totaled 0.97 million tons in 2003, 2.5 million tons below 1990 levels but 0.08 million tons above 2002 levels. Since 1995, SO₂ emissions from Phase I and II affected units in Pennsylvania averaged 0.99 million tons, an 18.4% reduction over 1990 emissions (Table 1). Percentage reductions in SO₂ emissions since 1995 averaged 42.2% in Ohio, 37.7% in West Virginia, 33.6% in Kentucky, 40.9% in Indiana, and 7.7% 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. 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 2003 (Phase II), NO_x emissions averaged 4.15 million tons, 1.25 million tons below 1995 levels and 0.65 million tons below 1999 emissions (Figure 4). The reductions in NO_x emissions are primarily from fuel combustion sources, which are dominated by utility boilers (EPA, 2004a).

Nitrogen oxides emissions reductions in Pennsylvania and in selected upwind states are listed in Table 1 (EPA, 2004b). The average percent reduction in NO_x emissions in PA, OH, MD, WV, KY, and IN from 1996 through 2003 relative to 1995 emissions was 14.9% (range 2.1% to 25.9%). The percent reduction in 2003 NO_x emissions relative to 1995 emissions averaged 34.5% (range 13.3% to 53.1%). The largest overall reduction in NO_x emissions occurred in Kentucky. The substantial increase in the percent reductions in 2003 relative to the 1996-2002 mean percent reductions reflects changes since implementation of Phase II controls, as well as

Table 1. Sulfur dioxide (SO₂) and nitrogen oxides (NO_x) emissions (1000 tons) from all Phase I and Phase II affected sources in Pennsylvania, Ohio, West Virginia, Kentucky, Indiana and Maryland since implementation of the Title IV of the Clean Air Act Amendments of 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, 2004b).

Year	PA	OH	WV	KY	IN	MD	Total
<u>Sulfur Dioxide Emissions from Phase I and II Affected Sources</u>							
1990	1213.4	2211.6	968.6	905.1	1499.2	282.5	7080.4
1995	1054.5	1199.9	606.8	676.3	894.6	230.0	4662.1
1996	1013.7	1479.0	658.3	642.3	933.6	253.7	4980.6
1997	1071.7	1448.5	663.6	671.4	977.4	259.8	5092.4
1998	1072.9	1415.0	667.9	625.1	968.3	289.0	5038.2
1999	964.2	1309.9	694.5	659.0	941.9	281.8	4851.3
2000	935.2	1209.5	593.3	584.9	874.6	254.5	4450.3
2001	944.9	1125.5	498.1	535.4	795.5	254.5	4153.9
2002	889.9	1132.1	507.1	482.7	778.9	255.4	4046.0
2003	967.2	1175.9	539.9	531.5	803.6	269.0	4287.1
Mean 1995-2003	990.5	1277.3	603.3	601.0	885.4	260.7	4618.0
Average % Reduction ¹	18.4	42.2	37.7	33.6	40.9	7.7	34.8
<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
Mean 1995-2003	217.7	433.0	261.0	276.3	330.4	95.7	1614.0
Average % Reduction ²	17.7	18.1	5.7	25.9	6.9	2.1	14.9
% Reduction ³	34.1	33.8	26.5	53.1	28.4	13.3	34.5

¹Average % reduction in SO₂ emissions from 1995-2003 relative to 1990 emissions.

²Average percent reduction in NO_x emissions from 1996-2003 relative to 1995 emissions.

³Percent reduction in 2003 NO_x emissions relative to 1995 emissions.

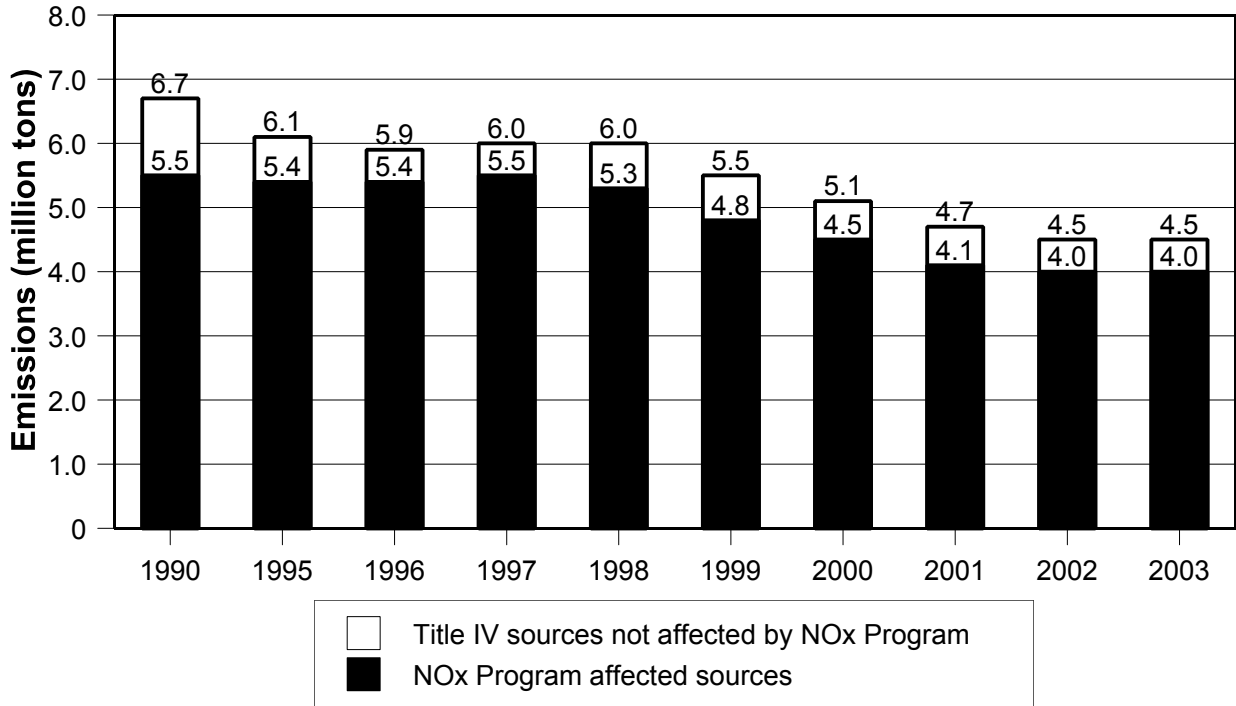


Figure 4. Nitrogen oxides emissions from Title IV affected sources of the Clean Air Act Amendments of 1990 for 1990 and 1995 through 2003 (EPA, 2004a).

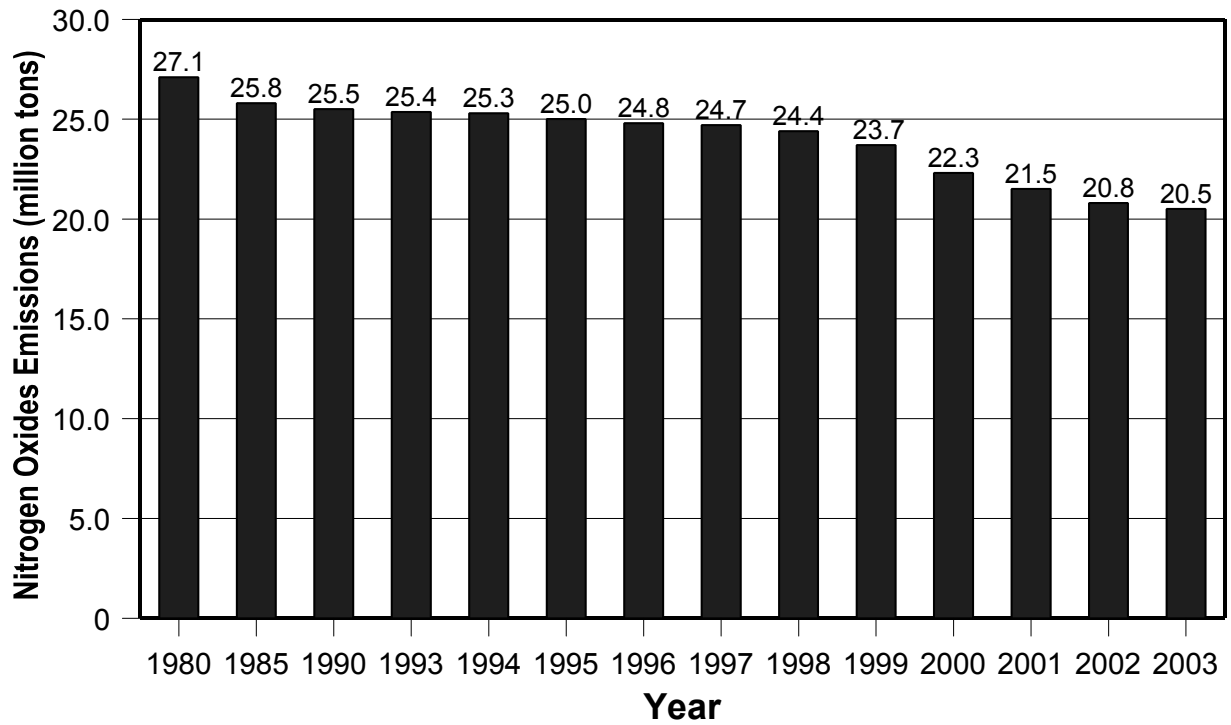


Figure 5. Nitrogen oxides emissions trends from all point and area sources in the United States (EPA, 2004b). Emission estimates for 2003 are preliminary.

other emissions control programs aimed at reducing ozone levels. In Pennsylvania, the average reduction in NO_x emissions since 1996 was 17.7% (46,900 tons). Nitrogen oxides emissions at all Title IV affected sources in PA in 2003 were 90,300 tons lower than in 1995 (Table 1).

Nitrogen oxides emissions from all sources in the United States for 1980, 1985, 1990, and 1993 through 2003 are shown in Figure 5. Clearly, NO_x emissions from all Title IV affected sources represent a relatively small percentage (approximately 24% on average) of total NO_x emissions from all sources (Figures 4 vs. Figure 5). Likewise, reductions in NO_x emissions from Title IV sources from 1996 to 1999 (0.60 million tons) represent 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 4.0 million tons in 2003 (Figure 4). Nitrogen oxides emissions from all sources (except fire) in 2003 totaled 20.5 million tons, 3.9 million tons below 1996 emissions. The greater reduction in total NO_x emissions relative to reductions from Title IV sources represents a decrease in NO_x emissions from other sources, primarily mobile sources. In 1990, fuel combustion sources accounted for 43.3% of all NO_x emissions in the United States; in 2003 these sources represented 38.3%. In contrast, on-road and non-road mobile emission sources in 1990 accounted for 53.1% of the annual total; in 2003 these sources accounted for 56.0% of all NO_x emissions. Although both fuel combustion and on-road and non-road sources decreased in 2003 relative to 1995 (EPA, 2004a), the percent reductions were much greater from fuel combustion sources (-26.5%) than on-road and non-road sources (-11.6%). When compared to 1990 emissions the percent reductions are 26.9% and 14.1%, respectively. Clearly, Title IV and other Titles in the CAAA have reduced NO_x emissions in the United States, with relatively larger reductions occurring from fuel combustion sources (industries/utilities) than from other sources. Consequently, the mix of emissions sources and their relative importance have changed since 1990 and even 1995 with on-road and non-road sources accounting from a larger percentage of all NO_x emissions. Changes in the relative contribution of emission sources in a region likely influence the distribution and magnitude of nitrate reductions in precipitation across that region.

Methods

Evaluation of the effects of a step-function change 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 (1995-2003), weekly precipitation volume and ionic concentration measurements were accumulated into bi-monthly precipitation totals and volume-weighted mean concentrations and wet depositions for each ionic species (i.e., H⁺, 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, 1998). This model was developed by the authors for detecting and quantifying trends in precipitation chemistry data that exhibit strong seasonal patterns (Lynch et al., 1995). The form of the model for both stages was:

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

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

Log-transformed concentrations and depositions were used to normalize the distribution of the model residuals (Lynch et al., 1995). After initially fitting the model to a site's concentration or deposition observations (expressed as $\mu\text{eq/L}$ or 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 2003 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 2003 (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 the two periods.

Results and Discussion

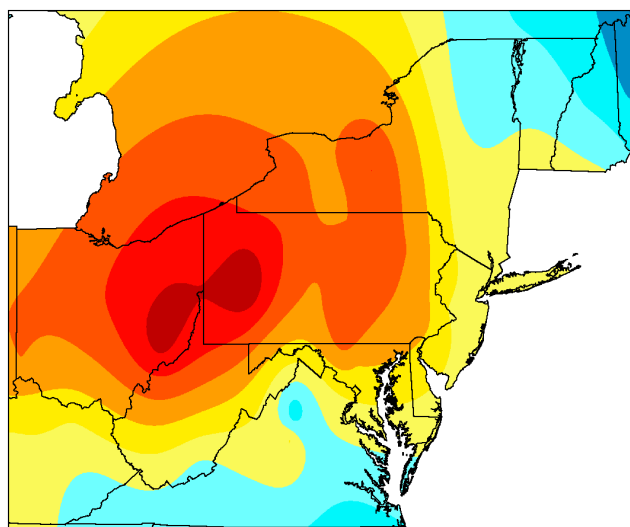
Sulfate - Sulfate concentrations (Figure 6) and wet deposition (Figure 7) have decreased substantially across Pennsylvania since implementation of the CAAA. These reductions are in response to lower SO_2 emissions (Figures 2 and 3) following implementation of Phase I of CAAA, Title IV on 1 January 1995 and Phase II on 1 January 2000. A comparison of mean annual and seasonal sulfate concentrations and wet depositions (Table 2) at each of the long-term monitoring sites during pre- (1983-1994) and post-CAAA (1995-2003) periods illustrates the magnitude of the reductions. Statistically significant ($p < 0.05$) reductions in mean annual sulfate concentrations are evident at all Pennsylvania sites and range from 0.578 mg/L at Laurel Hill (Somerset County) to 0.876 mg/L at Hills Creek (Tioga County). The average reduction is slightly greater in central Pennsylvania (0.769 mg/L) than in either the eastern (0.756 mg/L) or western (0.720 mg/L) regions of the state. The overall average reduction in mean annual sulfate concentrations across the state since 1995 has been 0.749 mg/L (Table 2).

