ATMOSPHERIC DEPOSITION: SPATIAL AND TEMPORAL VARIATIONS IN PENNSYLVANIA
2006

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TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

INTRODUCTION

Precipitation plays an important role in biogeochemical cycling by cleansing the atmosphere of many pollutants and delivering dissolved substances to aquatic and terrestrial ecosystems. Atmospheric pollutants are also returned to the Earth's surfaces via dry depositional processes, e.g., solid particulate fallout, aerosol impaction, and gaseous adsorption. Atmospheric pollutants can affect water quality and human health and impact aquatic, terrestrial, cultural, and material resources. Accordingly, the detailed study of the spatial and temporal chemistry of precipitation and dry deposition serves four principle functions: (1) it provides basic data needed for calculations involving specific air pollutants; (2) it provides data needed for evaluating possible impacts of these pollutants on aquatic and terrestrial ecosystems, cultural and material resources, and human health; (3) it provides for comparisons of both beneficial and detrimental substances associated with atmospheric deposition; and (4) it provides quantitative means of evaluating the effectiveness of present and future air pollution control legislation, such as the Clean Air Act Amendments of 1990, Title IV aimed at reducing acidic deposition in the United States.

Because of the importance of precipitation in providing water and its dissolved substances to the biosphere, an atmospheric deposition monitoring network was established in Pennsylvania in 1981 under a Cooperative Agreement between The Pennsylvania State University and The Pennsylvania Department of Environmental Resources, currently the Pennsylvania Department of Environmental Protection. The objectives of this project were to (1) determine the magnitude and distribution of wet atmospheric deposition and associated toxic and nutrient elements in Pennsylvania and (2) to assess their potential environmental impacts. The project was revised in 1986 and additional objectives added to: (3) determine temporal trends in the chemistry of precipitation in the state; (4) evaluate the influence of local emissions and variations in precipitation amounts on wet deposition patterns; (5) determine the optimum number of sites needed to define spatial variability in atmospheric deposition in Pennsylvania; and (6) evaluate the effectiveness of the Clean Air Act Amendments of 1990, Title IV in reducing acidic deposition to the Commonwealth.

This report represents a summary of precipitation chemistry and wet deposition data collected at 17 atmospheric deposition-monitoring sites in Pennsylvania in 2006. The Pennsylvania Department of Environmental Protection (DEP), Bureau of Air Quality Control, supported 11 of the monitoring sites. These sites are located in Mercer, Armstrong, Cambria, Somerset, Tioga, Lycoming, Perry, Luzerne, Erie, Lancaster, and Montgomery counties. The remaining six sites are part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). The 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, in Pike County near Milford, in Adams County near Arendtsville, and in Clinton County near North Bend (Young Women's Creek). The U.S. Forest Service, Northern Forest Experiment Station, supported the NADP/NTN sites near Kane and Milford. The Pennsylvania Agricultural Experiment Station through the National Research Support Project-3 (NRSP-3) supported the Leading Ridge NADP/NTN site. The National Oceanic and Atmospheric Administration supported the Penn State NADP/NTN site. The U.S. Environmental Protection Agency and The U.S. Geological Survey supported the Arendtsville and Young Women's Creek sites, respectively. The DEP supported monitoring site near Millersville University (Lancaster County) is also an NADP/NTN site. This site is located on an active farm and was selected to provide additional information on ammonium concentrations and wet deposition close to agricultural ammonia emission sources.

NETWORK DESIGN AND OPERATION

Monitoring Site Locations

Seventeen atmospheric deposition-monitoring sites were in operation in Pennsylvania during 2006. Included in this network were 11 sites supported by The Pennsylvania Department of Environmental Protection (DEP), Bureau of Air Quality Control and six National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites. One of the DEP supported sites (Millersville) is also part of the NADP/NTN. Site locations are plotted in Figure 1. The latitude, longitude, elevation, county, and date sampling was initiated for each site are given in Table 1.

Collection Site Specifications

All sites were equipped with an Aerochem Metrics wet/dry precipitation collector. This instrument consists of a two-container system with a movable lid designed to expose the wet container and cover the dry container during periods of precipitation, and vice versa. A sensor mounted on the instrument reacts electrically to the onset of precipitation causing the lid to move thereby exposing the wet-side container. Heaters mounted below the sensor serve to both melt snow and ice as well as evaporate moisture from the sensing element.

Standard recording and non-recording rain gages were installed at each site. Each recording rain gage was equipped with a timer/chart recorder keyed to the sampling interval of one week. The times of opening and closing of the wet/dry sampler were determined from an event recorder mounted on the recording rain gage. The standard non-recording rain gage was used to determine the total amount of precipitation. All of the monitoring sites in the Pennsylvania Network meet NADP/NTN standards and were instrumented with equipment selected for use in the NADP/NTN Network (Bigelow, 1984).

Protocols for Operation of Monitoring Network

All precipitation samples were collected following procedures established by the Illinois State Water Survey (Peden et al., 1979) and the NADP/NTN (Bigelow and Dossett, 1988). Sampling was conducted according to a specific weekly schedule and the entire collection bucket was shipped by United Parcel Service (UPS) in specially provided containers to a water quality lab at the Penn State Institutes of the Environment at the University Park campus of The Pennsylvania

Pennsylvania Atmospheric Deposition Monitoring Network

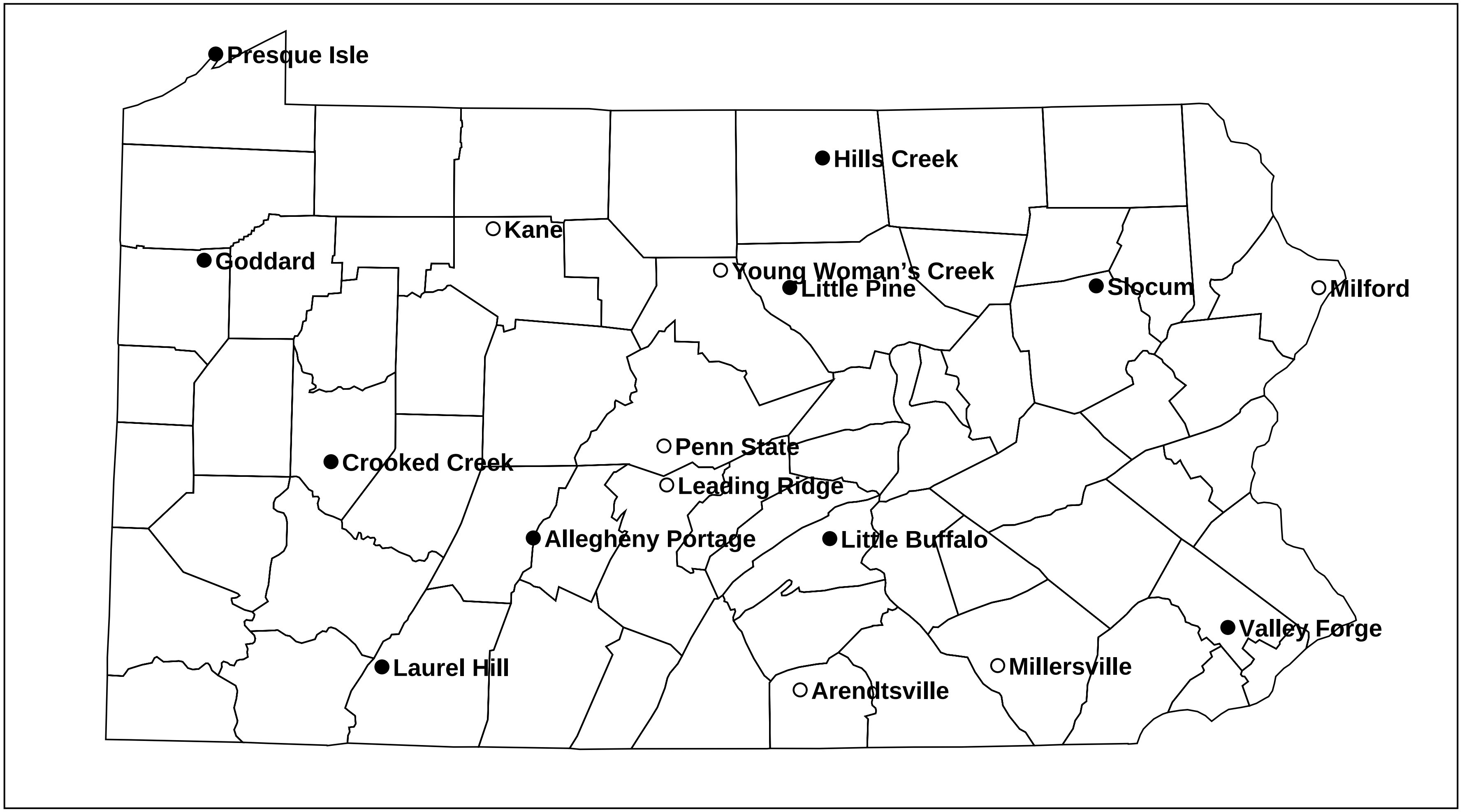


Figure 1. Site locations of the 2006 Pennsylvania Atmospheric Deposition Monitoring Network. Sites marked with an empty circle are part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN).

Table 1. Location and description of sites in the Pennsylvania Atmospheric Deposition Monitoring Network.

Site Name	Latitude	Longitude	County	Elevation (Meters)	Sampling Started
Western Pennsylvania					
Presque Isle State Park	42.1558	-80.1133	Erie	177	06/20/2000
M.K.Goddard State Park	41.4167	-80.1417	Mercer	384	11/10/1981
Crooked Creek Lake	40.7167	-79.5167	Armstrong	296	12/08/1981
Laurel Hill State Park	39.9869	-79.2544	Somerset	616	11/03/1981
Kane NADP/NTN	41.5978	-78.7675	Elk	618	07/17/1978
Allegheny Portage NHS	40.4572	-78.5600	Cambria	739	01/07/1997
Central Pennsylvania					
Arendtsville NADP/NTN	39.9231	-77.3078	Adams	269	01/26/1999
Hills Creek State Park	41.8044	-77.1903	Tioga	476	11/01/1981
Little Pine State Park	41.3800	-77.9397	Lycoming	238	01/03/1984
Leading Ridge NADP/NTN	40.6575	-77.9397	Huntingdon	287	04/25/1979
Little Buffalo State Park	40.4500	-77.1667	Perry	122	08/04/1981
Penn State NADP/NTN	40.7883	-77.9458	Centre	393	06/07/1983
Young Women Ck NADP/NTN	41.4133	-77.6939	Clinton	273	04/20/1999
Eastern Pennsylvania					
Milford NADP/NTN	41.3275	-74.8203	Pike	212	11/03/1981
Frances Slocum State Park	41.3333	-75.8833	Luzerne	366	11/03/1981
Valley Forge NHS	40.1167	-75.8917	Montgomery	46	11/03/1981
Millersville NADP/NTN	39.9900	-76.3862	Lancaster	85	11/21/2002

State University. NADP/NTN samples were shipped by UPS to the NADP/NTN Central Analytical Laboratory (CAL) at the Illinois State Water Survey in Champaign, Illinois. Prior to shipment of NADP/NTN samples, site operators took "field" pH and conductivity measurements Starting on 3 January 1994 all NADP/NTN precipitation samples were transferred to 1000 mL polyethylene bottles before shipment to the CAL. Prior to that date, all NADP/NTN samples were shipped to the CAL in the collection container.