The largest seasonal reductions in sulfate concentrations occurred during the growing season (Table 2). Average growing season reductions ranged from 0.913 mg/L at Slocum State Park in Luzerne County to 1.492 mg/L at the Leading Ridge NADP/NTN site in Huntingdon County with all sites exhibiting statistically significant ($p < 0.05$) decreasing trends. As with annual concentration means, the mean growing season reduction in central Pennsylvania (1.222 mg/L) was slightly larger than in the western (1.119 mg/L) and eastern (0.999 mg/L) regions of the state (Table 2). The overall average growing season reduction in sulfate concentrations since 1995 was 1.130 mg/L, a 30% decrease when compared to the pre-CAAA mean (Table 2).

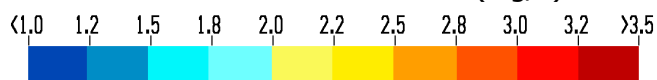
Mean dormant season sulfate concentrations also decreased since 1995 (Table 2), although the drop was not as large as they were for growing season mean concentrations. Reductions in mean dormant season concentrations ranged from 0.250 mg/L at Laurel Hill to 0.594 mg/L at the Slocum site. Reductions in mean dormant season concentrations were significant ($p < 0.05$) at all sites except M.K. Goddard State Park in Mercer County. Unlike growing season reductions in sulfate concentrations, mean dormant season reductions since 1995 were actually greater in eastern Pennsylvania (0.530 mg/L) than in either the central (0.375 mg/L) or western (0.303 mg/L) portions of the state (Table 2). With some exceptions (e.g., Kane, Hills Creek, and Penn State) there is an increasing west to east pattern in the decline of dormant season sulfate concentrations. The reason for this pattern and its deviation from the growing season pattern is uncertain but may be associated with seasonal differences in the conversion of sulfur dioxide to sulfate as well as differences in emissions and long-range transport processes.

As would be expected given the large reductions in sulfate concentrations since 1995, wet sulfate deposition across the state has also decreased (Table 2, Figure 7). On an annual basis, the average reduction in sulfate deposition at each of the long-term monitoring sites ranged from 13.14 kg/ha at the Kane NADP/NTN site in Elk County to 5.20 kg/ha at the Penn State

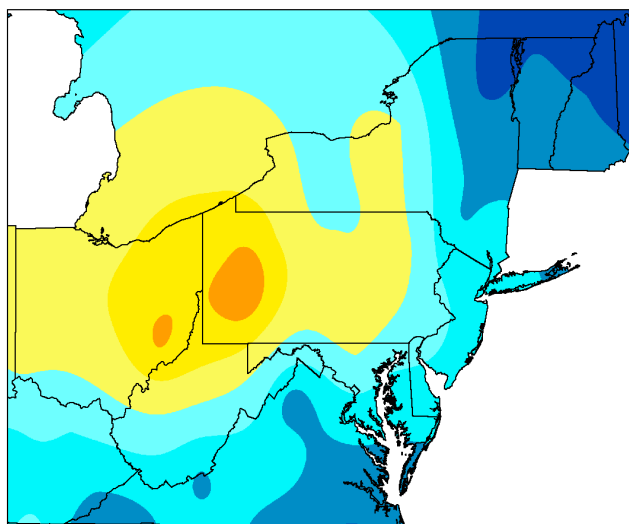
1983-1994



Annual Sulfate Concentration (mg/L)



1995-2003



Annual Sulfate Concentration (mg/L)



Figure 6. Mean annual sulfate concentrations across Pennsylvania and neighboring states before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

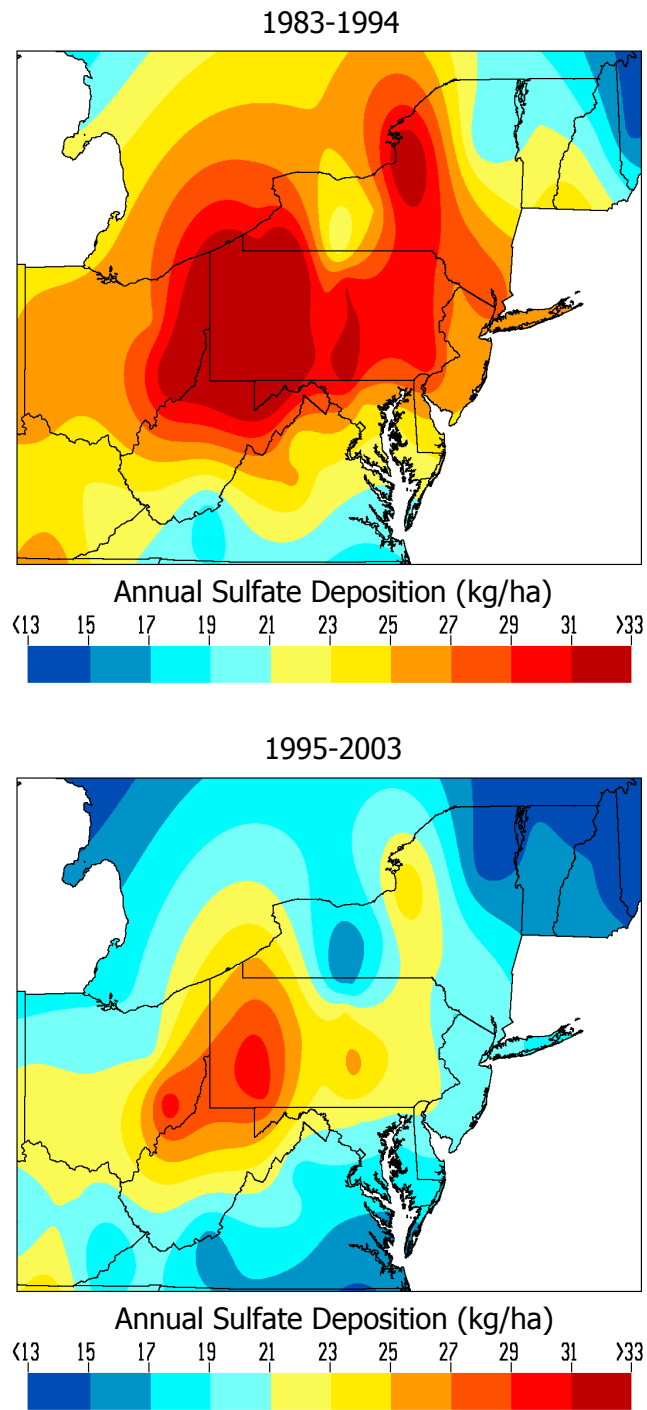


Figure 7. Mean annual sulfate deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

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 (1995-2003) 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-CAA Mean	Post-CAA Mean	Difference	Pre-CAA Mean	Post-CAA Mean	Difference	Pre-CAA Mean	Post-CAA Mean	Difference
Laurel Hill	2.943	2.365	-0.578*	4.022	3.029	-0.993*	1.977	1.727	-0.250*
M.K. Goddard	3.179	2.433	-0.746*	3.957	2.843	-1.114*	2.211	1.959	-0.252
Crooked Creek Lake	3.558	2.809	-0.749*	4.746	3.578	-1.167*	2.242	1.940	-0.302*
Kane-NADP	3.032	2.224	-0.808*	3.909	2.706	-1.202*	2.118	1.711	-0.407*
Western Region	3.178	2.458	-0.720*	4.158	3.039	-1.119*	2.137	1.834	-0.303*
Little Buffalo	2.917	2.271	-0.646*	3.889	2.805	-1.084*	1.982	1.675	-0.307*
Hills Creek	2.793	1.917	-0.876*	3.659	2.420	-1.239*	1.690	1.250	-0.440*
Leading Ridge-NADP	3.036	2.187	-0.849*	4.165	2.673	-1.492*	1.978	1.603	-0.375*
Little Pine	2.965	2.270	-0.694*	3.894	2.825	-1.069*	1.951	1.644	-0.308*
Penn State-NADP	2.935	2.150	-0.785*	3.915	2.689	-1.227*	1.939	1.483	-0.455*
Central Region	2.928	2.159	-0.769*	3.904	2.682	-1.222*	1.906	1.531	-0.375*
Valley Forge	2.576	1.875	-0.701*	3.227	2.247	-0.980*	1.919	1.474	-0.445*
Milford-NADP	2.397	1.595	-0.801*	3.052	1.950	-1.103*	1.762	1.211	-0.550*
Slocum	2.797	2.032	-0.765*	3.504	2.591	-0.913*	1.968	1.375	-0.594*
Eastern Region	2.590	1.834	-0.756*	3.261	2.263	-0.999*	1.883	1.353	-0.530*
Statewide	2.927	2.177	-0.749*	3.827	2.696	-1.130*	1.979	1.588	-0.391*

Site/Region	Sulfate Ion Wet Depositions (kg/ha)								
	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
Laurel Hill	39.132	30.798	-8.335*	25.335	19.584	-5.751*	13.797	11.210	-2.588*
M.K. Goddard	35.841	26.333	-9.507*	24.701	16.800	-7.901*	11.142	9.533	-1.609
Crooked Creek Lake	38.112	29.761	-8.351*	26.751	20.252	-6.499*	11.358	9.509	-1.849*
Kane-NADP	38.584	25.448	-13.136*	25.792	16.224	-9.568*	12.790	9.223	-3.567*
Western Region	37.917	28.085	-9.832*	25.645	18.215	-7.430*	12.272	9.869	-2.403*
Little Buffalo	31.324	25.427	-5.898*	21.045	16.673	-4.372*	10.278	8.753	-1.525
Hills Creek	26.186	17.508	-8.678*	19.372	12.544	-6.827*	6.813	4.962	-1.851*
Leading Ridge-NADP	32.865	22.762	-10.103*	22.624	15.280	-7.344*	10.238	7.481	-2.757*
Little Pine	31.004	23.424	-7.580*	21.793	15.528	-6.265*	9.213	7.899	-1.314
Penn State-NADP	29.401	24.200	-5.201*	20.380	16.816	-3.564	9.019	7.383	-1.636*
Central Region	30.168	22.664	-7.503*	21.053	15.368	-5.685*	9.114	7.296	-1.818*
Valley Forge	30.327	22.192	-8.135*	19.238	13.876	-5.363*	11.090	8.316	-2.774*
Milford-NADP	28.733	18.838	-9.895*	19.062	12.072	-6.990*	9.671	6.763	-2.908*
Slocum	30.880	21.492	-9.388*	21.517	14.889	-6.628*	9.363	6.603	-2.760*
Eastern Region	29.980	20.841	-9.139*	19.939	13.612	-6.327*	10.041	7.227	-2.814*
Statewide	32.758	24.015	-8.743*	22.332	15.878	-6.453*	10.426	8.136	-2.289*

NADP/NTN site in Centre County. The nine-year average statewide reduction in sulfate deposition was 8.74 kg/ha. The smallest reductions in wet deposition occurred in central Pennsylvania (7.50 kg/ha) despite the fact that reductions in sulfate concentrations (Table 2) were actually greater in central Pennsylvania than other regions of the state. Reductions in central Pennsylvania were about 2.0 kg/ha less than those in western (9.83 kg/ha) or eastern (9.14 kg/ha) portions of Pennsylvania. This discrepancy between changes in concentrations and wet deposition is largely a result of variability in the timing and volume of precipitation across regions and summary periods.

Reductions in wet sulfate deposition during the growing season were significant ($p < 0.05$) at all long-term network sites except the Penn State NADP/NTN site in Centre County. The largest average decrease during the past nine growing seasons (9.57 kg/ha) was measured at the Kane NADP/NTN site; the smallest significant ($p < 0.05$) reduction (4.37 kg/ha) was measured at Little Buffalo State Park in Perry County (Table 2). The average statewide growing season reduction was 6.45 kg/ha. The smallest regional reduction in growing season sulfate deposition was measured in central Pennsylvania (5.68 kg/ha); the largest regional reduction (7.43 kg/ha) was observed in western Pennsylvania.

The average post-CAAA statewide decrease in sulfate deposition during the dormant season was 2.29 kg/ha (Table 2). Although all sites reported lower dormant season sulfate deposition since 1995, the reductions were significant ($p < 0.05$) at only 9 of the 12 long-term sites (Table 2). These sites included Hills Creek (1.85 kg/ha), Kane (3.57 kg/ha), Laurel Hill (2.59 kg/ha), Leading Ridge (2.76 kg/ha), Milford (2.91 kg/ha), Penn State (1.64 kg/ha), Slocum (2.76 kg/ha), Crooked Creek Lake (1.85 kg/ha) and Valley Forge (2.77 kg/ha). Interestingly, the greatest regional reduction in sulfate deposition during the dormant season occurred in eastern Pennsylvania. This pattern is consistent with dormant season concentration trends at eastern sites but a departure from growing season deposition differences since 1995. As noted above, precipitation volume differences between sites as well as year to year variability strongly influence seasonal deposition trends and their significance. For example, significantly lower dormant season sulfate concentrations were evident at all but one site (M.K. Goddard) since 1995; however, reductions in wet deposition at three of sites (M.K. Goddard, Little Buffalo, and Little Pine) were not significant ($p < 0.05$). Consequently, when evaluating trends in wet deposition it is important that deviations in precipitation volumes between the pre- and post-CAAA periods as well as between sites and seasons be considered in assessing the impact of reductions in emissions on wet deposition.

Yearly reductions in post-CAAA sulfate concentrations and wet deposition relative to pre-CAAA levels are highly variable. The average annual decrease in sulfate concentrations and deposition over the 9-year post-CAAA period (Table 2) are largely the result of a step-function decrease in SO₂ emissions in 1995, not a gradual decrease in emissions over time. Fluctuations in annual SO₂ emissions since 1995 (Figures 2 and 3) resulted in fluctuations in annual sulfate concentrations and wet deposition. Compounding this relationship is year to year variability in climatic patterns that also influence ionic concentrations and the amount and timing of wet deposition that falls on the Commonwealth. Trend analyses of pre- and post-CAAA ionic concentrations and wet deposition are shown in Tables 3 and 4, respectively. Clearly, sulfate

Table 3. Changes in trends of ionic concentrations in precipitation in Pennsylvania before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

Site	1983-94 trend (%/yr)	1995-2003 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2003 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2003 trend (%/yr)	Change in trends (%/yr)	p	
----- hydrogen ion -----					----- sulfate -----					----- nitrate -----			
CROOKCRK	-1.86	-4.25	-2.40	0.0287	-1.09	-1.80	-0.71	0.5469	-1.64	-3.76	-2.12	0.1189	
GODDARD	-3.11	-3.58	-0.48	0.6401	-1.54	-2.84	-1.30	0.1800	-2.40	-3.65	-1.25	0.1653	
HILLSCRK	-0.91	-1.76	-0.86	0.4647	-0.96	1.08	2.04	0.1761	-1.28	-1.38	-0.10	0.9441	
LAURHILL	-2.06	-3.38	-1.32	0.3324	-0.96	-1.43	-0.47	0.7351	-2.16	-3.24	-1.07	0.4288	
LITTBUFF	-4.03	-1.35	2.68	0.1128	-1.80	0.42	2.22	0.1681	-3.01	-1.50	1.51	0.3404	
SLOCUM	-1.53	-1.30	0.23	0.8662	-0.54	1.87	2.41	0.1559	-1.20	-0.84	0.36	0.8191	
VALLFORG	-1.88	-2.06	-0.18	0.9125	-1.28	-0.74	0.53	0.7308	-2.42	-0.97	1.45	0.3724	
LITTPINE	-0.46	-7.08	-6.62	0.0005	-0.19	-3.39	-3.20	0.0896	-1.57	-5.83	-4.26	0.0218	
PSUNADP	-2.61	-0.79	1.82	0.1960	-2.43	0.53	2.96	0.0632	-2.55	-0.43	2.12	0.1939	
KANE	-1.66	-1.96	-0.30	0.7749	-1.44	0.09	1.53	0.1745	-0.59	-1.30	-0.71	0.4987	
LEADRIDG	-1.51	-1.55	-0.04	0.9803	-2.05	0.98	3.04	0.0797	-1.55	-1.31	0.24	0.8854	
MILFORD	-1.91	-3.01	-1.10	0.4875	-2.58	-1.61	0.98	0.5458	-1.33	-2.64	-1.32	0.3620	
----- ammonium -----					----- calcium -----					----- magnesium -----			
CROOKCRK	-0.14	-1.11	-0.97	0.5470	-2.38	-1.61	0.77	0.7359	-9.00	-0.08	8.92	0.0020	
GODDARD	0.46	-2.11	-2.57	0.0551	-4.53	-1.86	2.67	0.1972	-7.29	-1.09	6.20	0.0098	
HILLSCRK	1.77	1.41	-0.35	0.8663	-5.63	2.05	7.67	0.0106	-9.27	4.15	13.42	0.0001	
LAURHILL	0.00	-2.13	-2.13	0.2142	-4.26	-1.01	3.25	0.2010	-8.31	2.21	10.52	0.0007	
LITTBUFF	1.48	-0.92	-2.40	0.2456	-6.96	1.31	8.26	0.0013	-7.84	-0.52	7.32	0.0146	
SLOCUM	1.77	2.84	1.07	0.6242	-2.72	2.88	5.60	0.0282	-7.98	3.48	11.46	0.0001	
VALLFORG	2.37	-1.17	-3.53	0.0431	-3.81	0.01	3.81	0.1021	-5.86	-8.33	-2.47	0.3315	
LITTPINE	-0.01	-1.49	-1.48	0.4632	-2.23	-4.83	-2.60	0.3416	-4.70	0.60	5.30	0.0569	
PSUNADP	-0.53	1.56	2.08	0.3141	-5.54	-0.32	5.21	0.0202	-7.12	-1.80	5.32	0.0298	
KANE	-0.13	0.54	0.67	0.6755	-2.20	1.49	3.69	0.0525	-5.01	-0.52	4.48	0.0284	
LEADRIDG	-0.89	3.25	4.14	0.0779	-3.47	-0.35	3.12	0.2086	-5.93	-0.77	5.16	0.0491	
MILFORD	0.85	-0.32	-1.17	0.5846	-4.74	1.69	6.43	0.0019	-5.74	-3.40	2.35	0.2774	
----- potassium -----					----- sodium -----					----- chloride -----			
CROOKCRK	0.66	5.94	5.28	0.1742	-1.68	4.72	6.41	0.0483	1.76	-5.58	-7.34	0.0001	
GODDARD	2.04	9.78	7.74	0.0393	-2.36	5.17	7.52	0.0059	0.01	1.89	1.87	0.2736	
HILLSCRK	5.15	8.09	2.94	0.4977	-0.30	6.66	6.95	0.0267	-1.40	1.96	3.36	0.0583	
LAURHILL	4.30	6.77	2.47	0.5628	-1.08	3.07	4.15	0.2098	-0.80	0.07	0.87	0.5838	
LITTBUFF	4.27	5.84	1.57	0.7213	-1.87	-0.25	1.63	0.6177	-0.39	-2.10	-1.70	0.3667	
SLOCUM	2.55	8.86	6.30	0.1402	-1.78	4.65	6.43	0.0291	0.17	1.56	1.39	0.4471	
VALLFORG	4.55	5.84	1.30	0.7479	-0.28	-10.57	-10.29	0.0010	0.48	-8.46	-8.94	0.0005	
LITTPINE	2.44	12.96	10.51	0.0342	2.22	7.27	5.05	0.2290	0.89	1.37	0.48	0.8301	
PSUNADP	-3.10	-0.22	2.88	0.3571	-3.49	-8.44	-4.94	0.1026	-2.81	-1.28	1.52	0.3950	
KANE	-0.38	-0.38	0.00	0.9998	-1.53	-8.19	-6.66	0.0030	-1.70	-2.60	-0.90	0.5012	
LEADRIDG	-5.43	-3.07	2.36	0.4889	-3.20	-6.63	-3.42	0.2244	-1.41	-2.63	-1.23	0.5231	
MILFORD	-6.75	0.11	6.85	0.0221	-0.53	-6.50	-5.98	0.0187	-2.55	-4.41	-1.87	0.3853	

Table 4. Changes in trends of ionic wet deposition in Pennsylvania before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

site	1983-94 trend (%/yr)	1995-2003 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2003 trend (%/yr)	Change in trends (%/yr)	p	1983-94 trend (%/yr)	1995-2003 trend (%/yr)	Change in trends (%/yr)	p	
----- hydrogen ion -----					----- sulfate -----					----- nitrate -----			
CROOKCRK	-0.50	-3.23	-2.73	0.0949	0.27	-0.76	-1.03	0.5222	-0.24	-2.73	-2.49	0.1709	
GODDARD	-3.43	-3.01	0.43	0.8115	-2.11	-2.26	-0.15	0.9281	-2.98	-3.07	-0.08	0.9585	
HILLSCRK	-1.62	-0.93	0.69	0.7247	-2.14	1.94	4.08	0.0330	-2.46	-0.54	1.92	0.3262	
LAURHILL	-1.45	-5.75	-4.31	0.0189	-0.37	-3.85	-3.48	0.0527	-1.56	-5.61	-4.05	0.0164	
LITTBUFF	-4.05	-2.13	1.92	0.3240	-1.85	-0.38	1.48	0.4246	-3.03	-2.28	0.75	0.6528	
SLOCUM	-1.46	2.22	3.68	0.0363	-0.48	5.51	5.99	0.0026	-1.10	2.69	3.79	0.0288	
VALLFORG	-2.52	-1.86	0.66	0.7681	-1.93	-0.54	1.40	0.4961	-3.00	-0.76	2.24	0.2967	
LITTPINE	1.39	-5.33	-6.71	0.0001	1.66	-1.57	-3.24	0.0467	0.28	-4.06	-4.34	0.0074	
PSUNADP	-0.41	-0.84	-0.43	0.8211	-0.23	0.45	0.68	0.7202	-0.35	-0.50	-0.15	0.9347	
KANE	-1.43	-1.05	0.38	0.8194	-1.95	1.00	2.94	0.0771	-1.06	-0.38	0.68	0.6310	
LEADRIDG	-1.34	-0.91	0.44	0.8024	-1.88	1.62	3.50	0.0526	-1.37	-0.68	0.69	0.6684	
MILFORD	-0.40	-2.31	-1.92	0.4239	-0.83	-0.90	-0.07	0.9708	-0.09	-1.94	-1.85	0.3047	
----- ammonium -----					----- calcium -----					----- magnesium -----			
CROOKCRK	1.22	-0.05	-1.28	0.5248	-1.98	-0.56	1.42	0.5856	-8.39	0.98	9.38	0.0013	
GODDARD	-0.32	-1.52	-1.20	0.5463	-3.99	-1.27	2.72	0.2189	-7.57	-0.48	7.09	0.0067	
HILLSCRK	0.55	2.28	1.73	0.4672	-6.76	2.92	9.68	0.0014	-10.34	5.02	15.36	0.0001	
LAURHILL	0.58	-4.53	-5.10	0.0156	-3.71	-3.44	0.26	0.9142	-8.55	-0.30	8.25	0.0045	
LITTBUFF	0.86	-1.70	-2.56	0.1921	-6.97	0.51	7.49	0.0177	-7.90	-1.29	6.62	0.0676	
SLOCUM	1.85	6.51	4.66	0.0503	-2.58	6.54	9.13	0.0025	-7.91	7.18	15.08	0.0001	
VALLFORG	1.71	-0.96	-2.67	0.2178	-4.29	0.21	4.50	0.1182	-6.00	-8.14	-2.13	0.5130	
LITTPINE	1.86	0.36	-1.50	0.4033	-0.39	-3.05	-2.66	0.3332	-3.99	2.50	6.49	0.0351	
PSUNADP	0.88	1.45	0.57	0.7744	-3.28	-0.48	2.80	0.2191	-5.03	-1.82	3.21	0.1905	
KANE	-0.61	1.43	2.04	0.2840	-2.71	2.42	5.12	0.0079	-5.42	0.43	5.85	0.0070	
LEADRIDG	-0.71	3.85	4.55	0.0220	-3.31	0.30	3.61	0.0943	-6.12	-0.16	5.96	0.0125	
MILFORD	2.40	0.36	-2.04	0.3346	-3.27	2.45	5.72	0.0087	-5.09	-2.64	2.45	0.3295	
----- potassium -----					----- sodium -----					----- chloride -----			
CROOKCRK	0.97	7.10	6.13	0.1271	-0.97	5.82	6.79	0.0560	3.15	-4.57	-7.72	0.0014	
GODDARD	1.72	10.48	8.76	0.0348	-2.10	5.78	7.88	0.0195	-0.26	2.50	2.76	0.2712	
HILLSCRK	3.92	9.07	5.15	0.2717	-1.50	7.55	9.05	0.0202	-1.26	2.83	4.09	0.1283	
LAURHILL	2.91	4.10	1.20	0.7918	-0.52	0.53	1.05	0.7506	-0.23	-2.39	-2.16	0.2596	
LITTBUFF	5.27	5.02	-0.26	0.9574	-2.23	-1.03	1.20	0.7439	-0.68	-2.88	-2.19	0.3013	
SLOCUM	2.62	12.73	10.11	0.0385	-1.69	8.38	10.08	0.0042	0.22	5.18	4.96	0.0332	
VALLFORG	4.72	6.12	1.41	0.7438	-0.40	-10.38	-9.98	0.0077	0.35	-8.27	-8.62	0.0100	
LITTPINE	4.00	15.33	11.33	0.0478	4.08	9.29	5.21	0.2836	2.73	3.28	0.54	0.8411	
PSUNADP	-1.00	-0.27	0.73	0.8289	-1.33	-8.53	-7.20	0.0342	-0.63	-1.34	-0.71	0.7484	
KANE	-2.45	0.51	2.96	0.3623	-3.07	-7.36	-4.29	0.1104	-2.23	-1.69	0.54	0.7758	
LEADRIDG	-5.83	-2.48	3.35	0.3033	-3.04	-6.00	-2.95	0.3418	-1.51	-1.97	-0.47	0.8430	
MILFORD	-5.56	0.75	6.30	0.0414	0.28	-5.79	-6.07	0.0397	-0.66	-3.69	-3.02	0.2542	