At the time of collection, a clean collection container provided by the water quality labs was placed in the sampler. The "wet" sample containers were shipped to the laboratory each week regardless of whether precipitation occurred. Sample containers were removed each Tuesday at approximately 9:00 a.m. unless it was raining or snowing, but in no case later than the end of the working day on Tuesday.

Precautions were taken to preclude changes in or contamination of precipitation samples during collection, transport, and storage prior to analysis. Analyses were performed as soon as possible after receipt of the samples. Although ionic concentrations in weekly precipitation samples may be subject to change (Peden and Skowron, 1978; de Pena et al., 1985; Coscio et al., 1982; Ridder et al., 1985), the feasibility of daily or event sampling was unwarranted because of the high cost involved.

Laboratory Analyses

Precipitation samples were analyzed for the following parameters provided a sufficient volume was present: pH (H^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), chloride (CL^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), and specific conductance. In the event that insufficient volume was present for complete analysis, the priority on analysis was as listed. Specific analytical techniques and laboratory equipment used in this monitoring program are listed in Table 2.

Sample Handling Procedures

Upon receipt at the water quality lab, samples were assigned a number that is traceable to a specific sampling period and site. Following immediate measurement of volume, pH, and specific conductance (if sufficient volume was present), each sample was filtered. After filtration, nitrate, ammonium, sulfate, and chloride concentrations were measured within 1-3 working days; calcium, magnesium, sodium, and potassium samples were acidified and stored; analyses usually followed within 3-5 weeks. Precipitation samples that were grossly contaminated were discarded. For samples arriving with a twig, leaf, pine needle, beetle, bumblebee, etc., the contaminant was removed by filtration and the sample processed like any other precipitation sample. At the time of sample check-in, comments were placed in the site record to indicate the visual appearance and the presence of odor of each sample.

Table 2. Summary of analytical techniques used to measure ionic concentrations, pH, and specific conductance of precipitation samples collected in The Pennsylvania Atmospheric Deposition Monitoring Network.

Parameter	Methodology (Reference, EPA, 1983)	Equipment
pH	EPA Electrometric (150.1)	Beckman 360
Specific Conductance	EPA Specific Conductance (120.1)	YSI 3200
Sulfate	EPA Ion Chromatrography (300.0)	Dionex Ion Chromatrography
Chloride	EPA Ion Chromatrography (300.0)	Dionex Ion Chromatrography
Ammonium-Nitrogen	EPA-Phenate Method (350.1)	SEAL AQ2 Discrete Analyzer
Oxidized Nitrogen Reduction	Standard Methods-Cadium (353.3)	SEAL AQ2 Discrete Analyzer
Extractable Metals		Perkin Ekmer Atomic Absorption Model 5100ZL
Calcium	EPA AA Direct Aspiration (215.1)	
Magnesium	EPA AA Direct Aspiration (242.1)	
Potassium	EPA AA Direct Aspiration (7610)	
Sodium	EPA AA Direct Aspiration (273.1)	

Quality Assurance Quality Control Protocols

The quality control (QC) and quality assurance (QA) policies for atmospheric deposition monitoring that have been followed throughout this project were designed to provide maximum credibility of the data, including documented accuracy, precision, and completeness. Major components of this QA plan include sound QC programs addressing field operations, laboratory analyses, and data management. The QA/QC programs discussed below apply to Pennsylvania network sites supported by The Pennsylvania Department of Environmental Protection. A separate QA/QC program is maintained by the NADP for all precipitation chemistry data from NADP/NTN sites that are included in this report. The NADP/NTN Quality Assurance Report is available on the Internet at http://nadp.sws.uiuc.edu.

Field Measurements: Precipitation samples were collected following procedures established under the NADP/NTN and discussed in detail in the NADP/NTN Instruction Manual on Site Operations (Bigelow and Dossett, 1988). Recording rain gage calibrations were conducted each fall and spring or whenever discrepancies exist for two consecutive weeks between the recording rain gage and the non-recording gage. Weekly comparison of precipitation volume from the Aerochem Metrics wet/dry collector and the non-recording rain gage were made to assure that the sensor was properly activating the precipitation sampler. Using the event recorder, the opening and closing of the roof on the precipitation sampler was compared each week with the recording rain gage chart to determine if the sample had been exposed to the atmosphere during rain free periods and to determine if the sampler was responding to precipitation. Any contamination in the sample or any field sampling problems noted on the field form by the site operator were reviewed weekly by the Project Assistant and entered into each site's permanent record. Information on site operations is used in screening precipitation chemistry data to eliminate contaminated samples.

Analytical Laboratory and External Audits: Quality assurance for the analytical measurements given in Table 2 is a multi-tiered program that includes bench level quality control, laboratory management quality assurance, and external quality assurance monitoring. The analytical laboratory is expected to achieve at least the detection limits in Table 3 with maximum allowable variance in accuracy of ±100 percent of the detection limit, of ±20 percent at ten times the detection limit, and ±10 percent at 100 times the detection limit. Analytical methodology and specific references are given in Table 2. Instruments are maintained and calibrated according to manufacturer specifications. Standard preparation and instrument calibrations are among the most critical procedures in laboratory quality control. For QA of the preparation of stock standard solutions, the Lab Manager arranges for (1) independent laboratory confirmation of each standard and (2) compares the results of new standard solutions to those obtained with prior standards. In some cases, the lab may also obtain confirmation by an independent analytical procedure within the lab, such as is the case with nitrate standards that are used to calibrate both the automated colorimetric apparatus and the ion chromatograph. Procedure 1 is accomplished by the simultaneous measurement of stock solution standards and U.S. EPA mineral and nutrient standards. All standard solutions are reformulated at or before shelve-life of the solution.

Table 3. Minimum detection limit criteria for Laboratory analyses. Units in mg/L unless otherwise noted.

Ion	Detection Limit	
Na^+	0.005	
K^+	0.005	
Ca^{2+}	0.005	
Mg^{2+}	0.005	
NH_4^+	0.005	
SO_4^{2-}	0.2	
NO_3^-	0.005	
Cl^-	0.02	
	Accuracy	Precision
pH < 5.0	± 0.05	± 0.03
pH > 5.0	± 0.05	± 0.01
Specific Conductance		
10-100 μS/cm	± 5%	± 3%
>100 μS/cm	± 2%	± 1%

Quality control exercised by the analyst is also an essential component of the overall program. Immediately following instrument calibration, one or more reference samples are analyzed to ensure that the system is functioning properly. Subsequently, at a frequency of no less than 1 sample in 10, the analyst inserts a reference material duplicate or single-point standard to verify correct operation. The observed values for these QC samples must not differ from the theoretical value by more than ±5% for all parameters, except nitrate and ammonium that must not differ by more than ±10% of the theoretical value. When an unacceptable value for the calibration QC sample is obtained, the instrument is re-calibrated and all samples that were analyzed after the last acceptable QC sample are re-analyzed. One sample per batch is also prepared and must be within the control limit that is ±5% of the relative standard deviation. An Ion Chromatography Resolution Test is also performed for each analytical run. Records of all QC data are maintained in a bound notebook at each workstation and periodically reviewed by the Lab Manager. Maintenance of current information on the characteristics (precision, bias, detection limit, etc.) of each analytical method was provided by a continuous quality assurance monitoring program operated by the Lab Manager and Project Supervisor. The program includes "blind" insertion into the normal sample flow of split samples, spiked samples, and standard reference solutions. "Blind audit samples" using simulated rain water provided by the National Atmospheric Deposition Program Coordination Office and the Central Analytical Lab of the Illinois State Water Survey are also periodically submitted to the lab, generally at a rate of one per month.

In addition to the above QC program, cation/anion balance, conductance balance, and percent ion difference are calculated for each sample with complete chemical analyses. Samples with poor cation/anion balance (<0.85 or >1.15) are checked for possible cause and re-analyzed. An approximation of the conductance of each sample is calculated by adding together the equivalent conductance of each measured ion at infinite dilution. The calculated conductance is determined by multiplying the concentration of each ion by the appropriate factor. The percent conductance difference is calculated by dividing the difference between the calculated conductance and the measured conductance by the measured conductance. Samples are screened based on the conductance criterion of +10% or -40%. The larger negative percentage is based on the fact that calculated conductance is always less than measured conductance due to the presence of ions in precipitation that are not measured.

The water quality laboratory participates in an inter-laboratory comparison study sponsored by the National Water Research Institute of Canada. The LRTAP (Long Range Transport of Air Pollution) Inter-laboratory Study for major ions and nutrients is conducted bi-annually.

Data Management: All analytical results and field measurements are entered into a computer database by the Lab Manager or Project Assistant. The data are entered twice and automatically checked to assure correct entry. All of the data are manually verified against the original laboratory and field forms. All of the laboratory data are evaluated based on available QA/QC data using established procedures. The objective of the data verification process is to identify and correct, flag, or delete data of unacceptable quality. All data are rigorously validated to identify outliers and detect possible systematic errors in the measurement and analytical processes. Outliers are identified using uni-variate, bi-variate, and multi-variate analyses.

DATA REDUCTION

Precipitation-Weighted Means

Seasonal and annual precipitation-weighted mean concentrations discussed in this report were calculated according to the formula:

$$C_w = \frac{\sum_{i=1}^{n} C_i P_i}{\sum_{i=1}^{n} P_i}$$

where the precipitation-weighted mean concentration, $\mathbf{C_w}$, for a given ion was calculated from the n valid samples in the season or year under consideration. Individual sample concentrations,

$\mathbf{C_i}$, were weighted by the measured precipitation, $\mathbf{P_i}$, from the standard non-recording rain gage, with values substituted from the recording gage or sample volume for those infrequent cases where the standard non-recording rain gage was out of service or where rain gage measurements were otherwise invalid.

The quantity of precipitation measured by the rain gage is usually greater than that captured in the sample bucket. Non-recording rain gage amounts, rather than the actual sample volumes, were used in the calculation of precipitation-weighted means. This practice is based on the assumption that the chemistry of the sample captured in the bucket represents that which was missed.