concentrations at all sites during the pre-CAAA period were decreasing and this trend changed in magnitude and, at some sites, direction since 1995 when SO₂ emission reductions mandated by the CAAA were implemented. At six of the long-term sites, post-CAAA trend analyses indicate that sulfate concentrations have increased over the past nine years, while at the remaining six sites the pre-CAAA decreasing patterns continued into the post-CAAA period. Although none of the post-CAAA trend patterns are statistically significant, the patterns are fairly consistent with SO₂ emissions (Figures 2 and 3). After the initial reduction in 1995, SO₂ emissions from Title IV affected sources increased until 1998 and did not fall below 1995 levels until 2000. After 2000 they declined to their lowest level in 2002 before increasing slightly in 2003. Increasing SO₂ emissions from 1995 to 1998 followed by a decreasing pattern from 1999 through 2002 has resulted in an increasing pattern in sulfate concentrations during the post-CAAA period at some sites (Table 3). Also contributing to the temporal and spatial patterns is the fact that the impact of emissions and emissions reduction programs on sulfate concentrations are not uniform across the state. This latter observation is supported by the fact that pre- and post-CAAA mean annual sulfate concentrations (Table 2) are highly variable across the Commonwealth, differing by more than 1.5 mg/L during both the pre- and post-CAAA periods.

Pre- and post-CAAA wet sulfate deposition trends are even more variable than the concentration patterns (Table 4). Pre-CAAA deposition patterns were decreasing at 10 of the 12 long-term sites and increasing at two sites (Little Pine in Lycoming County and Crooked Creek Lake in Armstrong County). Post-CAAA trend analyses indicate that the decreasing pre-CAAA pattern continued at five sites (three of which were enhanced) and was reversed at five sites, two of which are statistically significant ($p < 0.05$). The post-CAAA trend pattern at both of the sites with increasing pre-CAAA trends were also reversed, with the largest change occurring at the Little Pine site. With one exception (Little Buffalo State Park in Perry County), wet sulfate deposition trends since 1995 are similar to the concentration trends. However, fluctuation in precipitation volumes between and within summary periods has been an influencing factor. For example, the average yearly precipitation in Pennsylvania between the pre- and post-CAAA periods is nearly identical (43.96 inches versus 43.92 inches). However, in six of the last nine years annual precipitation was below the pre-CAAA mean. The three years that precipitation was above the pre-CAAA mean were some of the wettest on record. Such variability influences concentration and wet deposition patterns as well as trends. Consequently, the post-CAAA trend results should not be interpreted to mean that sulfate concentrations and wet deposition have not changed as a result of the CAAA. Instead they are included to illustrate that the trends between the pre- and post-CAAA periods changed since 1995 and that sulfate concentrations and wet deposition since then have been variable, reflecting to a great extent patterns in SO₂ emissions from Title IV affected sources and climatic variability, particularly the amount and seasonal distribution of precipitation across the state.

Nitrate - Like sulfate, mean annual nitrate concentrations have decreased across Pennsylvania since 1995 (Table 5, Figure 8); however, the reductions are statistically significant ($p < 0.05$) at only half of the long-term monitoring sites (Kane, Hills Creek, Leading Ridge, Penn State, Slocum, and Milford). The largest statistically significant reduction in mean annual nitrate concentrations (0.381 mg/L) occurred at the Milford site in eastern Pennsylvania. The smallest significant reduction (0.246 mg/L) was measured at the Kane site. With the exception of the

Table 5. Comparison of mean annual and seasonal nitrate ion concentrations and depositions at 12 atmospheric deposition monitoring stations in Pennsylvania before (1983-1994) and after (1995-2003) 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
Laurel Hill	1.846	1.767	-0.078	1.949	1.800	-0.149	1.780	1.758	-0.022
M.K. Goddard	2.076	1.942	-0.134	2.188	1.976	-0.211	1.987	1.939	-0.048
Crooked Creek Lake	2.141	1.965	-0.175	2.374	2.109	-0.265	1.899	1.810	-0.089
Kane-NADP	1.899	1.653	-0.246*	1.958	1.645	-0.313*	1.850	1.687	-0.163
Western Region	1.990	1.832	-0.158*	2.117	1.883	-0.235*	1.879	1.799	-0.080
Little Buffalo	2.011	1.878	-0.133	2.214	1.997	-0.217	1.877	1.750	-0.127
Hills Creek	1.851	1.525	-0.327*	1.967	1.569	-0.398*	1.748	1.482	-0.265*
Leading Ridge-NADP	2.001	1.717	-0.284*	2.228	1.717	-0.511*	1.828	1.732	-0.095
Little Pine	2.059	1.868	-0.190	2.185	1.857	-0.328	1.973	1.904	-0.069
Penn State-NADP	1.877	1.574	-0.302*	2.135	1.635	-0.500*	1.672	1.516	-0.156
Central Region	1.961	1.712	-0.248*	2.145	1.755	-0.390*	1.822	1.677	-0.145*
Valley Forge	1.718	1.465	-0.253	1.926	1.583	-0.343	1.541	1.342	-0.199
Milford-NADP	1.784	1.403	-0.381*	1.987	1.446	-0.541*	1.666	1.364	-0.302*
Slocum	1.954	1.639	-0.314*	2.033	1.722	-0.312*	1.935	1.546	-0.390
Eastern Region	1.818	1.502	-0.316*	1.982	1.584	-0.399*	1.714	1.417	-0.297*
Statewide	1.935	1.700	-0.235*	2.094	1.755	-0.339*	1.814	1.653	-0.161*

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
Laurel Hill	24.615	23.018	-1.597	12.286	11.633	-0.652	12.331	11.383	-0.947
M.K. Goddard	23.435	20.856	-2.579	13.679	11.437	-2.243	9.757	9.423	-0.334
Crooked Creek Lake	22.874	20.724	-2.150	13.327	11.888	-1.439	9.548	8.833	-0.715
Kane-NADP	24.014	18.796	-5.219*	12.856	9.742	-3.114*	11.163	9.054	-2.108*
Western Region	23.735	20.848	-2.886*	13.037	11.175	-1.862*	10.700	9.674	-1.026*
Little Buffalo	21.713	21.063	-0.650	12.072	11.990	-0.082	9.640	9.072	-0.568
Hills Creek	17.346	13.908	-3.438*	10.417	8.033	-2.384*	6.927	5.876	-1.052
Leading Ridge-NADP	21.583	17.811	-3.771*	12.128	9.788	-2.341*	9.454	8.022	-1.432*
Little Pine	21.586	19.319	-2.267	12.310	10.211	-2.099*	9.278	9.107	-0.172
Penn State-NADP	18.890	17.633	-1.257	11.065	10.172	-0.893	7.824	7.462	-0.362
Central Region	20.246	17.947	-2.299*	11.605	10.039	-1.566*	8.641	7.908	-0.734*
Valley Forge	20.248	17.303	-2.945	11.501	9.798	-1.703	8.745	7.506	-1.239
Milford-NADP	21.339	16.528	-4.811*	12.387	8.949	-3.439*	8.953	7.580	-1.373
Slocum	21.565	17.261	-4.304*	12.579	9.886	-2.694*	8.989	7.376	-1.614*
Eastern Region	21.051	17.031	-4.020*	12.156	9.544	-2.612*	8.896	7.487	-1.409*
Statewide	21.639	18.685	-2.954*	12.233	10.294	-1.939*	9.407	8.391	-1.016*

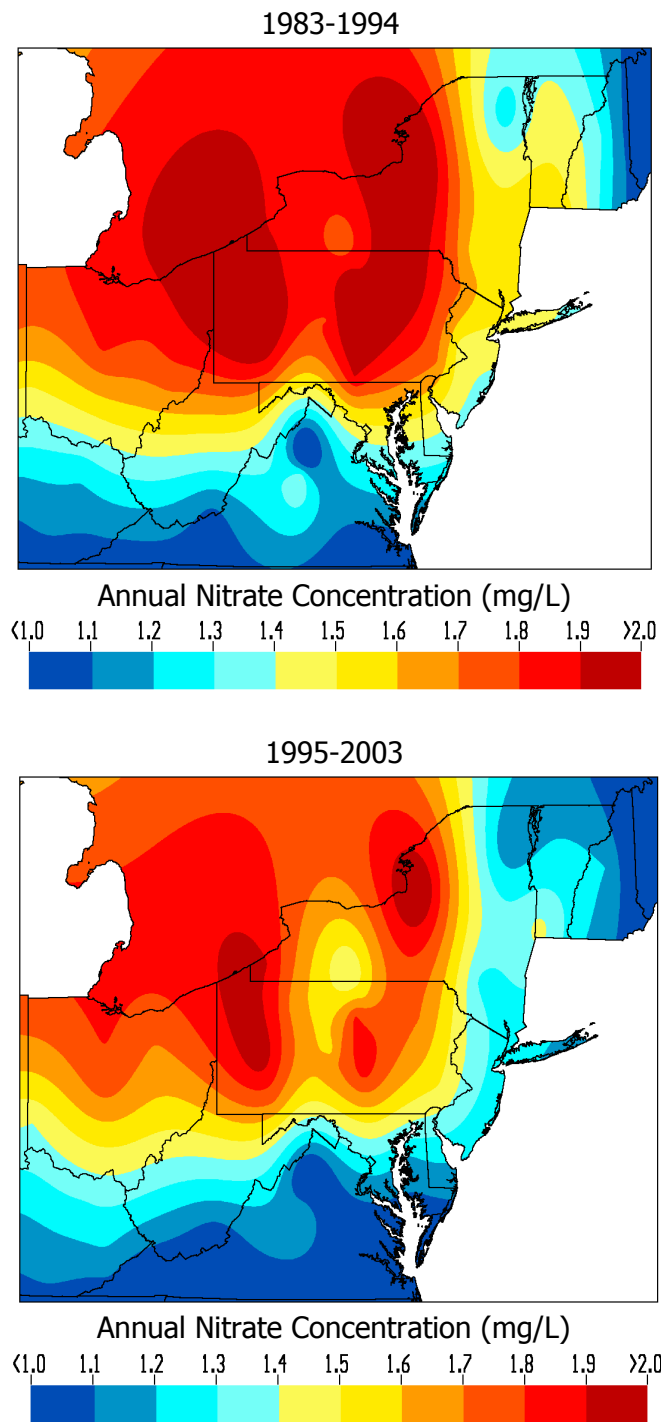


Figure 8. Mean annual nitrate concentrations across Pennsylvania and neighboring states before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

Kane site in western Pennsylvania, decreases in mean annual nitrate concentrations since 1995 were larger in the eastern (0.316 mg/L) and central (0.248 mg/L) portions of the state than in the western region (0.158 mg/L). The reductions in concentrations also appear to be larger in the northern tier counties than in the southern half of Pennsylvania.

Although decreasing nitrate concentrations patterns are evident at all sites for both growing and dormant seasons (Table 5), the largest and most statistically significant seasonal reductions occurred during the growing season. The statewide growing season mean concentration was 0.339 mg/L lower the past nine years than during the previous 13-year pre-CAAA period. At six sites (Kane, Hills Creek, Leading Ridge, Milford, Penn State, and Slocum), the reductions are significant ($p < 0.05$). These are the same sites that exhibit statistically significant reductions in mean annual nitrate concentrations. The largest significant ($p < 0.05$) reduction during the growing season (0.541 mg/L) was measured at the Milford site in Pike County. The smallest significant reduction (0.312 mg/L) was measured at the Slocum site. The smallest overall reduction (0.149 mg/L) was measured at Laurel Hill State Park. Reductions in growing season nitrate concentrations since 1995 were greater in eastern (0.399 mg/L) and central (0.390 mg/L) Pennsylvania and lowest in the western third (0.235 mg/L) of the state (Table 5).

Dormant season nitrate concentrations since 1995 have also been lower than the pre-CAAA reference period; however, the reductions are relatively small and significant ($p < 0.05$) at only the Milford (0.302 mg/L) and Hills Creek (0.265 mg/L) sites. Despite the lack of statistically significant reductions at most sites, the central (0.145 mg/L) and eastern (0.297 mg/L) regional means were significantly lower as was the statewide reduction of 0.161 mg/L. On a regional basis, changes in dormant season nitrate concentrations since 1995 have been much greater in eastern Pennsylvania than in either the central or western portions of the state (Table 5).