Weekly, Seasonal, and Annual Wet Deposition Estimates

Weekly measured wet deposition (kg/ha) of each ion was obtained by multiplying the product of the concentration data (mg/L) and precipitation depth (mm) by 0.01. Ionic concentrations for each weekly sampling period were converted to depositions and then summed over desired periods. Total annual and seasonal depositions were calculated by adding to the measured deposition an estimate of the amount of deposition that occurred during those precipitation events that were not analyzed. The estimate of unmeasured deposition was based on the amount of precipitation measured but not analyzed and the precipitation-weighted average concentration of each ion for their respective summary periods.

Concentration and Wet Deposition Maps

Color-shaded raster maps depict the annual and seasonal precipitation-weighted mean estimates of ion concentrations and wet depositions for precipitation across Pennsylvania in 2006. The concentrations and depositions were estimated from data collected at the 11 Pennsylvania Network and six NADP/NTN monitoring sites within Pennsylvania (Figure 1) and 31 NADP/NTN monitoring sites located around the periphery of the state (Table 4). Estimates of concentration and deposition for each pixel in an 1820-column by 1365-row grid superimposed on Pennsylvania were obtained by applying the multi-quadric equation spatial interpolation algorithm (Harding, 1974) to the coordinates and chemistry data from the 42 monitoring sites. The resulting estimated grids were mapped by applying a color gradient to the range of values in each grid and overlaying the state boundaries and monitoring sites on the colorized grids.

Concentration and wet deposition maps included in this report are also available in an electronic version at http://www.dep.state.pa.us. Concentration and wet deposition maps from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) are available at http://nadp.sws.uiuc.edu.

Concentration and Wet Deposition Trends

Statistical analyses of long-term trends in ion concentration and wet deposition at each monitoring site in Pennsylvania were based on a least squares general linear model which

Table 4. Peripheral NADP/NTN monitoring sites used to estimate spatial distributions of ionic concentrations and wet depositions across Pennsylvania.

State (ID No.)	Location
Connecticut (CT15)	Abington
Maryland (MD07)	Catoctin Mountain Park
Maryland (MD08)	Piney Reservoir
Maryland (MD13)	Wye
Maryland (MD18)	Assateague Island
Maryland (MD99)	Beltsville
New Jersey (NJ00)	E. B. Forsythe
New Jersey (NJ99)	Washington Crossing
New York (NY01)	Alfred
New York (NY08)	Aurora
New York (NY10)	Chautaugua
New York (NY20)	Huntingdon
New York (NY 22)	St. Lawrence River Valley
New York (NY52)	Bennett Bridge
New York (NY68)	Biscuit Brook
New York (NY98)	Whiteface Mountain
New York (NY99)	West Point
Ohio (OH09)	Oxford
Ohio (OH15)	Lykens
Ohio (OH17)	Delaware
Ohio (OH49)	Caldwell
Ohio (OH54)	Deer Creek State Park
Ohio (OH71)	Wooster
Virginia (VA00)	Charlottesville
Virginia (VA28)`	Shenandoah National Park
Virginia (VA10)	Mason Neck
Virginia (VA24)	Prince Edward
Virginia (VA27)	James Madison University
West Virginia (WV04)	Babcock State Park
West Virginia (WV05)	Cedar Creek State Park
West Virginia (WV28)	Parsons

controlled for the cyclical seasonal variability inherent in precipitation chemistry and volume. The trend model incorporated precipitation chemistry data that was summarized into 6, bi-monthly seasons for each year during the 1983 through 2005 trend analysis period. Concentrations were summarized as precipitation-weighted means. Seasonal deposition values were calculated from the corresponding seasonal precipitation-weighted mean concentration and the total seasonal precipitation volume.

The components of the model are as follows:

$$C_{ys} = b_0 + b_s + y_{by} + e$$

where, C_{ys} = estimated concentration or deposition during season, s, and year, y.
b_0 = estimated intercept of the linear model.
b_s = estimated shift in concentration or deposition during season, s, relative to the latest season (i.e., Nov-Dec).
y = date at the mid-point of the season, expressed as decimal years (e.g., the first season of 1994 would be 1994.0833).
b_y = estimated long-term linear trend in concentration or deposition.

Inferences on the direction and significance of long-term trends in concentration or deposition were based on the estimated value of b_y and on the F-statistic of the linear effect associated with b_y.

Units

The standard units used in this report are **mg/L** (milligrams per liter) or **µeq/L** (micro-equivalents per liter) for concentrations and **kg/ha** (kilograms/hectare) for wet deposition amounts. Conversion factors appear in Tables 5 and 6. Table 5 presents factors for converting among various deposition units and for converting ion concentrations to deposition amounts, given precipitation measurements in cm (centimeters). Table 6 presents factors to convert mass per unit volume to micro-moles or micro-equivalents per unit volume for direct elemental comparisons.

Summary Periods

For this report, the annual period started at 9:00 a.m. on 3 January 2006 and ended at 9:00 a.m. on 2 January 2007. The growing season (or warm period) started 28 March 2006 and ended 31 October 2006. The dormant season (or cold period) included precipitation samples collected from 3 January 2006 to 28 March 2006 and from 31 October 2006 to 2 January 2007. The annual and seasonal periods in this report are the same as those used in summarizing the 2006 atmospheric deposition data of the National Atmospheric Deposition Program/National Trends Network.

Table 5. Conversion factors for concentration and deposition units.

From	To	Multiply by
mg/m2	lb/ac	0.00892
mg/m2	kg/ha	10-2
mg/L	g/m2	10-2 x cm rainfall
mg/L	kg/ha	10-1 x cm rainfall
mg/L	lb/ac	0.0892 x cm rainfall

Appendices

A summary of weekly chemical analyses (mg/L) of all precipitation samples collected throughout Pennsylvania during 2006 appears in Appendix I. Weekly measured wet depositions (kg/ha) for each ion are summarized in Appendix II. Annual and seasonal mean concentration and wet deposition trends from 1982 through 2006 are given in Appendix III. Correlation coefficient matrices are given in Appendix IV. Micro-equivalent concentrations and ionic balances of weekly precipitation chemistry observations are given in Appendix V. Annual and seasonal concentration and wet deposition maps are shown in Appendix VI.

Table 6. Conversion factors from mass to micro-moles or micro-equivalents.

Ion	Ion as	Factor From mg/L to µmoles/L	Factor From mg/L to µeq/L
		Multiply by	Multiply by
Hydrogen	H^+	1000	1000
Calcium	Ca^{2+}	24.950	49.900
Magnesium	Mg^{2+}	41.144	82.287
Potassium	K^+	25.577	25.577
Sodium	Na^+	43.498	43.498
Ammonium	NH_4^+	55.473	55.438
Sulfate	SO_4^{2-}	10.410	20.821
Nitrate	NO_3^-	16.128	16.128
Chloride	Cl^-	28.206	28.216

2006 NETWORK PERFORMANCE

Catch Efficiency

The precipitation catch efficiency of the Aerochem Metrics precipitation sampler and the handling protocols of site operators were very good in 2006. On an annual basis, the amount of precipitation that arrived at the water quality lab (determined from the volume of precipitation in the wet-side bucket) as a ratio of the amount of precipitation measured in the standard non-recording rain gage varied from 0.80 at the Allegheny-Portage site in Cambria County to 0.97 at the Leading Ridge and Millersville NADP/NTN sites in Huntingdon and Lancaster counties (Table 7). A ratio of 1.0 indicates that 100% of the precipitation was collected by the sampler and that no precipitation was lost in transit to the lab. The annual network mean catch efficiency ratio was 0.90, with 8 of 17 sites having a catch efficiency ratio of 0.90 or higher. Considering that the Aerochem Metrics sampler, because of its design and aerodynamics, is less efficient in catching precipitation than a standard non-recording rain gage, the annual ratios are indicative of very good network performance. Studies comparing the sampler to a standard rain gage have shown that the sampler underestimates total annual precipitation by 5% to 10% of the rain gage measurement. Discrepancies between measured precipitation and the sampler's volume are also influenced by equipment failure (especially the sensor) and electrical outages.

The form of precipitation (rain versus snow) and site exposure also influence the catch efficiency of the Aerochem Metrics sampler. This is evident when comparing the ratios of the weekly bucket volumes to the standard non-recording rain gage amounts for warm and cold periods (Table 7). At all sites, except the Millersville NADP/NTN site in Lancaster County and the Little Pine site in Lycoming County, the sampler was more efficient during the warm period (28 March 2006 through 30 October 2006) when precipitation was dominated by rain than during the cold period (3 January 2006 to 28 March 2006 and 30 October 2006 to 2 January 2007) when precipitation frequently occurred as snow or ice. The network mean ratio during the warm period was 0.91 compared to 0.86 during the cold period. The lower ratios during the cold period reflect the sensor's sensitivity in detecting light, dry snow, as well as other problems associated with freezing conditions. The relatively low cold period catch efficiency at the Presque Isle site in Erie County and the Hills Creek site in Tioga County were caused by frequent weather related electrical failures at these sites.

Site exposure also affects the collection efficiency of the sampler. Where the Aerochem Metrics sampler is exposed (in an open field or on a ridge), as it is at M. K. Goddard State Park in Mercer County and the Allegheny Portage National Historic Site in Cambria County it is subject to higher wind velocities (which lowers catch efficiency) than samplers located at more protected (shielded) sites, such as the Leading Ridge and Young Women's Creek NADP/NTN sites. The Allegheny Portage site is also often subjected severe icing problems which can affect sampler performance.

Table 7. Precipitation catch efficiency of the Aerochem Metric precipitation sampler during 2006.

Monitoring Site	Ratio of Bucket Volume to Non-recording Raingage Amount[1] Annual	Warm Period[2]	Cold Period[3]
Western Pennsylvania			
Laurel Hill State Park	0.91	0.91	0.91
M. K. Goddard State Park	0.89	0.92	0.80
Crooked Creek Lake	0.84	0.85	0.80
Allegheny Portage N. R.	0.80	0.85	0.66
Presque Isle State Park	0.85	0.88	0.79
Kane - NADP	0.89	0.90	0.84
Central Pennsylvania			
Little Buffalo State Park	0.89	0.90	0.84
Hills Creek State Park	0.87	0.89	0.79
Little Pine State Park	0.91	0.90	0.92
Young Woman's Creek - NADP	0.94	0.95	0.91
Leading Ridge - NADP	0.97	0.97	0.97
Penn. State Univ. - NADP	0.91	0.91	0.90
Arendtsville - NADP	0.94	0.96	0.91
Eastern Pennsylvania			
Valley Forge National Park	0.90	0.92	0.84
Slocum State Park	0.88	0.88	0.87
Millersville - NADP	0.97	0.97	0.98
Milford - NADP	0.92	0.93	0.91
State Mean	0.90	0.91	0.86

[1] Ratio of volume of precipitation collected in wet bucket of Aerochem Metric Sampler as measured at the water quality lab to the amount of precipitation measured in the non-recording standard raingage.