Annual wet nitrate deposition since 1995 has decreased throughout the state (Table 5, Figure 9). Significant ($p < 0.05$) reductions in mean annual nitrate deposition were measured at Kane (5.22 kg/ha), Hills Creek (3.44 kg/ha), Leading Ridge (3.77 kg/ha), Milford (4.81 kg/ha) and Slocum (4.30 kg/ha). Except for Leading Ridge, all of these sites are located in the northern tier counties of the state. Decreases in mean annual nitrate deposition are significant ($p < 0.05$) for all three regions, with the greatest regional reductions occurring in the eastern (4.02 kg/ha) and western (2.89 kg/ha) regions and the state; the reduction in wet nitrate deposition in central Pennsylvania averaged 2.30 kg/ha since 1995 (Table 5).

Like nitrate concentrations, the majority of the decrease in annual nitrate deposition since 1995 occurred during the growing season (Table 5). With two exceptions, significant reductions in mean growing season deposition were measured at each of the sites that reported significantly lower growing season concentrations. The two exceptions include Little Pine State Park in Lycoming County where the decrease in growing season nitrate deposition was significant even though the decline in nitrate concentrations was not. The reverse was evident at the Penn State site that had significantly lower growing season nitrate concentrations, although wet deposition levels at this site were not significantly different from pre-CAAA levels. The largest growing season reduction was measured at the Milford site (3.44 kg/ha); the smallest significant reduction

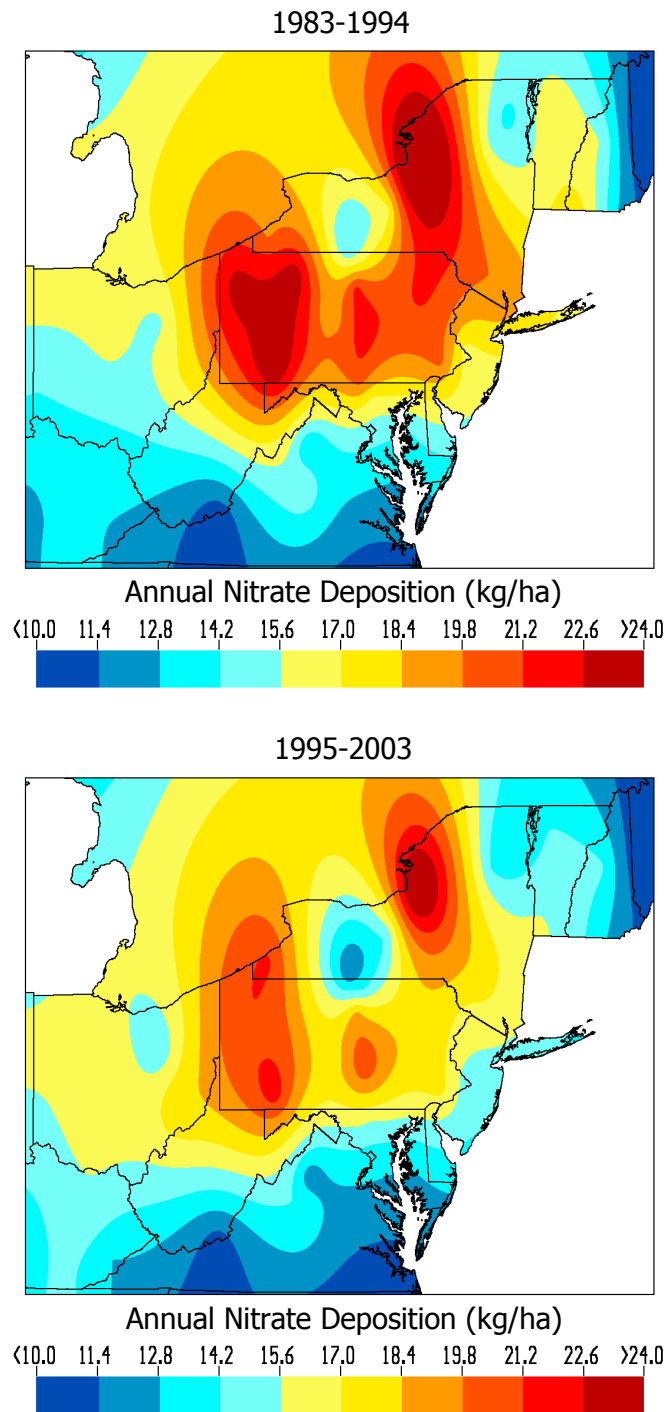


Figure 9. Mean annual nitrate deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

(2.10 kg/ha) was observed at Little Pine. The overall average statewide reduction in growing season nitrate deposition since 1995 was 1.94 kg/ha, which was statistically significant ($p < 0.05$) as were each average regional reduction.

Dormant season nitrate depositions since 1995 were also lower than the pre-CAAA reference period (Table 5). However, the reductions were much smaller when compared to the growing season and averaged around 1.0 kg/ha. Despite the fact that only three sites (Kane, Leading Ridge, and Slocum) recorded significantly lower dormant season nitrate deposition levels since 1995, the statewide decrease (1.02 kg/ha) as well as the western (1.03 kg/ha), central (0.73 kg/ha) and eastern (1.41 kg/ha) regional mean reductions were significant ($p < 0.05$).

Deviations in pre- and post-CAAA nitrate concentrations and depositions (Table 5) at individual sites and across summary periods reflect to some extent differences in precipitation between pre- and post-CAAA summary periods. Changes in regional nitrate concentrations were consistently greater in eastern Pennsylvania and decreased to their lowest levels in western Pennsylvania. Regional changes in wet nitrate deposition were also greater in eastern Pennsylvania; however, the smallest change occurred in central Pennsylvania despite the fact that concentrations changes were greater. This regional inconsistency between changes in pre- and post-CAAA concentrations and deposition results from differences in precipitation volumes between pre- and post-CAAA periods. As indicated earlier, the average annual precipitation across Pennsylvania was the same during both the pre- and post-CAAA periods. This was also the case for the statewide seasonal mean volumes. However, on a regional basis, growing season precipitation during the post-CAAA period in central Pennsylvania was 4.0 inches lower than the pre-CAAA mean, even though precipitation in western and eastern portions of the state were identical for both summary periods. The lower precipitation volumes during the growing season in central Pennsylvania influenced both concentration and deposition levels in this region and contributed to the inconsistency between concentration and deposition reductions between pre- and post-periods. Regional differences in emission reductions may also be important, although such an analysis is beyond the scope of this report.

Year to year reductions in nitrate concentrations and wet deposition during the post-CAAA period relative to the pre-CAAA reference period (1983-1994) are not as variable as was evident for sulfate concentrations and wet depositions (Tables 3 and 4, respectively). The reason for this is that the average annual decrease in nitrate concentrations and depositions over the 9-year post-CAAA period are largely the result of a more consistent and gradual decrease in NO_x emissions starting around 1996 (Figures 4 and 5) as opposed to the step-function change that occurred with SO_2 emissions reductions. Pre- and post-CAAA trend analyses indicate decreasing patterns in nitrate concentrations at all sites prior to 1995 and that this pattern continued at all sites during the post-CAAA period, with seven sites (Crooked Creek Lake, M.K. Goddard, Hills Creek, Little Pine, Laurel Hill, Kane and Milford) exhibiting even greater reductions in nitrate concentrations since 1995 (Table 3). Pre-CAAA nitrate deposition trends were also decreasing at all sites except Little Pine. Post-CAAA analyses indicate that the pre-CAAA decreasing pattern continued during the post-CAAA period, with six sites (Crooked Creek Lake, M.K. Goddard, Laurel Hill, Little Pine, Penn State and Milford) exhibiting even greater reductions since 1995. 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 since 1995 (Table 4). In contrast, an increasing post-CAAA nitrate deposition trend is evident at Slocum, a statistically significant change from the decreasing pattern that was evident at this site from 1983-1994. Why this pattern occurred at Slocum is unclear but may be related to precipitation patterns between summary periods and/or local emissions.

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

Hydrogen Ion (pH) - The pH of precipitation in Pennsylvania since 1995 has increased (become less acidic, H^+ concentrations lower, pH higher) throughout the Commonwealth (Table 6, Figure 10). The average increase in mean annual pH at each site relative to the pre-CAAA reference period is statistically significant ($p < 0.05$). The greatest increase in mean annual pH was measured at the Leading Ridge and Milford sites (0.17 unit); the smallest increase was measured at Crooked Creek Lake and Laurel Hill State Park (0.10 unit). Both of these sites are located in western Pennsylvania. The increase in mean annual pH across the state was 0.14 pH unit. On a regional basis, the largest increase in pH was measured in eastern (0.15 unit) and central (0.14 unit) Pennsylvania; the increase in western Pennsylvania was 0.12 unit. The increase in pH across the state is fairly consistent with observed decreases in sulfate concentrations (Table 2) and to a lesser extent nitrate concentrations (Table 5), although fluctuations in ammonium and base cation concentrations exert some influence.

Growing season pH means since 1995 have also increased substantially when compared to the pre-CAAA means (Table 6). All of the increases are statistically significant ($p < 0.05$). The statewide average increase in growing season pH since 1995 was 0.15 pH unit. The increase in mean growing season pH from 4.09 before 1995 to 4.24 after 1995 represents a decrease in H^+ concentrations of nearly 29%. The largest increase in mean growing season pH (0.22 unit) was measured at the Leading Ridge site in Huntingdon County. This change represents a 40% reduction in H^+ concentrations since 1995. Even the relatively small increase in pH at Crooked Creek Lake between the pre- and post-CAAA periods (3.99 versus 4.10) represents a reduction in H^+ concentrations of 22%.

Table 6. Comparison of mean annual and seasonal pH and hydrogen ion depositions at 12 atmospheric deposition monitoring stations in Pennsylvania before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

Site/Region	pH								
	Annual			Growing Season			Dormant Season		
	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference
Laurel Hill	4.156	4.255	0.099*	4.060	4.170	0.110*	4.266	4.357	0.092*
M.K. Goddard	4.148	4.282	0.135*	4.091	4.237	0.146*	4.226	4.344	0.118*
Crooked Creek Lake	4.078	4.177	0.098*	3.995	4.097	0.102*	4.193	4.289	0.096*
Kane-NADP	4.162	4.314	0.152*	4.077	4.258	0.181*	4.272	4.387	0.115*
Western Region	4.136	4.257	0.121*	4.056	4.191	0.135*	4.239	4.344	0.105*
Little Buffalo	4.164	4.299	0.135*	4.082	4.235	0.153*	4.262	4.386	0.125*
Hills Creek	4.184	4.335	0.150*	4.101	4.259	0.158*	4.320	4.463	0.143*
Leading Ridge-NADP	4.147	4.313	0.166*	4.042	4.263	0.221*	4.277	4.385	0.108*
Little Pine	4.135	4.244	0.109*	4.052	4.183	0.130*	4.253	4.326	0.073*
Penn State-NADP	4.179	4.333	0.154*	4.095	4.265	0.170*	4.286	4.436	0.150*
Central Region	4.161	4.305	0.143*	4.074	4.241	0.167*	4.280	4.399	0.120*
Valley Forge	4.248	4.393	0.145*	4.172	4.332	0.159*	4.345	4.477	0.133*
Milford-NADP	4.222	4.387	0.165*	4.148	4.336	0.188*	4.316	4.453	0.137*
Slocum	4.191	4.332	0.141*	4.129	4.262	0.133*	4.277	4.437	0.160*
Eastern Region	4.220	4.371	0.151*	4.150	4.310	0.160*	4.313	4.456	0.143*
Statewide	4.168	4.305	0.137*	4.087	4.241	0.154*	4.274	4.395	0.121*

Site/Region	Hydrogen Ion Wet Depositions (kg/ha)								
	Annual			Growing Season			Dormant Season		
	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference	Pre-CAAA Mean	Post-CAAA Mean	Difference
Laurel Hill	0.947	0.736	-0.211*	0.561	0.447	-0.114*	0.387	0.291	-0.096*
M.K. Goddard	0.820	0.576	-0.244*	0.516	0.347	-0.169*	0.303	0.227	-0.077*
Crooked Creek Lake	0.908	0.716	-0.193*	0.577	0.459	-0.118*	0.330	0.258	-0.072*
Kane-NADP	0.902	0.558	-0.344*	0.569	0.336	-0.234*	0.329	0.223	-0.106*
Western Region	0.894	0.646	-0.248*	0.556	0.397	-0.159*	0.337	0.250	-0.088*
Little Buffalo	0.757	0.576	-0.181*	0.469	0.358	-0.111*	0.288	0.214	-0.074*
Hills Creek	0.623	0.430	-0.193*	0.430	0.290	-0.140*	0.192	0.139	-0.054*
Leading Ridge-NADP	0.788	0.510	-0.278*	0.505	0.318	-0.187*	0.282	0.197	-0.085*
Little Pine	0.780	0.599	-0.181*	0.513	0.371	-0.142*	0.268	0.230	-0.038
Penn State-NADP	0.678	0.530	-0.148*	0.429	0.347	-0.082	0.247	0.184	-0.063*
Central Region	0.726	0.529	-0.197*	0.470	0.337	-0.133*	0.256	0.193	-0.063*
Valley Forge	0.678	0.491	-0.187*	0.414	0.299	-0.115*	0.264	0.192	-0.072*
Milford-NADP	0.733	0.491	-0.241*	0.457	0.294	-0.162*	0.275	0.201	-0.074*
Slocum	0.731	0.501	-0.230*	0.470	0.321	-0.149*	0.260	0.179	-0.081*
Eastern Region	0.714	0.494	-0.219*	0.447	0.305	-0.142*	0.266	0.191	-0.076*
Statewide	0.780	0.559	-0.221*	0.493	0.349	-0.144*	0.286	0.211	-0.075*