[2] Warm Period: 28 March through 30 October 2006 represents the period when precipitation was primarily rain.

[3] Cold Period: 3 January through 27 March 2006 and 31 October 2006 through 2 January 2007 represent periods when precipitation was primarily snow and/or ice.

Sampling Frequency

The maximum number of valid precipitation samples that could have been collected by the Pennsylvania Atmospheric Deposition Monitoring Network during 2006 was 884 (Table 8). Since 47 of these sampling periods were without precipitation, the maximum number of potential samples available for complete or partial analysis was 837. Of this number, 723 samples (86.4%) contained sufficient volume for complete analysis. Of the 93 sampling periods with precipitation but no analyses, 25 samples involved precipitation amounts of 0.05 inch or less. Failure of the Aerochem Metrics sampler to detect and sample low intensity snow or rainfall accounts for many of the samples that contain insufficient volume for analysis.

The Millersville site in Lancaster County and the Slocum State Park site in Luzerne County collected the lowest number of samples (34 and 37, respectively) with complete analyses. At the Millersville NADP/NTN site, QA/QC procedures coded 5 of the 18 samples with precipitation but no analyses as "contaminated" with varies forms of materials, most noticeably bird droppings. These samples were so badly contaminated that all chemical analyses were omitted from all summary statistics for this site. In addition, 7 samples were coded as trace samples with insufficient volumes for analyses while two samples were identified as "undefined samples" meaning the samples may have been exposed to dry deposition during the course of the week and thus treated as potentially contaminated samples. A similar situation existed at the Arendtsville site in Adams County where 9 of the 14 samples without analyses were coded as trace samples while two samples were identified as contaminated. At Young Women's Creek in Clinton County 8 of 14 samples with no analyses were coded at trace samples while at the Kane site in Elk County 7 of the 11 samples with no analyses were thus identified. The greatest number of samples with volumes large enough to permit complete analyses was collected at Laurel Hill State Park in Somerset County (49); the second largest number of samples (47) was collected at the Penn State NADP/NTN site in Centre County. The number of measurements in 2006 by site and parameter is given in Table 8.

Percentage of Annual Precipitation Analyzed

Another means of evaluating network performance is to compare the percentage of annual precipitation that was analyzed with the total volume of measured precipitation at each site. Such a comparison is given in Table 9 for each precipitation quality parameter. Because of the previously discussed sample contamination problems at sites such as the Millersville NADP/NTN site, less than 94% of the mean annual precipitation in Pennsylvania was analyzed for pH in 2006. This network-wide average is obviously distorted by the nearly 25% of the annual precipitation that was lost at Slocum State Park, the nearly 13% lost at the Little Buffalo site, and the nearly 11% lost at Crooked Creek Lake. Sample contamination accounted for nearly all of the unanalyzed precipitation at the Slocum site, including one 6.75-inch sample. At Little Buffalo, three samples totaling 5.50 inches were discarded due to contamination problems while at Crooked Creek Lake contamination accounted for 5.25 inches (9.6%) of the unanalyzed volume. Power outages also accounted for some of the lost sample volumes at Millersville (3.12 inches, 6.4%). On an individual site basis, excluding the three sites with severe contamination

Table 8. Number of precipitation quality measurements in Pennsylvania in 2006 by site and quality parameter.

Region/ Site Name	Maximum Number of Samples	Number of Measurements of Each Parameter											No. of Samples with Complete Analyses	No. of Samples with Partial Analyses	No. of Sample Periods with no Analyses	No. of Sample Periods with no Precip.
		pH	Conduct- ance	SO_4	NO_3	Cl	NH_4	Ca	Mg	K	Na	Sum				
Western Pennsylvania																
M. K. Goddard	52	49	49	46	46	46	46	46	46	46	46	466	46	3	3	2
Crooked Creek	52	43	43	42	42	42	42	42	42	42	42	422	42	1	9	4
Laurel Hill	52	51	51	49	49	49	49	49	49	49	49	494	49	2	1	0
Allegheny Portage	52	43	43	42	42	42	42	42	42	42	42	422	42	1	9	2
Presque Isle	52	48	47	46	46	46	46	46	46	46	46	463	46	2	4	2
Kane-NADP	52	41	41	41	41	41	40	41	41	41	41	409	40	1	11	1
Central Pennsylvania																
Little Pine	52	46	46	45	45	45	45	45	45	45	45	452	45	1	6	3
Hills Creek	52	46	47	45	45	45	45	45	45	45	45	453	45	2	5	3
Little Buffalo	52	45	45	43	43	43	43	43	43	43	43	434	43	2	7	2
Penn State-NADP	52	47	47	47	47	47	47	47	47	47	47	470	47	0	5	2
Leading Ridge-NADP	52	47	47	47	47	47	46	47	47	47	47	469	46	1	5	1
Arendtsville-NADP	52	38	38	38	38	38	38	38	38	38	38	380	38	0	14	6
Y. Woman Creek-NADP	52	38	38	38	38	38	38	38	38	38	38	380	38	0	14	3
Eastern Pennsylvania																
Slocum	52	39	39	37	37	37	37	37	37	37	37	374	37	2	13	3
Valley Forge	52	45	44	44	44	44	44	44	44	44	44	441	44	1	7	4
Millersville-NADP	52	34	34	34	34	34	34	34	34	34	34	340	34	0	18	5
Milford-NADP	52	43	43	43	43	43	41	43	43	43	43	428	41	2	9	4
State Sum*	884	743	742	727	727	727	723	727	727	727	727	7297	723	21	140	47

Table 9. Annual and seasonal distribution of precipitation in Pennsylvania during 2006 and the percent of annual precipitation not analyzed.

Region and Site Name	Measured Precipitation (Inches)			Percent of Annual Precipitation Not Analyzed									
	Annual	Growing Season	Dormant Season	pH	SO_4	NO_3	NH_4	Cl	Cond	Ca	Mg	Na	K
Western Pennsylvania													
M. K. Goddard	52.83	38.08	14.75	0.02	0.42	0.42	0.42	0.42	0.02	0.42	0.42	0.42	0.42
Crooked Creek	54.84	38.36	16.48	10.72	11.11	11.11	11.11	11.11	10.72	11.11	11.11	11.11	11.11
Laurel Hill	46.20	27.54	18.66	4.78	4.96	4.96	4.96	4.96	4.78	4.96	4.96	4.96	4.96
Allegheny Portage	47.90	29.83	18.07	5.32	6.49	6.49	6.49	6.49	5.32	6.49	6.49	6.49	6.49
Presque Isle	45.00	28.80	16.20	0.40	0.58	0.58	0.58	0.58	0.42	0.58	0.58	0.58	0.58
Kane-NADP	60.64	41.77	18.87	7.48	7.48	7.48	11.76	7.48	7.48	7.48	7.48	7.48	7.48
Central Pennsylvania													
Little Pine	40.18	25.75	14.43	2.31	2.51	2.51	2.51	2.51	2.31	2.51	2.51	2.51	2.51
Hills Creek	41.93	29.02	12.91	1.60	1.91	1.91	1.91	1.91	1.48	1.91	1.91	1.91	1.91
Little Buffalo	45.28	27.50	17.78	12.90	12.96	12.96	12.96	12.96	12.90	12.96	12.96	12.96	12.96
Penn State-NADP	39.73	24.83	14.90	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28	2.28
Leading Ridge-NADP	37.77	22.65	15.12	6.38	6.38	6.38	13.19	6.38	6.38	6.38	6.38	6.38	6.38
Arendtsville-NADP	40.01	22.95	17.05	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38	3.38
Y. Woman Creek-NADP	43.98	28.50	15.48	9.64	9.64	9.64	9.64	9.64	9.64	9.64	9.64	9.64	9.64
Eastern Pennsylvania													
Slocum	53.00	33.96	19.04	25.43	25.85	25.85	25.85	25.85	25.43	25.85	25.85	25.85	25.85
Valley Forge	55.04	35.24	19.80	3.69	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Milford-NADP	53.09	31.58	21.51	4.48	4.48	4.48	5.59	4.48	4.48	4.48	4.48	4.48	4.48
Millersville-NADP	48.65	28.93	19.72	11.30	11.30	11.30	11.30	11.30	11.30	11.30	11.30	11.30	11.30
State Mean	47.42	30.31	17.10	6.60	6.81	6.81	7.52	6.81	6.61	6.81	6.81	6.81	6.81

problems, the percentage varied from 99.8% at the M. K. Goddard State Park site in Mercer County to approximately 90% at the Young Women's Creek NADP/NTN site in Clinton County which also reported contamination problems for part of the year. Despite the contamination problems, the network still analyzed approximately 93% of the annual precipitation for sulfate, nitrate, chloride, and ammonium concentrations in 2006 and a similar amount for the base cations (calcium, magnesium, potassium, and sodium) concentrations. The percent of precipitation analyzed for these parameters at individual sites varied from nearly 100% at the M.K. Goddard and Presque Isle sites to approximately 90% at the Young Women's Creek and Kane NADP/NTN sites (Table 9).

Quality Control/Quality Assurance

The distribution of precipitation samples having "flagged" cation/anion balances (ratios <0.85 or >1.15) among intervals of precipitation volume, specific conductance, and total ionic strength for all valid samples collected at the 17 atmospheric deposition monitoring sites in Pennsylvania in 2006 is shown in Table 10. About 94% of the samples with complete analyses were within the specified cation/anion criterion. Of the 47 samples that were flagged, 26% (12 samples) of them were from low volume storms (<0.3 inch), while another 13% (6 samples) were from storms that fell into the 0.3 inch to 0.5 inch range. Collectively, this group of 18 samples represented approximately 0.5% of the total volume of precipitation measured in Pennsylvania in 2006 (Table 10). Nineteen percent of the "flagged" samples were from storms ranging in size from 0.5 inch to 1.0 inch. This group of nine samples represented 0.9% of the total volume of precipitation measured in the state in 2006. Overall, the analyses of samples from 93.5% of the precipitation collected in the state met the cation/anion criterion. It should be noted that failure to meet the cation/anion criterion does not in itself mean that the analytical results for these samples are in error. The list of cations and anions that are measured represents the major ions found in precipitation. However, other ions, such as phosphorous, may be present, and if present would affect the ionic strength and subsequently the cation/anion balance. Furthermore, samples with low ionic strength and low specific conductance are more likely to be flagged than higher ionic strength samples.