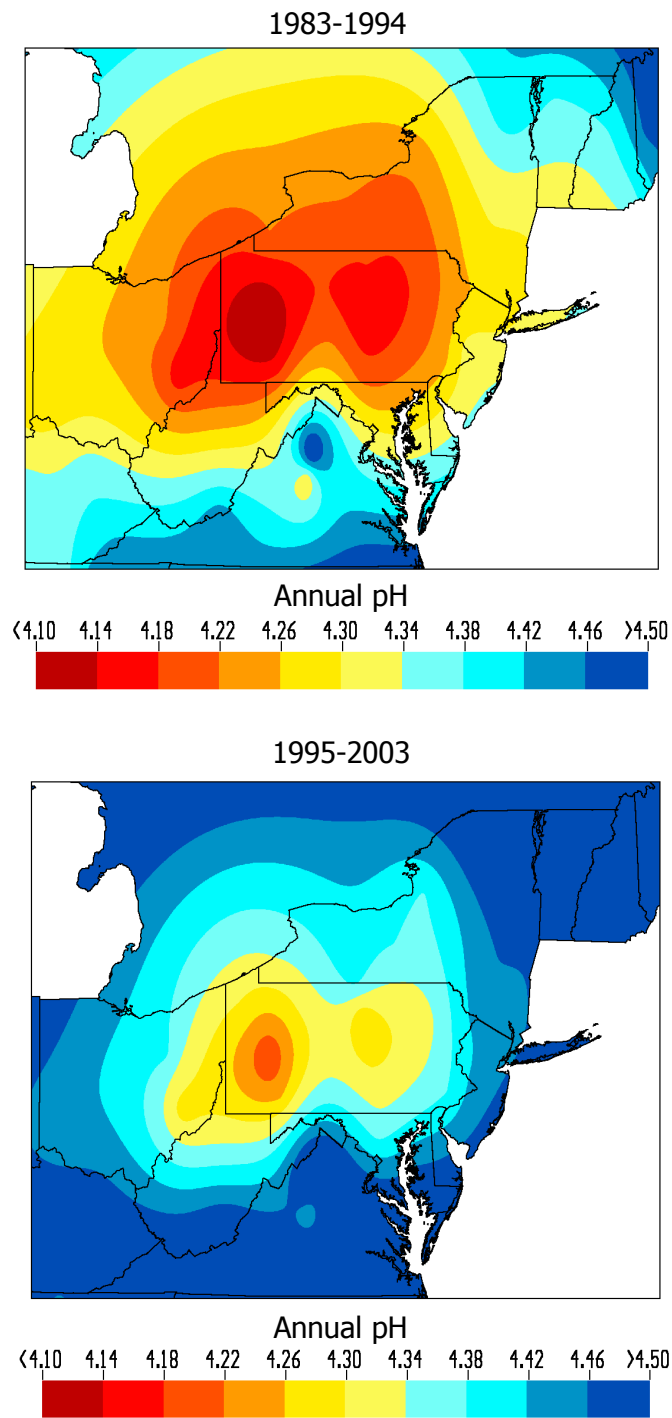


Figure 10. Mean annual pH across Pennsylvania and neighboring states before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

Significantly ($p < 0.05$) higher dormant season pH means were evident at all long-term monitoring sites since 1995 (Table 6). The higher dormant season pH mean differences ranged from 0.16 unit at Slocum to 0.07 unit at Little Pine. The statewide increase in mean dormant season pH was 0.12 unit. Regional increases in post-CAAA dormant season mean pH values were about 0.03 unit lower than measured changes in post-CAAA growing season means. Although the smallest increases in growing and dormant season mean pH were observed in western Pennsylvania, the largest increases varied by season with the highest dormant season increase occurring in eastern Pennsylvania while the highest growing season pH increase was reported in the center region (Table 6). Regional differences between seasons are likely the result of regional and seasonal differences in measured reductions in nitrate (Table 5) and sulfate (Table 2) concentrations, both of which were largest in eastern Pennsylvania during the dormant season.

Mean annual wet H^+ deposition has decreased across the entire state with all sites reporting significant ($p < 0.05$) drops since 1995 (Table 6, Figure 11). The largest decreases were measured at Kane (0.34 kg/ha) and Leading Ridge (0.28 kg/ha). The smallest annual decreases were measured at Penn State (0.15 kg/ha), Little Pine (0.18 kg/ha), and Little Buffalo (0.18 kg/ha) all of which are located in central Pennsylvania. On a regional basis, the decrease in annual H^+ deposition was greater in western Pennsylvania (0.25 kg/ha) than either the central (0.20 kg/ha) or eastern (0.22 kg/ha) regions. The statewide mean reduction was 0.22 kg/ha (Table 6).

Approximately 65% of the reduction in annual H^+ deposition resulted from higher pH values (lower H^+ concentrations) during the growing season (Table 6). Decreases in mean growing season H^+ deposition since 1995 ranged from 0.23 kg/ha at Kane to 0.08 kg/ha at Penn State. All decreases in growing season H^+ deposition since 1995 are significant ($p < 0.05$) except for the Penn State site in Centre County. The statewide decrease in mean growing season H^+ deposition is 0.14 kg/ha; the largest (0.16 kg/ha) and smallest (0.13 kg/ha) regional reductions were observed in western and eastern Pennsylvania, respectively.

Reductions in dormant season H^+ depositions were much smaller than growing season reductions, but still statistically significant at all sites except Little Pine State Park in Lycoming County (Table 6). The largest post-CAAA drop in dormant season deposition since 1995 was 0.11 kg/ha at Kane; the smallest significant decrease (0.05 kg/ha) was measured at the Hills Creek site in Tioga County. The average statewide dormant season reduction in H^+ deposition since 1995 relative to the pre-CAAA reference period was 0.075 kg/ha (Table 6). Regional reductions in dormant season H^+ deposition ranged from 0.06 kg/ha in central Pennsylvania to 0.09 kg/ha in the western third of the state.

The acidity (as pH) of precipitation results from a balance between the acid anions (primarily sulfate and nitrate), the base cations (e.g., calcium, magnesium, etc.) and ammonium concentrations. Consequently, year to year variability in mean annual pH during pre- and post-CAAA years represents a balance between year to year fluctuations in anion and cation concentrations in precipitation as well as year to year variability in the amount and distribution

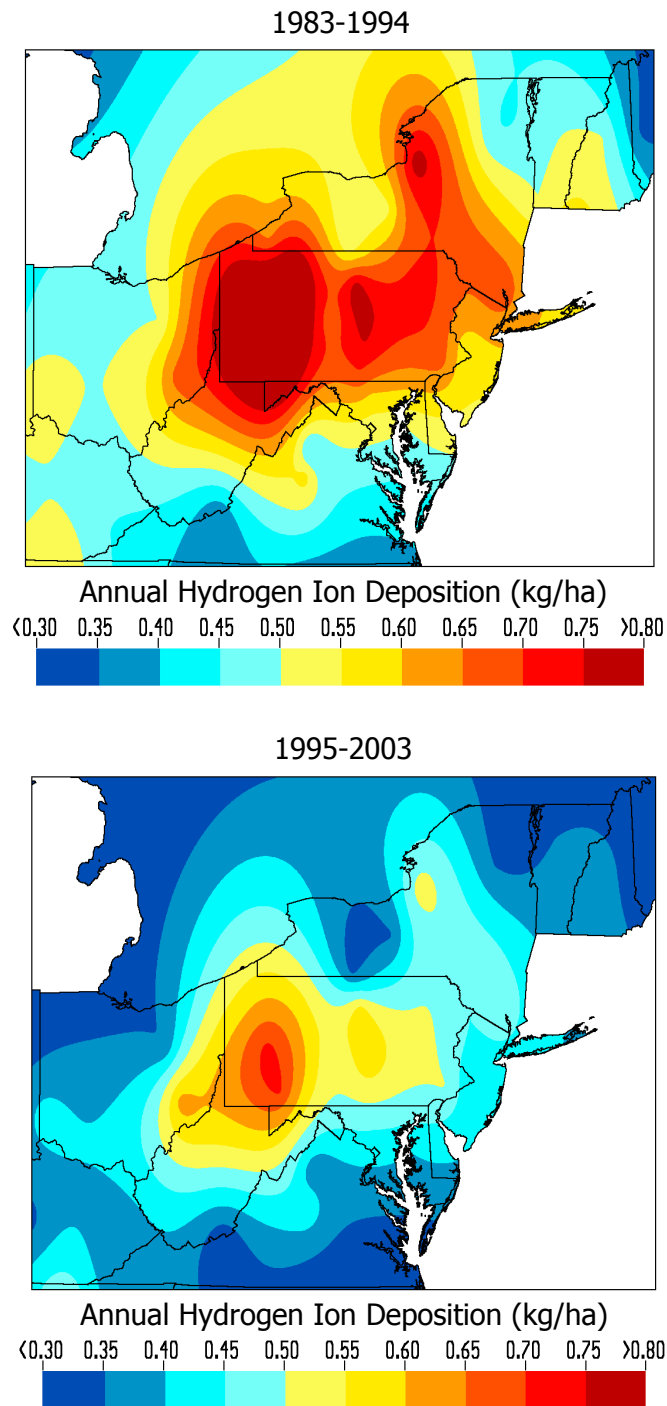


Figure 11. Mean annual hydrogen ion deposition across Pennsylvania and neighboring states before (1983-1994) and after (1995-2003) implementation of Title IV of the Clean Air Act Amendments of 1990.

of precipitation. As a result, post-CAAA trends in H^+ concentrations (Table 3) as well as year to year variability during summary periods tend to reflect the composite changes observed in acid anion and cation concentrations as well as fluctuations in climatic conditions.

Prior to implementation of the CAAA, H^+ concentrations were decreasing at all sites (Table 3). Since 1995, the decreasing pattern has continued at all sites with the rate of change increasing at 9 of the 12 sites. At the three sites where the rate of change during the post-CAAA period is smaller than the pre-CAAA period (Little Buffalo, Slocum, and Penn State), post-CAAA sulfate concentrations were increasing while nitrate concentrations continued to decline although at a much smaller rate. At the Penn State NADP/NTN site, the relatively small decreasing post-CAAA H^+ trend also reflects an increasing ammonium concentration trend (Table 3) at that site. Ammonium in precipitation can act to neutralize some of the acidity resulting in a smaller net change in pH. An increasing ammonium concentration trend during the post-CAAA period also influenced the relatively small difference in the rate of increase in pH between pre- and post-CAAA periods at the Leading Ridge site. Changes in post-CAAA calcium and magnesium concentrations also influenced the post-CAAA H^+ concentration trends at Slocum and Little Buffalo State Parks (Table 3).

Prior to implementation of the CAAA, wet H^+ depositions were decreasing at all sites except Little Pine. Since 1995, wet H^+ deposition at Little Pine has decreased as has deposition levels of at all other sites, except Slocum State Park. The increasing pattern at Slocum is consistent with the increasing trends in sulfate, nitrate, and some cation concentrations at that site since 1995. The statistically significant decrease in H^+ deposition at Little Pine during the post-CAAA period is consistent with statistically significant post-CAAA decreases in H^+ and nitrate concentrations and to a lesser extent sulfate concentrations (Table 3).

A comparison of mean annual and seasonal ionic concentrations in precipitation and wet depositions before (1983-1994) and after (1995-2003) implementation of emissions control requirements under Title IV of the CAAA are listed in Table 7. The “p” values indicate the level of significance with all sites exhibiting very significant reductions in hydrogen, sulfate, and nitrate ion concentrations and wet depositions since 1995. Changes in post-CAAA base cations, ammonium, and chloride concentrations are much smaller and generally not statistically significant. However, their influence on the acidity of precipitation needs to be considered when evaluating the magnitude of spatial patterns and temporal trends in acid rain across Pennsylvania.

Summary and Recommendations

The results presented in this report demonstrate clearly that implementation of Title IV of the Clean Air Act Amendments of 1990 in 1995 has resulted in lower sulfur dioxide emissions in Pennsylvania and upwind states (EPA, 2004b). The reductions in sulfur dioxide have subsequently lowered sulfate concentrations in precipitation throughout the state. The average statewide reduction in sulfate concentrations since 1995 was 0.749 mg/L, a reduction of 34% over the pre-CAAA mean. Concurrent with the drop in sulfate concentrations has been a significant statewide average reduction in wet sulfate deposition of 8.74 kg/ha (23%). Likewise,

Table 7. Comparison of mean annual and seasonal ionic concentrations in precipitation and wet depositions before (1983-1994) and after (1995-2003) implementation of emissions control requirements under Title IV of the Air Act Amendments of 1990.

Site	Hydrogen Ion																	
	Annual						Growing Season						Dormant Season					
	pH			Deposition (kg/ha)			pH			Deposition (kg/ha)			pH			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	4.078	4.177	0.0005	0.908	0.716	0.0017	3.995	4.097	0.0013	0.577	0.459	0.0138	4.192	4.289	0.0018	0.330	0.258	0.0081
GODDARD	4.148	4.282	0.0001	0.820	0.576	0.0011	4.091	4.237	0.0001	0.516	0.347	0.0047	4.226	4.344	0.0014	0.303	0.227	0.0082
HILLSCRK	4.184	4.335	0.0001	0.623	0.430	0.0001	4.101	4.259	0.0001	0.430	0.290	0.0001	4.320	4.463	0.0001	0.193	0.139	0.0035
KANE	4.162	4.314	0.0001	0.902	0.558	0.0001	4.077	4.258	0.0001	0.569	0.336	0.0005	4.272	4.387	0.0001	0.329	0.223	0.0002
LAURHILL	4.156	4.255	0.0017	0.947	0.736	0.0058	4.060	4.170	0.0070	0.561	0.447	0.0257	4.266	4.357	0.0041	0.387	0.291	0.0063
LEADRIDG	4.147	4.313	0.0001	0.787	0.510	0.0001	4.042	4.263	0.0001	0.505	0.318	0.0001	4.277	4.385	0.0048	0.282	0.197	0.0009
LITTBUFF	4.164	4.299	0.0008	0.757	0.576	0.0117	4.082	4.235	0.0031	0.469	0.358	0.0227	4.262	4.386	0.0008	0.288	0.214	0.0272
LITTPINE	4.135	4.244	0.0017	0.780	0.599	0.0005	4.052	4.183	0.0073	0.513	0.371	0.0006	4.253	4.326	0.0132	0.268	0.230	0.0626
MILFORD	4.222	4.387	0.0001	0.733	0.491	0.0001	4.148	4.336	0.0001	0.457	0.294	0.0001	4.316	4.453	0.0012	0.275	0.201	0.0191
PSUNADP	4.179	4.333	0.0001	0.678	0.530	0.0081	4.095	4.265	0.0009	0.429	0.347	0.0619	4.286	4.436	0.0001	0.247	0.184	0.0048
SLOCUM	4.191	4.332	0.0002	0.731	0.501	0.0001	4.129	4.262	0.0033	0.470	0.321	0.0011	4.277	4.437	0.0018	0.260	0.179	0.0013
VALLFORG	4.248	4.393	0.0005	0.678	0.491	0.0013	4.172	4.332	0.0048	0.414	0.299	0.0056	4.345	4.477	0.0005	0.264	0.192	0.0301

Site	Sulfate																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	3.558	2.809	0.0001	38.112	29.761	0.0009	4.746	3.578	0.0001	26.751	20.252	0.0061	2.242	1.940	0.0425	11.358	9.509	0.0532
GODDARD	3.179	2.433	0.0001	35.841	26.333	0.0012	3.957	2.843	0.0001	24.701	16.800	0.0025	2.211	1.959	0.0377	11.143	9.533	0.0873
HILLSCRK	2.793	1.917	0.0001	26.186	17.508	0.0001	3.659	2.420	0.0001	19.372	12.544	0.0001	1.690	1.250	0.0001	6.813	4.962	0.0127
KANE	3.032	2.224	0.0001	38.584	25.448	0.0001	3.909	2.706	0.0001	25.793	16.224	0.0001	2.118	1.711	0.0002	12.790	9.223	0.0001
LAURHILL	2.943	2.365	0.0001	39.133	30.798	0.0006	4.022	3.029	0.0001	25.335	19.584	0.0045	1.977	1.727	0.0234	13.798	11.210	0.0199
LEADRIDG	3.036	2.187	0.0001	32.865	22.762	0.0001	4.165	2.673	0.0001	22.624	15.280	0.0001	1.978	1.603	0.0081	10.238	7.481	0.0002
LITTBUFF	2.917	2.271	0.0006	31.324	25.427	0.0038	3.889	2.805	0.0036	21.045	16.673	0.0024	1.982	1.675	0.0016	10.278	8.753	0.1795
LITTPINE	2.965	2.270	0.0009	31.005	23.424	0.0002	3.894	2.825	0.0029	21.793	15.528	0.0002	1.951	1.644	0.0257	9.213	7.899	0.0785
MILFORD	2.397	1.595	0.0001	28.733	18.838	0.0001	3.052	1.950	0.0001	19.063	12.072	0.0001	1.762	1.211	0.0007	9.671	6.763	0.0047
PSUNADP	2.935	2.150	0.0001	29.401	24.200	0.0130	3.915	2.689	0.0001	20.380	16.816	0.0297	1.939	1.483	0.0016	9.019	7.383	0.0211
SLOCUM	2.798	2.032	0.0001	30.880	21.492	0.0001	3.504	2.591	0.0022	21.517	14.889	0.0005	1.968	1.375	0.0024	9.363	6.603	0.0082
VALLFORG	2.576	1.875	0.0001	30.327	22.192	0.0001	3.227	2.247	0.0012	19.238	13.876	0.0004	1.919	1.474	0.0006	11.090	8.316	0.0456

Site	Nitrate																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	3.558	2.809	0.0001	38.112	29.761	0.0009	4.746	3.578	0.0001	26.751	20.252	0.0061	2.242	1.940	0.0425	11.358	9.509	0.0532
GODDARD	3.179	2.433	0.0001	35.841	26.333	0.0012	3.957	2.843	0.0001	24.701	16.800	0.0025	2.211	1.959	0.0377	11.143	9.533	0.0873
HILLSCRK	2.793	1.917	0.0001	26.186	17.508	0.0001	3.659	2.420	0.0001	19.372	12.544	0.0001	1.690	1.250	0.0001	6.813	4.962	0.0127
KANE	3.032	2.224	0.0001	38.584	25.448	0.0001	3.909	2.706	0.0001	25.793	16.224	0.0001	2.118	1.711	0.0002	12.790	9.223	0.0001
LAURHILL	2.943	2.365	0.0001	39.133	30.798	0.0006	4.022	3.029	0.0001	25.335	19.584	0.0045	1.977	1.727	0.0234	13.798	11.210	0.0199
LEADRIDG	3.036	2.187	0.0001	32.865	22.762	0.0001	4.165	2.673	0.0001	22.624	15.280	0.0001	1.978	1.603	0.0081	10.238	7.481	0.0002
LITTBUFF	2.917	2.271	0.0006	31.324	25.427	0.0038	3.889	2.805	0.0036	21.045	16.673	0.0024	1.982	1.675	0.0016	10.278	8.753	0.1795
LITTPINE	2.965	2.270	0.0009	31.005	23.424	0.0002	3.894	2.825	0.0029	21.793	15.528	0.0002	1.951	1.644	0.0257	9.213	7.899	0.0785
MILFORD	2.397	1.595	0.0001	28.733	18.838	0.0001	3.052	1.950	0.0001	19.063	12.072	0.0001	1.762	1.211	0.0007	9.671	6.763	0.0047
PSUNADP	2.935	2.150	0.0001	29.401	24.200	0.0130	3.915	2.689	0.0001	20.380	16.816	0.0297	1.939	1.483	0.0016	9.019	7.383	0.0211
SLOCUM	2.798	2.032	0.0001	30.880	21.492	0.0001	3.504	2.591	0.0022	21.517	14.889	0.0005	1.968	1.375	0.0024	9.363	6.603	0.0082
VALLFORG	2.576	1.875	0.0001	30.327	22.192	0.0001	3.227	2.247	0.0012	19.238	13.876	0.0004	1.919	1.474	0.0006	11.090	8.316	0.0456

Table 7 (continued).

Site	Ammonium																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.325	0.331	0.7965	3.478	3.482	0.9721	0.402	0.378	0.3304	2.257	2.143	0.5559	0.243	0.277	0.2692	1.220	1.338	0.3454
GODDARD	0.379	0.396	0.5404	4.282	4.268	0.9475	0.454	0.445	0.8104	2.857	2.599	0.4540	0.290	0.344	0.0934	1.425	1.670	0.0793
HILLSCRK	0.284	0.273	0.5198	2.667	2.500	0.3966	0.349	0.323	0.2441	1.875	1.662	0.2190	0.203	0.209	0.8161	0.789	0.837	0.7328
KANE	0.292	0.267	0.2006	3.694	3.074	0.0329	0.354	0.299	0.0765	2.317	1.797	0.0269	0.230	0.237	0.7932	1.376	1.279	0.4556
LAURHILL	0.292	0.324	0.0494	3.908	4.232	0.2684	0.329	0.357	0.1592	2.082	2.353	0.2828	0.264	0.292	0.2625	1.825	1.879	0.6264
LEADRIDG	0.300	0.280	0.3586	3.233	2.912	0.1624	0.379	0.313	0.0519	2.056	1.794	0.1615	0.228	0.241	0.5066	1.178	1.117	0.4580
LITTBUFF	0.375	0.414	0.1034	4.043	4.622	0.0942	0.466	0.480	0.7500	2.540	2.851	0.2472	0.301	0.341	0.0999	1.503	1.770	0.0351
LITTPINE	0.310	0.323	0.5358	3.254	3.356	0.7615	0.377	0.366	0.7474	2.135	2.040	0.6094	0.243	0.275	0.2623	1.122	1.314	0.1163
MILFORD	0.213	0.203	0.5475	2.545	2.413	0.5083	0.277	0.240	0.1374	1.728	1.506	0.1405	0.152	0.162	0.5311	0.817	0.908	0.3458
PSUNADP	0.278	0.264	0.5429	2.776	2.948	0.5834	0.360	0.305	0.1708	1.866	1.901	0.9723	0.196	0.213	0.2933	0.911	1.047	0.0819
SLOCUM	0.302	0.324	0.4027	3.334	3.439	0.8073	0.368	0.401	0.3969	2.275	2.306	0.9772	0.231	0.237	0.7810	1.061	1.136	0.4554
VALLFORG	0.293	0.319	0.2361	3.435	3.781	0.2061	0.359	0.373	0.6914	2.138	2.307	0.3771	0.234	0.259	0.2633	1.298	1.473	0.2402

Site	Calcium																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.175	0.160	0.4017	1.849	1.690	0.2822	0.206	0.175	0.2048	1.130	0.991	0.1850	0.142	0.145	0.8834	0.720	0.701	0.9873
GODDARD	0.181	0.157	0.2452	2.013	1.692	0.1460	0.209	0.169	0.1319	1.285	0.958	0.0548	0.150	0.151	0.9283	0.726	0.737	0.9207
HILLSCRK	0.109	0.095	0.3356	1.017	0.879	0.3367	0.130	0.098	0.1679	0.675	0.496	0.0793	0.087	0.094	0.6930	0.343	0.384	0.6517
KANE	0.123	0.111	0.2652	1.551	1.263	0.0226	0.135	0.116	0.1682	0.879	0.671	0.0041	0.112	0.110	0.8753	0.673	0.592	0.3186
LAURHILL	0.125	0.131	0.6457	1.659	1.686	0.8906	0.140	0.132	0.5886	0.880	0.842	0.6992	0.112	0.132	0.2494	0.777	0.846	0.5094
LEADRIDG	0.123	0.105	0.0855	1.317	1.092	0.0520	0.144	0.106	0.0060	0.783	0.597	0.0065	0.105	0.105	0.9706	0.537	0.496	0.5236
LITTBUFF	0.138	0.108	0.0565	1.497	1.227	0.2034	0.154	0.122	0.0943	0.852	0.734	0.2862	0.129	0.092	0.1621	0.647	0.491	0.2609
LITTPINE	0.109	0.108	0.8923	1.140	1.132	0.8212	0.120	0.113	0.5799	0.671	0.621	0.4296	0.102	0.104	0.8599	0.468	0.510	0.7027
MILFORD	0.092	0.073	0.0706	1.099	0.866	0.0540	0.096	0.072	0.0114	0.603	0.443	0.0055	0.092	0.076	0.2859	0.498	0.421	0.3551
PSUNADP	0.120	0.101	0.1881	1.194	1.137	0.6722	0.144	0.101	0.0097	0.768	0.632	0.2198	0.092	0.101	0.4114	0.424	0.507	0.1539
SLOCUM	0.107	0.090	0.0843	1.171	0.966	0.0501	0.121	0.096	0.0913	0.738	0.548	0.0129	0.093	0.086	0.4795	0.434	0.418	0.6967
VALLFORG	0.134	0.090	0.0029	1.577	1.081	0.0061	0.136	0.092	0.0080	0.807	0.582	0.0155	0.136	0.087	0.0318	0.768	0.501	0.0629

Site	Magnesium																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.034	0.031	0.6318	0.358	0.328	0.6332	0.040	0.034	0.4457	0.219	0.193	0.4934	0.028	0.027	0.9779	0.138	0.133	0.9067
GODDARD	0.035	0.029	0.3277	0.392	0.312	0.2045	0.041	0.031	0.1687	0.257	0.173	0.0934	0.028	0.029	0.8001	0.136	0.140	0.7992
HILLSCRK	0.028	0.019	0.1130	0.263	0.178	0.1216	0.034	0.020	0.0867	0.177	0.101	0.0537	0.021	0.019	0.5315	0.085	0.077	0.6874
KANE	0.023	0.017	0.0044	0.291	0.192	0.0009	0.025	0.018	0.0166	0.166	0.107	0.0018	0.021	0.016	0.0351	0.125	0.084	0.0065
LAURHILL	0.026	0.023	0.4295	0.348	0.299	0.2898	0.030	0.022	0.1229	0.185	0.141	0.0613	0.023	0.024	0.7999	0.165	0.159	0.8699
LEADRIDG	0.025	0.018	0.0100	0.268	0.183	0.0095	0.029	0.019	0.0019	0.160	0.108	0.0047	0.021	0.017	0.1308	0.108	0.079	0.0804
LITTBUFF	0.031	0.028	0.5559	0.351	0.323	0.7437	0.032	0.031	0.8176	0.182	0.190	0.8870	0.032	0.025	0.3064	0.169	0.132	0.4508
LITTPINE	0.023	0.022	0.5020	0.246	0.226	0.5202	0.025	0.022	0.4094	0.143	0.122	0.4294	0.022	0.021	0.8927	0.101	0.103	0.8839
MILFORD	0.030	0.018	0.0093	0.358	0.214	0.0204	0.028	0.016	0.0047	0.172	0.101	0.0051	0.033	0.019	0.0237	0.185	0.113	0.0884
PSUNADP	0.021	0.015	0.0113	0.215	0.174	0.0955	0.025	0.017	0.0014	0.133	0.103	0.0935	0.018	0.015	0.1741	0.081	0.070	0.3210
SLOCUM	0.027	0.020	0.0986	0.303	0.219	0.0784	0.031	0.021	0.1115	0.188	0.121	0.0338	0.025	0.020	0.3027	0.116	0.097	0.3299
VALLFORG	0.057	0.040	0.0409	0.676	0.509	0.1275	0.053	0.040	0.1796	0.314	0.270	0.3901	0.062	0.040	0.0111	0.362	0.239	0.0988

Table 7 (continued).