Inter-laboratory Comparisons

A summary of analytical results from three inter-laboratory comparison studies of water samples submitted to the water quality lab at The Penn State Institutes of Energy and the Environment in 2006 are shown in Tables 11, 11a, and 11b. Overall, the Penn State water lab compared favorably with other labs participating in the inter-laboratory comparisons, although a number of potential problems were detected and corrected as a result of the external audits. The audits were conducted by the National Water Research Institute in Ontario, Canada. In all of these audits, the "expected value" was the mean concentration of all the labs participating in the comparison minus the results from those samples with coded or flagged results. Samples are flagged, if the reported results are greater than or less than two times the standard deviation of the reported results from all participating labs.

Table 10. Distribution of precipitation samples having "flagged" cation:anion balances (ratios < 0.85 or > 1.15) among intervals of precipitation volume, specific conductance, and total ionic strength for valid samples collected at 17 sites in Pennsylvania during 2006. Only those observations having complete chemical analyses were included.

Parameter and Interval	# of Obs.	Percent (#) of Obs. with cation:anion ratios < 0.85 or > 1.15	Distribution of precip. vol. by interval (%) $(100.0*v_i/v_t)$	Vol. of flagged precip. by interval as a % of total precip. vol. $(100.0*x_i/v_t)$	Distribution of flagged precip. vol. by interval (%) $(100.0*x_i/x_t)$	Percent of precip. vol. that was flagged by interval (%) $(100.0*x_i/v_i)$
Precip. (Inches)						
0.0 - 0.3	161	7.5 (12)	3.4	0.2	3.6	6.9
0.3 - 0.5	111	5.4 (6)	5.8	0.3	4.6	5.2
0.5 - 1.0	162	5.6 (9)	15.3	0.9	13.4	5.8
1.0 - 1.5	113	5.3 (6)	18.4	1.0	15.3	5.5
1.5 - 2.0	73	9.6 (7)	17.2	1.7	26.5	10.1
2.0 - 2.5	39	10.3 (4)	11.5	1.1	17.4	10.0
2.5+	64	4.7 (3)	28.4	1.3	19.2	4.4
Conductance (µS/cm)						
0 - 16	213	14.5 (26)	38.5	4.6	70.5	12.0
16 - 32	325	3.9 (14)	46.3	1.5	23.3	3.3
32 - 48	110	3.4 (4)	11.5	0.3	5.0	2.9
48 - 64	41	4.7 (2)	2.8	0.0	0.6	1.5
64 - 80	16	5.9 (1)	0.7	0.0	0.6	5.2
80+	8	0.0 (0)	0.2	0.0	0.0	0.0
Total Ionic Strength						
0 - 100	207	8.9 (14)	35.6	2.9	44.4	8.2
100 - 200	293	6.4 (21)	47.0	2.7	40.7	5.7
200 - 300	137	3.3 (5)	12.8	0.7	10.6	5.5
300 - 400	44	7.1 (4)	3.4	0.2	3.0	5.8
400 - 500	17	9.5 (2)	0.8	0.1	1.1	8.4
500+	15	9.1 (1)	0.3	0.0	0.1	2.8

v_i = volume of precipitation samples for the given interval, summed over all sites.
v_t = total volume of precipitation samples for 2006, summed over all intervals and sites.
x_i = volume of flagged precipitation samples for the given interval, summed over all sites.
x_t = total volume of flagged precipitation samples for 2006, summed over all intervals and sites.

Table 11. Results of inter-laboratory analyses of water samples submitted to the water quality lab at Penn State's Institutes of Energy and the Environment. The expected value is the mean of all of labs participating in the comparison minus those with coded or flagged results. Samples were submitted January 2006.

Audit	pH[1]	Sulfate[2]	Nitrate[3]	Chloride[4]	Potassium[5]
Sample	Reported-Mean	Reported-Mean	Reported-Mean	Reported-Mean	Reported-Mean
1	4.67-4.65	1.29-1.31	0.261-0.257	0.278-0.300	0.02-0.031
2	4.86-4.90	1.72-1.72	0.231-0.227	2.070-2.055	0.18-0.132
3	5.52-5.63	2.32-2.34	0.073-0.060	4.710-4.740	0.37-0.303
4	5.26-5.26	2.40-2.44	0.006-0.004	5.980-5.880	0.31-0.225
5	6.37-6.42	1.51-1.50	0.468-0.475	0.117-0.130	0.04-0.023
6	6.73-6.82	4.87-4.88	0.089-0.076	1.720-1.740	0.55-0.523
7	6.85-6.90	1.94-1.95	0.474-0.477	0.177-0.201	0.20-0.178
8	6.92-6.95	4.12-4.10	0.623-0.610	0.520-0.555	0.20-0.170
9	6.97-6.97	2.47-2.51	0.066-0.050	0.589-0.647	0.40-0.361
10	7.11-7.11	4.64-4.53	0.173-0.167	0.826-0.852	0.46-0.454

[1] Mean difference −0.035 pH unit. All values within range of expected values. No analytical bias.

[2] Mean difference +0.00 mg/L. All values within range of expected values. No analytical bias.

[3] Mean difference +0.006 mg/L. Samples #3, #6, and #9 flagged high. No analytical bias.

[4] Mean difference −0.01 mg/L. All values within range of expected values. No analytical bias.

[5] Mean difference +0.03 mg/L. Samples #2, #3, #4 and #5 flagged high, sample #1 flagged low. Possible high analytical bias indicated.

Table 11. Continued.

Audit	Calcium[6]	Magnesium[7]	Sodium[8]	Ammonium[9]
Sample	Reported-Mean	Reported-Mean	Reported-Mean	Reported-Mean
1	0.14-0.12	0.04-0.04	0.16-0.17	0.129-0.120
2	0.34-0.34	0.20-0.20	1.25-1.37	0.039-0.005
3	0.79-0.82	0.38-0.40	2.65-2.93	0.019-0.007
4	0.80-0.85	0.46-0.46	3.35-3.79	0.043-0.027
5	1.55-1.59	0.29-0.28	0.05-0.05	0.021-0.005
6	2.42-2.55	0.60-0.62	2.12-2.27	0.059-0.042
7	2.86-2.83	0.58-0.58	0.12-0.11	0.021-0.006
8	2.78-2.78	1.03-1.07	0.29-0.30	0.428-0.410
9	2.49-2.66	0.44-0.46	1.35-1.40	0.035-0.024
10	4.26-4.53	0.80-0.85	1.01-1.07	0.036-0.006

[6] Mean difference −0.06 mg/L. All values within range of expected values. No analytical bias.

[7] Mean difference −0.01 mg/L. All values within range of expected values. No analytical bias.

[8] Mean difference −0.11 mg/L. Sample #4 flagged low. No analytical bias.

[9] Mean difference +0.02 mg/L. Six of 10 samples flagged high. High analytical bias indicated.

Table 11a. Results of inter-laboratory analyses of water samples submitted to the water quality lab at Penn State's Institutes Energy and the Environment. The expected value is the mean of all of labs participating in the comparison minus those with coded or flagged results. Samples were submitted June 2006.

Audit	pH[1]	Sulfate[2]	Nitrate[3]	Chloride[4]	Potassium[5]
Sample	Reported-Mean	Reported-Mean	Reported-Mean	Reported-Mean	Reported-Mean
1	4.52-4.48	5.84-5.68	2.52-2.260	0.557-0.580	0.22-0.160
2	4.51-4.54	5.14-5.04	2.16-1.960	0.499-0.520	0.36-0.280
3	4.81-4.90	1.28-1.28	0.26-0.260	0.200-0.222	0.12-0.026
4	5.35-5.45	7.26-7.02	0.08-0.065	0.718-0.740	0.32-0.199
5	7.11-7.03	3.03-3.03	0.09-0.078	1.610-1.600	0.33-0.219
6	6.72-6.45	2.70-2.70	0.74-0.740	0.397-0.420	0.19-0.060
7	6.74-6.65	4.67-4.62	1.20-1.150	0.715-0.750	0.26-0.160
8	5.21-4.90	2.07-2.10	0.35-0.350	0.122-0.140	0.12-0.024
9	6.24-6.54	5.90-5.82	0.10-0.092	4.270-3.880	0.46-0.339
10	6.55-6.87	3.86-3.86	0.18-0.176	2.160-2.160	0.47-0.352

[1] Mean difference −0.005 pH unit. Samples #6 and #8 flagged high; samples #9 and #10 flagged low. No analytical bias indicated.

[2] Mean difference +0.06 mg/L. All values within range of expected values. No analytical.

[3] Mean difference +0.055 mg/L. Samples #1 and #2 flagged high. Possible high analytical bias indicated.

[4] Mean difference +0.023 mg/L. Sample #9 flagged high. No analytical bias.

[5] Mean difference +0.10 mg/L. All samples flagged high. High analytical bias indicated.

Table 11a. Continued.

Audit	Calcium[6]	Magnesium[7]	Sodium[8]	Ammonium[9]
Sample	Reported-Mean	Reported-Mean	Reported-Mean	Reported-Mean
1	2.72-2.85	0.97-1.00	0.33-0.30	0.196-0.185
2	2.75-2.88	0.63-0.66	0.22-0.15	0.220-0.213
3	0.17-0.19	0.03-0.04	0.22-0.18	0.240-0.240
4	2.09-2.16	0.53-0.55	0.81-0.79	0.007-0.003
5	3.24-3.34	0.71-0.73	1.58-1.60	0.007-0.005
6	1.79-1.92	0.53-0.56	0.29-0.22	0.007-0.001
7	3.18-3.26	0.90-0.92	0.41-0.39	0.007-0.002
8	0.67-0.70	0.16-0.16	0.11-0.06	0.093-0.089
9	2.40-2.51	0.60-0.61	2.62-2.70	0.048-0.048
10	2.81-2.98	0.53-0.55	2.02-2.01	0.007-0.006

[6] Mean difference −0.10 mg/L. All values within range of expected values. Possible low analytical bias indicated.

[7] Mean difference −0.02 mg/L. All values within range of expected values. No analytical bias.

[8] Mean difference +0.02 mg/L. Samples #1, #2, #3, #6, and #8 flagged High. Possible high analytical bias indicated.

[9] Mean difference +0.004 mg/L. All values within range of expected values. No analytical bias.

Table 11b. Results of inter-laboratory analyses of water samples submitted to the water quality lab at Penn State's Institutes of Energy and the Environment. The expected value is the mean of all of labs participating in the comparison minus those with coded or flagged results. Samples were submitted December 2006.