Site	Potassium																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.038	0.049	0.1738	0.403	0.517	0.2262	0.046	0.055	0.4279	0.258	0.310	0.4096	0.029	0.042	0.0663	0.145	0.212	0.0889
GODDARD	0.034	0.045	0.0509	0.384	0.480	0.1805	0.036	0.041	0.4616	0.230	0.239	0.8558	0.031	0.048	0.0051	0.152	0.241	0.0154
HILLSCRK	0.036	0.044	0.4367	0.332	0.404	0.3961	0.044	0.048	0.8063	0.219	0.249	0.6292	0.030	0.038	0.2309	0.113	0.157	0.1493
KANE	0.030	0.021	0.0783	0.379	0.233	0.0178	0.044	0.026	0.0553	0.285	0.150	0.0214	0.015	0.016	0.9782	0.094	0.084	0.6009
LAURHILL	0.042	0.051	0.2854	0.572	0.657	0.4247	0.051	0.059	0.4778	0.326	0.371	0.5473	0.034	0.043	0.2591	0.246	0.286	0.4682
LEADRIDG	0.037	0.027	0.1159	0.399	0.281	0.0670	0.047	0.040	0.4634	0.259	0.216	0.4263	0.028	0.013	0.0105	0.142	0.063	0.0018
LITTBUFF	0.038	0.065	0.0324	0.426	0.733	0.0446	0.046	0.080	0.0787	0.258	0.483	0.0600	0.033	0.047	0.0689	0.168	0.248	0.0752
LITTPINE	0.032	0.041	0.1905	0.344	0.428	0.3180	0.030	0.038	0.2760	0.170	0.224	0.3219	0.035	0.041	0.5137	0.174	0.204	0.5999
MILFORD	0.022	0.017	0.0105	0.269	0.209	0.0341	0.027	0.021	0.0987	0.168	0.136	0.1637	0.018	0.013	0.0344	0.101	0.076	0.0838
PSUNADP	0.033	0.019	0.1771	0.330	0.220	0.2678	0.050	0.026	0.1090	0.271	0.164	0.2774	0.012	0.011	0.2159	0.058	0.053	0.5058
SLOCUM	0.046	0.047	0.9599	0.508	0.506	0.9756	0.055	0.053	0.8704	0.349	0.318	0.6924	0.035	0.039	0.6309	0.160	0.190	0.4924
VALLFORG	0.041	0.045	0.6011	0.477	0.548	0.5091	0.045	0.045	0.9975	0.271	0.286	0.7782	0.037	0.045	0.4338	0.205	0.261	0.3532
Site	Sodium																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.052	0.060	0.1982	0.560	0.647	0.2226	0.043	0.052	0.2213	0.242	0.294	0.2847	0.062	0.071	0.3929	0.316	0.353	0.4935
GODDARD	0.052	0.064	0.0350	0.583	0.686	0.0991	0.045	0.045	0.9445	0.264	0.268	0.9798	0.066	0.086	0.0429	0.322	0.419	0.0161
HILLSCRK	0.043	0.050	0.2732	0.402	0.468	0.2682	0.041	0.042	0.9062	0.201	0.219	0.6418	0.052	0.061	0.3481	0.201	0.248	0.2539
KANE	0.053	0.038	0.0110	0.673	0.443	0.0031	0.044	0.031	0.0083	0.289	0.190	0.0062	0.064	0.047	0.0603	0.385	0.254	0.0192
LAURHILL	0.049	0.061	0.0235	0.647	0.813	0.0695	0.033	0.051	0.0125	0.214	0.336	0.0239	0.062	0.073	0.2481	0.434	0.477	0.5388
LEADRIDG	0.070	0.050	0.0195	0.754	0.551	0.0391	0.056	0.039	0.0122	0.311	0.234	0.1378	0.088	0.065	0.1864	0.443	0.316	0.0721
LITTBUFF	0.079	0.091	0.1530	0.869	1.037	0.2296	0.059	0.071	0.2459	0.347	0.439	0.2735	0.101	0.115	0.2869	0.524	0.598	0.3940
LITTPINE	0.053	0.063	0.1602	0.572	0.654	0.3852	0.038	0.056	0.1451	0.223	0.311	0.2267	0.072	0.071	0.8963	0.350	0.344	0.9357
MILFORD	0.119	0.097	0.1478	1.416	1.192	0.2260	0.080	0.065	0.1371	0.520	0.412	0.1877	0.166	0.132	0.2340	0.897	0.782	0.4220
PSUNADP	0.059	0.045	0.0164	0.599	0.517	0.2698	0.048	0.033	0.0130	0.257	0.218	0.3891	0.072	0.059	0.1513	0.342	0.299	0.3910
SLOCUM	0.082	0.065	0.2453	0.890	0.700	0.1641	0.064	0.052	0.5164	0.388	0.316	0.4918	0.108	0.080	0.0952	0.502	0.383	0.0803
VALLFORG	0.195	0.163	0.2329	2.324	2.102	0.4297	0.108	0.112	0.8204	0.651	0.750	0.5220	0.286	0.221	0.1125	1.673	1.350	0.2545
Site	Chloride																	
	Annual						Growing Season						Dormant Season					
	Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)			Concentration (mg/L)			Deposition (kg/ha)		
	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p	Before	After	p
CROOKCRK	0.287	0.302	0.6896	3.086	3.189	0.7266	0.285	0.255	0.5522	1.600	1.432	0.6129	0.294	0.355	0.1250	1.487	1.757	0.2196
GODDARD	0.188	0.203	0.3646	2.118	2.176	0.8784	0.177	0.184	0.7643	1.060	1.043	0.8274	0.212	0.235	0.2453	1.059	1.133	0.4265
HILLSCRK	0.176	0.161	0.4808	1.650	1.470	0.4010	0.191	0.155	0.3779	0.971	0.794	0.2850	0.168	0.168	0.9903	0.680	0.677	0.9565
KANE	0.150	0.114	0.0001	1.911	1.312	0.0002	0.135	0.104	0.0003	0.899	0.623	0.0035	0.168	0.127	0.0009	1.012	0.689	0.0002
LAURHILL	0.208	0.210	0.9024	2.800	2.744	0.9697	0.193	0.207	0.5489	1.236	1.368	0.4793	0.227	0.214	0.8113	1.565	1.378	0.5716
LEADRIDG	0.178	0.134	0.0018	1.910	1.431	0.0091	0.166	0.122	0.0014	0.917	0.730	0.1046	0.196	0.148	0.0742	0.996	0.701	0.0064
LITTBUFF	0.236	0.252	0.3289	2.566	2.826	0.3084	0.226	0.224	0.9542	1.275	1.340	0.6313	0.254	0.287	0.1917	1.289	1.483	0.1678
LITTPINE	0.192	0.193	0.9291	2.046	2.004	0.8726	0.179	0.190	0.5758	1.024	1.066	0.7175	0.210	0.194	0.3525	1.023	0.941	0.5923
MILFORD	0.239	0.189	0.0408	2.864	2.319	0.0954	0.192	0.142	0.0083	1.231	0.897	0.0329	0.304	0.241	0.1697	1.633	1.421	0.3146
PSUNADP	0.164	0.128	0.0004	1.658	1.452	0.1462	0.159	0.113	0.0009	0.841	0.717	0.2107	0.174	0.148	0.0669	0.816	0.733	0.3000
SLOCUM	0.212	0.189	0.2606	2.327	2.012	0.1309	0.199	0.188	0.6950	1.204	1.076	0.3351	0.238	0.195	0.1298	1.122	0.937	0.1782
VALLFORG	0.415	0.399	0.7391	4.883	5.097	0.8335	0.293	0.345	0.3886	1.778	2.294	0.3307	0.538	0.460	0.2821	3.103	2.804	0.4359

nitrate concentrations have also decreased across Pennsylvania, with significant drops occurring in most but not all regions of the state. Since 1996, the average statewide decrease in nitrate concentrations and wet deposition were 0.235 mg/L (12.1%) and 2.95 kg/ha (13.6%), respectively. The reductions in nitrate concentrations and wet deposition are a direct response to lower nitrogen oxides emissions in Pennsylvania and neighboring states, particularly from fuel combustion sources (EPA, 2004a). 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 2003 based on the 12 long-term monitoring sites was 4.43, an increase of 0.22 pH unit when compared to the pre-CAAA (1983-1994) average pH of 4.17 at these sites. The 0.22 unit increase represents a decrease of hydrogen ion concentrations of approximately 40%. The average reduction in pH at the 12 long-term monitoring sites during the entire post-CAAA period (1995-2003) was 0.14 unit (pre-CAAA pH of 4.17 versus a post-CAAA pH of 4.31) which resulted in a 28% reduction in hydrogen ion concentrations in precipitation. Increasing base cation and ammonium concentrations has also influenced the post-CAAA acidity at some sites although their overall influence has been relatively small from a statewide prospective.

The observed reductions in sulfate and nitrate concentrations and wet depositions as well as acidity exhibit substantial seasonal differences. Although significant ($p < 0.05$) reductions in seasonal sulfate concentrations and wet depositions have been evident throughout the state, the reductions were nearly three times greater during the growing season. For nitrate, all regions of the state have experienced decreasing growing and dormant season concentrations and wet depositions as well; however, the reductions are significant ($p < 0.05$) at only a few sites. The largest and most significant reductions occurred during the growing season and were generally twice as large as the measured reductions in dormant season concentrations and wet deposition. As one might expect, reductions in acidity and wet hydrogen ion depositions were also greatest during the growing season.

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

On an annual basis, post-CAAA reductions in nitrate concentrations were lowest in the west and increased to the east. Reductions in growing season concentrations followed a similar pattern, although the differences between central and eastern Pennsylvania are quite small. In contrast, reductions in dormant season nitrate concentrations were highest in eastern Pennsylvania and decreased to their lowest levels in western Pennsylvania. Reductions in wet nitrate deposition were consistently highest in eastern Pennsylvania and lowest in the center region regardless of season. Post-CAAA reductions in nitrate deposition appear to be greater across the northern tier

counties than the southern tier counties of Pennsylvania. Differences in emissions, emission sources and emissions reductions as well as deviations in precipitation volumes from the pre-CAAA reference period are likely the reasons these spatial patterns.

Despite the significant reductions in sulfate and nitrate concentrations in precipitation and its acidity as well as the reductions in wet deposition throughout the Commonwealth, Pennsylvania, particularly the western third of the state, still receives the most acidic precipitation of any region of North America. Sulfate and nitrate concentrations and wet depositions are also higher in Pennsylvania than most regions of North America. For a direct comparison of ionic concentrations and wet deposition measurements in Pennsylvania with the rest of the United States, readers are referred to the National Atmospheric Deposition Program 2003 Annual Summary (NADP, 2004) 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 likely be necessary to provide adequate protection of acid sensitive aquatic and terrestrial ecosystems and cultural and material resources in the Commonwealth, particularly in western Pennsylvania. Some of the year to year variability in post-CAAA reductions in wet acidic deposition can be attributed to above average precipitation. Since precipitation is an unmanageable parameter of climate, the only way to provide additional protection to the citizens of the Commonwealth and the environment is to reduce further sulfur dioxide and nitrogen oxides emissions in Pennsylvania and in upwind states. The expeditious implementation of a stringent national multi-pollutant strategy would not only reduce emissions and subsequently acidic deposition, but improve visibility as well. An assessment of source-receptor relationships should be undertaken to identify those sources that will provide the greatest opportunity for further reductions in acidic deposition in Pennsylvania. A detailed evaluation of spatial and temporal variations in precipitation and its influence on deposition patterns in the Commonwealth should also be undertaken. Such an analysis will provide valuable information to determine the level of emissions reductions that will be necessary to achieve adequate protection of the citizens of the Commonwealth and the environment.

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