Audit Sample	pH[1] Reported-Mean	Sulfate[2] Reported-Mean	Nitrate[3] Reported-Mean	Chloride[4] Reported-Mean	Potassium[5] Reported-Mean
1	4.99-4.84	1.61-1.62	0.244-0.242	0.143-0.143	0.04-0.032
2	4.63-4.58	3.16-3.17	1.320-1.285	0.302-0.310	0.10-0.103
3	5.91-6.33	7.09-6.83	0.623-0.630	0.441-0.490	0.21-0.200
4	6.66-6.92	3.33-3.33	0.235-0.235	0.893-0.961	0.38-0.360
5	6.64-6.84	6.38-6.15	0.098-0.086	3.130-3.160	0.46-0.438
6	6.72-6.89	2.11-2.10	0.226-0.224	-------------	0.44-0.390
7	6.50-6.50	1.49-1.50	0.451-0.470	0.128-0.130	0.04-0.025
8	6.53-6.50	1.92-1.94	0.006-0.006	-------------	0.31-0.294
9	5.59-5.33	2.31-2.30	0.051-0.033	-------------	0.24-0.220
10	5.86-5.98	5.18-5.10	0.184-0.180	0.423-0.460	0.35-0.330

[1] Mean difference −0.07 pH unit. Sample #3 flagged low, #9 flagged high. No analytical bias indicated.

[2] Mean difference +0.05 mg/L. All values within range of expected vales. No analytical bias indicated.

[3] Mean difference +0.05 mg/L. Sample #2 flagged high. No analytical bias indicated.

[4] Mean difference −0.028 mg/L. Samples #3 and #10 flagged low. No analytical bias indicated.

[5] Mean difference +0.02 mg/L. Sample #6 flagged high. No analytical bias indicated.

Table 11b. Continued.

Audit Sample	Calcium[6] Reported-Mean	Magnesium[7] Reported-Mean	Sodium[8] Reported-Mean	Ammonium[9] Reported-Mean
1	0.29-0.28	0.07-0.07	0.07-0.07	0.191-0.226
2	1.97-1.82	0.45-0.46	0.06-0.06	0.030-0.031
3	3.00-2.85	0.83-0.84	0.32-0.33	0.007-0.044
4	2.31-3.07	0.41-0.43	1.42-1.48	0.007-0.006
5	2.82-3.08	0.88-0.89	2.16-2.30	0.021-0.031
6	2.60-2.95	0.67-0.67	3.63-4.00	0.007-0.004
7	1.70-1.60	0.28-0.28	0.07-0.05	0.007-0.001
8	0.89-1.38	0.47-0.49	2.84-3.10	0.007-0.016
9	0.43-0.74	0.42-0.44	2.80-3.02	0.007-0.020
10	1.43-2.01	0.30-0.33	0.71-0.73	0.007-0.025

[6] Mean difference −0.23 mg/L. Sample #2 flagged high; samples #4, 6, 8, 9, and 10 flagged low. Low analytical bias indicated.

[7] Mean difference −0.01 mg/L. All values within range of expected values. No analytical bias indicated.

[8] Mean difference −0.11 mg/L. Samples #6, 8, and 9 flagged low. No analytical bias indicated.

[9] Mean difference −0.011 mg/L. Samples #1, 3, and 10 flagged low. No analytical bias indicated.

The mean difference in pH between reported and expected values for the three audits (30 samples) was -0.035 pH unit. The results from individual samples varied from -0.42 to +0.31 pH unit. Seven of the 30 samples were flagged, four low and three high. Four of the flagged samples occurred during the June audit. If these samples were eliminated from the mean difference calculations, the mean difference would be -0.037 pH unit. The results from all three performance audits indicate that no systematic or laboratory biases for pH existed at the Penn State lab during 2006. Although relatively large pH differences were detected for some samples, all of the flagged results were from samples with pH values that were higher than those normally found in precipitation samples collected in Pennsylvania.

The mean difference in sulfate concentrations between expected and reported values for all three audits was +0.038 mg/L. Results from individual samples varied from -0.04 mg/L to +0.26 mg/L. None of the results of the 30 audit samples were flagged. The results from all three performance audits indicate that no systematic or laboratory biases for sulfate existed at the Penn State lab during 2006.

The mean difference in nitrate concentrations between expected and reported values for all three audits was +0.022 mg/L. Results from individual samples varied from -0.02 mg/L to +0.26 mg/L. Results from 6 of the 30 audit samples were flagged, all high. If these samples were eliminated from the mean difference calculations, the mean difference would be +0.005. The results from all performance audits indicate that no systematic or laboratory biases for nitrate existed at the Penn State lab during 2006.

The mean difference in ammonium concentrations between expected and reported values for all three audits was +0.004 mg/L. Results from individual samples varied from -0.037 mg/L to +0.034 mg/L. Results from 6 of the 30 audit samples were flagged high while 3 were flagged low. The majority (7 of 9) of the flagged samples were for samples with very low concentrations (i.e., <0.05 mg/L). The results from all three audits indicate that a high analytical bias for ammonium measurements existed at the Penn State in January 2006 and that the bias was corrected. There were no analytical biases indicated for the June and December audit samples.

Chloride analyses were generally lower than the expected values, although the mean difference was only -0.001 mg/L largely because one sample was above the expected value by 0.39 mg/L which offset the 21 samples that had lower than expected values. The sample in question had a much higher concentration (3.88 mg/L) than normally encountered in precipitation in the state. If this sample was removed from the calculations, the mean difference of the remaining samples is -0.018 mg/L, with only two samples being flagged as unacceptable. Results from individual samples varied from -0.049 mg/L to +0.39 mg/L. The results from all three performance audits indicate no systematic or laboratory biases for chloride existed at the Penn State lab during 2006.

Potassium analyses produced mixed results. The mean difference for all the inter-lab comparison samples was +0.05 mg/L. Results from individual samples varied from -0.011 mg/L to +0.121 mg/L. Of the 30 audit samples, the results from 14 samples were flagged high while one sample was flagged low. A high analytical bias was indicated for the June audit; however, the January and December audits did not find any analytical bias for potassium measurements at the Penn State lab.

Calcium analyses were generally lower than the expected values (mean difference -0.13 mg/L), with the results from 6 of the 30 audit samples being flagged low, all of which occurred during the December audit. Results from individual samples varied from -0.58 mg/L to +0.15 mg/L. The majority of the mean difference in the audit samples was attributable to samples where the expected concentration was 2.0 mg/L or higher. Such concentrations are much higher than generally encountered in precipitation in Pennsylvania. The results from all three performance audits indicate no consistent laboratory bias for calcium measurements at the Penn State lab during 2006; however, 22 of the 30 audit samples were lower than expected and the June audit did detect a low analytical bias, with the results from 6 of the 10 audit samples being below acceptable levels.

The mean difference in magnesium concentrations between expected and reported values for all three audits was -0.015 mg/L. Results from individual samples varied from -0.05 mg/L to +0.01 mg/L and were flagged as unacceptable. The results from all three performance audits indicate that no systematic or laboratory biases for magnesium existed at the Penn State lab during 2006.

The mean difference in sodium concentrations between expected and reported values for all three audits was -0.065 mg/L. Results from individual samples varied from -0.44 mg/L to +0.07 mg/L. Results from 9 of the 30 samples were flagged, with 3 samples having lower than expected concentrations while 6 were higher than expected. Most of the samples that were flagged had expected concentrations above 2.0 mg/L. Such concentrations are generally much higher than normally encountered in precipitation in Pennsylvania. The results from all three performance audits were mixed and although no consistent analytical biases for sodium was found in 2006, the lab generally reported lower concentrations than expected for the majority of the audit samples.

Although results from some of the inter-laboratory performance audits were above or below expected values and were flagged as unacceptable and that analytical biases were indicated for some analytes, poor lab performance for some of the analytes may be the result of inappropriate calibration of the instruments for the range of concentrations found in the audit samples. Most analytical equipment has an optimum range of concentrations for which the instrument is calibrated. When concentrations are encountered that lie outside this range, it is standard laboratory procedure to re-calibrate the instrument and repeat the analyses. Since the actual concentrations of audit samples are unknown, re-calibration and re-analysis is not possible. Consequently, if poor lab performance in the inter-laboratory comparisons is a result of inappropriate calibration of the instruments for the range of concentrations in the audit samples, then the concentration data for all 2006 precipitation samples are less likely to be biased. In fact, other quality control and quality assurance procedures support this position. The cation/anion and conductive balances do not indicate any consistent problem. Nor do other statistical measures that are used to routinely screen data to detect and eliminate potential bias or questionable results.

EXECUTIVE SUMMARY
2006 PRECIPITATION CHEMISTRY AND WET DEPOSITION

A wet atmospheric deposition monitoring network was established in Pennsylvania in 1981 to determine the magnitude and distribution of acidic and nutrient elements in precipitation, to assess their potential environmental impacts, and to evaluate the effectiveness of current and future legislation designed to reduce acidic and nutrient deposition in the Commonwealth. Results from the 24th full-year of operation of this network are summarized in this report. Included in this summary are data from seven National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites and 10 sites supported by The Pennsylvania Department of Environmental Protection (DEP), Bureau of Air Quality Control (BAQC). One of the NADP/NTN sites is also supported by the BAQC. Additional information on atmospheric deposition monitoring in Pennsylvania and the United States can be obtained over the World Wide Web at http://www.dep.state.pa.us and http://nadp.sws.uiuc.edu.

Hydrogen Ion (H^+ as pH). The 2006 statewide mean annual pH (4.46) was the same as in 2005 and the highest pH (lowest acidity) measured in Pennsylvania since monitoring began in 1981 (Table 12). The hydrogen ion concentration (measured as pH) of precipitation in Pennsylvania has declined approximately 51% (40.0 μeq/L) over the last 24 years (Table 13). The decline in "acid rain" has been attributed to reductions in sulfur dioxide and nitrogen oxides emissions and to a much lesser extent increasing base cation and ammonium concentrations in some regions of the state (Lynch et al., 2007). Seasonal pH values in 2006 were very similar; the statewide mean growing season and dormant season pH was 4.43 and 4.51, respectively. Regional differences were also quite small (Table 12), with the highest pH values (lowest acidity) occurring in the eastern third of the state and the lowest pH values occurring in the central portion of Pennsylvania, although the mean difference between central and western Pennsylvania was very small. Despite the decrease in acidity, precipitation in the Commonwealth is still more acidic than nearly all other regions of the United States based on NADP/NTN data shown in Figure 2. Only three sites in the NADP/NTN, one in Ohio and two in West Virginia, recorded mean annual pH values in 2006 that were equal to or lower than the mean annual pH across most of Pennsylvania.

Sulfate (SO_4^{2-}). Sulfate concentrations have decreased approximately 39% (25.1 μeq/L) since 1983 (Table 13). The statewide mean annual sulfate concentration in 2006 was 2.034 mg/L (Table 14). Mean annual sulfate concentrations in 2006 were higher than in 2005 and generally higher than any year since 2002. Higher sulfate concentrations were observed at all sites, except the Millersville and Arendtsville NADP/NTN sites in south central Pennsylvania, with the largest increases reported in central and eastern Pennsylvania. Most of the increase in annual sulfate concentrations resulted from substantially higher concentrations during the dormant season, which averaged 1.717 mg/L across the state. Mean dormant season sulfate concentrations in 2006 were generally higher than values reported since 2001, except at Hills Creek (Tioga County) Little Pine (Lycoming County), and Leading Ridge (Huntingdon County)

Table 12. Annual and seasonal hydrogen ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

	Volume Weighted Mean pH			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
Region/Site	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	4.45	4.45	4.44	0.48	0.34	0.14	52.82	38.08	14.74	0.01	0.00	0.01
CROOKCRK	4.40	4.38	4.44	0.57	0.41	0.15	48.96	33.05	15.91	5.88	5.31	0.57
LAURHILL	4.39	4.33	4.50	0.49	0.33	0.15	43.99	25.33	18.66	2.21	2.21	0.00
ALLEPORT	4.42	4.40	4.46	0.47	0.31	0.16	45.35	28.66	16.69	2.55	1.17	1.38
PRESQISL	4.46	4.44	4.50	0.40	0.27	0.13	44.82	28.80	16.02	0.18	0.00	0.18
KANE	4.42	4.42	4.42	0.59	0.41	0.18	56.10	40.97	15.13	4.54	0.80	3.74
Region Mean	4.42	4.40	4.46	0.50	0.35	0.15	48.67	32.48	16.19	2.56	1.58	0.98
Central Pennsylvania												
LITTPINE	4.39	4.45	4.29	0.42	0.23	0.19	39.25	24.82	14.43	0.93	0.93	0.00
HILLSCRK	4.43	4.39	4.53	0.40	0.30	0.10	41.26	28.43	12.83	0.67	0.59	0.08
LITTBUFF	4.49	4.46	4.53	0.38	0.24	0.13	39.44	24.15	15.29	5.84	3.35	2.49
PSUNADP	4.39	4.36	4.44	0.41	0.28	0.14	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	4.38	4.34	4.45	0.40	0.27	0.14	35.36	21.72	13.64	2.41	0.93	1.48
YOWOCRK	4.39	4.37	4.42	0.46	0.31	0.15	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	4.50	4.50	4.49	0.33	0.19	0.14	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	4.42	4.41	4.45	0.40	0.26	0.14	38.93	24.54	14.40	2.34	1.35	0.99
Eastern Pennsylvania												
SLOCUM	4.56	4.55	4.58	0.37	0.24	0.13	39.52	24.10	15.42	13.48	9.86	3.62
VALLFORG	4.51	4.46	4.61	0.43	0.31	0.12	53.01	33.28	19.73	2.03	1.96	0.07
MILLERSV	4.66	4.56	4.90	0.27	0.20	0.06	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	4.51	4.47	4.57	0.42	0.27	0.15	50.71	29.63	21.08	2.38	1.95	0.43
Region Mean	4.56	4.51	4.67	0.37	0.26	0.12	46.60	28.53	18.07	5.85	3.90	1.95
State Mean	4.46	4.43	4.51	0.43	0.29	0.14	44.17	28.28	15.89	3.24	2.03	1.21

Table 13. Estimated changes in concentrations of individual ions in precipitation from 1983 to 2006.

	Hydrogen Ion		Sulfate		Nitrate		Chloride	
Site	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change
CROOKCRK	-53.751*	-53.543	-29.224*	-37.652	-13.332*	-34.542	-2.008*	-24.907
GODDARD	-43.289*	-51.649	-26.951*	-38.701	-12.530*	-33.181	0.839	17.039
HILLSCRK	-30.924*	-45.121	-18.145*	-33.374	-10.030*	-31.634	0.066	1.479
LAURHILL	-47.776*	-55.178	-31.913*	-45.594	-11.650*	-34.560	-0.321	-6.098
LITTBUFF	-41.332*	-51.773	-20.422*	-32.600	-10.649*	-30.169	-0.072	-1.103
SLOCUM	-33.984*	-47.191	-16.440*	-29.164	-6.384*	-20.254	0.465	8.842
VALLFORG	-34.004*	-50.879	-23.712*	-40.504	-9.080*	-29.966	-4.603*	-38.113
LITTPINE	-49.636*	-56.587	-24.822*	-39.198	-15.928*	-41.323	1.799*	39.044
PSUNADP	-36.246*	-48.267	-26.295*	-40.772	-12.866*	-38.075	-1.985*	-38.618
KANE	-37.701*	-49.567	-27.043*	-41.215	-11.225*	-34.166	-2.216*	-46.543
LEADRIDG	-29.403*	-41.757	-20.338*	-33.549	-9.246*	-28.069	-2.031*	-38.905
MILFORD	-35.698*	-53.291	-27.145*	-49.232	-12.167*	-38.576	-2.158*	-31.364
Mean[1]	-39.978	-50.692	-25.092	-39.308	-11.700	-34.024	-1.154	-15.281

* $p<0.05$

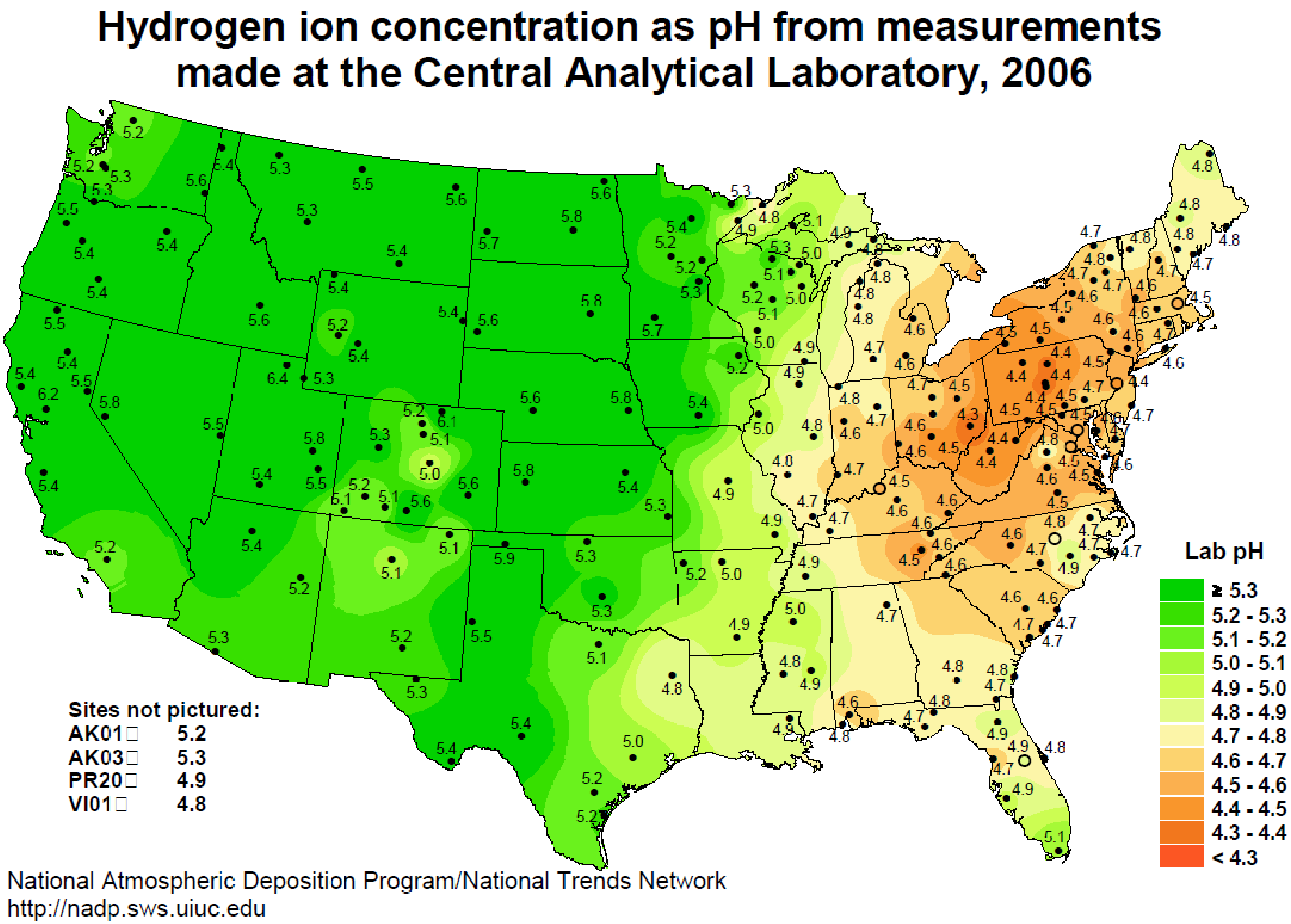
[1] Changes for Slocum State Park were excluded from calculation of the mean because of a malfunction of the Aerochemetric sampler unit from 22 September 2005 through 3 January 2006.

Table 13 (continued).

Site	Ammonium		Calcium		Magnesium		Potassium		Sodium	
	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change
CROOKCRK	0.458	2.640	-1.585	-18.819	-0.908*	-32.054	0.551*	79.777	1.033*	55.640
GODDARD	0.692	3.602	-2.446*	-26.830	-1.128*	-37.987	0.826*	144.282	1.253*	64.936
HILLSCRK	2.496	19.119	-0.736	-14.196	-0.579*	-28.284	1.041*	215.474	1.584*	114.384
LAURHILL	-1.502	-9.072	-0.856	-13.830	-0.912*	-40.034	0.659*	88.737	1.419*	84.619
LITTBUFF	1.412	7.225	-1.678*	-24.556	-0.655*	-25.255	0.982*	151.105	1.376*	46.476
SLOCUM	8.428*	63.220	0.514	11.272	-0.493	-23.075	1.005*	156.786	0.933	33.506
VALLFORG	2.175	13.989	-2.218*	-33.866	-3.821*	-65.690	0.814*	125.309	-2.877*	-34.744
LITTPINE	2.295	14.993	-0.386	-7.470	0.240	14.011	0.870*	183.170	2.851*	186.192
PSUNADP	1.816	14.347	-1.462*	-24.532	-0.778*	-42.415	-0.020	-4.771	-1.251*	-46.260
KANE	-0.173	-1.239	-0.868	-15.428	-0.721*	-40.819	-0.028	-6.854	-1.234*	-50.591
LEADRIDG	1.162	8.212	-1.002	-17.521	-0.732*	-38.093	-0.115	-18.849	-1.105*	-39.685
MILFORD	1.659	16.712	-0.807	-19.588	-0.863*	-41.441	-0.086	-18.067	-1.177	-24.486
Mean[1]	1.135	8.230	-1.277	-19.694	-0.987	-34.369	0.499	85.392	0.170	32.407

* $p<0.05$

[1] Changes for Slocum State Park were excluded from calculation of the mean because of a malfunction of the Aerochemetric sampler unit from 22 September 2005 through 3 January 2006.



Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2006

Sites not pictured:

AK01	5.2
AK03	5.3
PR20	4.9
VI01	4.8

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

Figure 2. Mean annual hydrogen ion concentrations (as pH) in precipitation collected in the USA in 2006 by the National Atmospheric Deposition Program/National Trends Network.

Table 14. Annual and seasonal sulfate ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

	Volume Weighted Mean Concentrations (mg/L)			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
Region/Site	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	2.135	2.176	2.026	28.64	21.05	7.59	52.61	38.08	14.53	0.22	0.00	0.22
CROOKCRK	2.315	2.477	1.975	32.40	24.14	8.27	48.75	33.05	15.70	6.09	5.31	0.78
LAURHILL	2.300	2.686	1.774	27.19	18.79	8.41	43.91	25.33	18.58	2.29	2.21	0.08
ALLEPORT	2.664	3.035	2.004	32.19	22.99	9.20	44.79	28.66	16.13	3.11	1.17	1.94
PRESQISL	2.219	2.202	2.248	25.36	16.11	9.25	44.74	28.79	15.95	0.26	0.01	0.25
KANE	1.904	1.998	1.648	29.09	21.20	7.90	56.10	40.97	15.13	4.54	0.80	3.74
Region Mean	2.256	2.429	1.946	29.15	20.71	8.43	48.48	32.48	16.00	2.75	1.58	1.17
Central Pennsylvania												
LITTPINE	2.389	2.460	2.265	24.39	16.09	8.30	39.17	24.82	14.35	1.01	0.93	0.08
HILLSCRK	2.023	2.266	1.482	21.56	16.70	4.86	41.13	28.43	12.70	0.80	0.59	0.21
LITTBUFF	1.940	2.199	1.531	22.27	15.36	6.92	39.41	24.15	15.26	5.87	3.35	2.52
PSUNADP	2.089	2.309	1.717	21.06	14.56	6.50	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	2.211	2.416	1.885	21.13	13.89	7.24	35.36	21.72	13.64	2.41	0.93	1.48
YOWOCRK	1.897	2.060	1.609	21.24	14.91	6.33	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	1.826	1.911	1.703	18.52	11.14	7.38	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	2.054	2.231	1.742	21.45	14.67	6.79	38.90	24.54	14.36	2.37	1.35	1.02
Eastern Pennsylvania												
SLOCUM	1.725	1.904	1.442	23.39	16.42	6.97	39.30	24.10	15.20	13.70	9.86	3.84
VALLFORG	1.842	2.031	1.522	25.83	18.17	7.65	52.84	33.28	19.56	2.20	1.96	0.24
MILLERSV	1.677	1.943	1.228	20.43	14.28	6.15	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	1.418	1.625	1.127	19.19	13.03	6.16	50.71	29.63	21.08	2.38	1.95	0.43
Region Mean	1.666	1.876	1.330	22.21	15.48	6.73	46.50	28.53	17.97	5.94	3.90	2.05
State Mean	2.034	2.217	1.717	24.35	16.99	7.36	44.07	28.28	15.79	3.35	2.03	1.31

where they were the highest since the early 1990's. At Leading Ridge, sulfate concentrations in 2006 were 42% higher than in 2005 (1.885 mg/L versus 1.327 mg/L) and the highest measured at the site since 1991 (2.108 mg/L). The impact across the region was so pronounced that the dormant season mean (1.742 mg/L) was the highest since 1992.

In contrast, 2006 growing season sulfate concentrations, which averaged 2.217 mg/L across the state, were near their lowest levels in western Pennsylvania and generally higher than in 2005 in central and eastern regions of the state, but still well within the range of values reported since 1995. The higher sulfate concentrations occurred despite a significant drop in SO_2 emissions in 2006 in Pennsylvania and upwind states (EPA, 2007). The higher sulfate concentrations in 2006 were likely due to either long-range emission sources, seasonal differences in emissions, and/or climatic influences. Since the 2006 nitrate concentrations (discussed below) were only slightly higher in 2006 than 2005 and well within the range of values reported since 1995, the higher sulfate concentrations were most likely due to emissions patterns, not climatic variability, since changes in climate would affect but sulfate and nitrate concentrations similarly (Lynch et al., 2007).

Reductions in sulfate concentrations since 1983 resulted in an average decrease of 11.8 kg/ha (34.9%) of wet sulfate deposition across the state (Table 15). Annual and growing season sulfate depositions were generally higher in 2006 than in 2005, but well within the range of values reported over the past five years. This was not the case for dormant season sulfate deposition. Despite the relatively high dormant season sulfate concentrations, wet depositions were below 2005 levels at most monitoring sites. In fact, the western regional mean deposition was the second lowest reported to date, while the statewide mean deposition was the fourth lowest value reported in the last ten years. Obviously the amount and distribution of precipitation during the year influenced wet sulfate deposition patterns in 2006 relative to 2005 and other years, especially in central Pennsylvania.

Annual and seasonal precipitation patterns and volumes in 2006 were very different than those in 2005. Although annual precipitation was generally higher in 2006 than in 2005 by two to four inches, seasonal distributions were very different. Regional growing season precipitation in 2006 averaged from seven inches (central Pennsylvania) to 12 inches (western Pennsylvania) above 2005 volumes and was nearly ten inches higher across the entire state. In contrast, 2006 statewide dormant season precipitation was 7 inches below 2005 levels with the largest deficits occurring in western (8 inches) and central (6.5 inches) Pennsylvania. Such differences can exert substantial influence on annual and seasonal concentrations and wet deposition patterns across the state as well as comparisons of 2006 ionic concentrations and wet deposition patterns with patterns measured in 2005 and earlier years. However, as previously noted, annual and seasonal nitrate concentrations in 2006 were not substantially different from 2005, even during the dormant season, which suggests that precipitation differences were not the driving force behind the differences in sulfate concentrations. To illustrate this point, nitrate concentrations were approximately 11% higher in central Pennsylvania during the 2006 dormant season than they were in 2005. The higher concentrations were likely the result of lower precipitation during the 2006 dormant season because concentrations are generally inversely related to precipitation

Table 15. Estimated changes in wet deposition of individual ions in precipitation from 1983 to 2006.

	Hydrogen Ion		Sulfate		Nitrate		Chloride	
Site	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change
CROOKCRK	-0.453*	-45.03	-11.098*	-29.28	-5.778*	-24.59	-0.194	-7.16
GODDARD	-0.436*	-48.69	-11.872*	-33.33	-6.667*	-27.33	0.490*	27.28
HILLSCRK	-0.221*	-36.96	-5.269*	-23.14	-3.314*	-20.29	0.255	19.76
LAURHILL	-0.704*	-61.02	-23.697*	-52.76	-11.849*	-43.09	-0.443	-18.17
LITTBUFF	-0.369*	-45.38	-7.227*	-23.54	-4.525*	-20.58	0.242	10.51
SLOCUM	-0.309*	-41.70	-6.121*	-21.80	-2.347	-11.96	0.372	20.15
VALLFORG	-0.388*	-51.05	-12.979*	-40.71	-5.572*	-27.32	-1.642*	-35.34
LITTPINE	-0.416*	-48.97	-8.438*	-28.53	-7.021*	-31.04	0.841*	54.18
PSUNADP	-0.281*	-39.07	-8.710*	-29.34	-5.104*	-26.10	-0.428*	-25.70
KANE	-0.475*	-51.24	-17.429*	-44.82	-8.847*	-36.35	-0.966*	-48.31
LEADRIDG	-0.329*	-43.95	-11.127*	-35.87	-6.460*	-30.40	-0.765*	-40.66
MILFORD	-0.333*	-47.76	-11.634*	-42.38	-6.638*	-32.51	-0.385	-16.13
Mean[1]	-0.400	-47.19	-11.771	-34.88	-6.525	-29.06	-0.272	-7.25

* $p<0.05$

[1] Changes for Slocum State Park were excluded from calculation of the mean because of a malfunction of the Aerochemetric sampler unit from 22 September 2005 through 3 January 2006.

Table 15 (continued).

Site	Ammonium		Calcium		Magnesium		Potassium		Sodium	
	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change
CROOKCRK	0.492	15.53	-0.089	-5.28	-0.071	-20.70	0.252*	88.72	0.360*	87.82
GODDARD	0.318	8.41	-0.273	-14.73	-0.125*	-32.52	0.393*	166.98	0.348*	75.72
HILLSCRK	0.806*	39.42	0.010	1.12	-0.037	-17.32	0.420*	264.93	0.370*	140.26
LAURHILL	-0.822*	-20.73	-0.413*	-25.07	-0.163*	-45.09	0.245*	65.27	0.313*	61.84
LITTBUFF	0.629	17.03	-0.219	-15.68	-0.052	-16.41	0.468*	180.87	0.404*	61.22
SLOCUM	1.997*	80.24	0.213	22.88	-0.040	-15.11	0.494*	188.68	0.300*	48.82
VALLFORG	0.428	13.47	-0.444*	-31.28	-0.501*	-65.60	0.371*	133.89	-0.653	-32.26
LITTPINE	0.940*	35.19	0.087	8.76	0.067	33.91	0.415*	235.27	0.767*	237.31
PSUNADP	0.664*	29.34	-0.126	-11.15	-0.068*	-32.15	0.020	12.70	-0.207*	-36.75
KANE	-0.261	-8.37	-0.250	-18.23	-0.112*	-42.74	-0.014	-6.98	-0.347*	-52.24
LEADRIDG	0.140	5.16	-0.241*	-19.90	-0.093*	-38.53	-0.058	-22.80	-0.279*	-42.72
MILFORD	0.344	17.15	-0.022	-2.70	-0.083*	-31.64	0.023	12.62	-0.144	-12.80
Mean[1]	0.334	13.78	-0.180	-12.12	-0.113	-28.07	0.230	102.86	0.085	44.31

* $p<0.05$

[1] Changes for Slocum State Park were excluded from calculation of the mean because of a malfunction of the Aerochemetric sampler unit from 22 September 2005 through 3 January 2006.

volumes. In contrast, the 2006 mean dormant season sulfate concentration in central Pennsylvania was 43% higher than in 2005. Obviously, below average precipitation was a contributing factor to the substantially higher sulfate concentrations in 2006; however, if precipitation was the main driving force behind the lower sulfate concentrations, nitrate concentrations should have been similarly affected, but were not. The only other contributing factor would be differences in dormant season sulfur dioxide emissions between 2005 and 2006 (Lynch et al., 2007).

Despite the dramatic reductions, sulfate concentrations and wet depositions in western Pennsylvania continue to be higher than in most regions in the United States (Figure 3). The highest mean annual sulfate concentration (2.6 mg/L) at NADP/NTN sites in 2006 was recorded at an Ohio site; the second highest concentration (2.2 mg/L) was recorded at the Leading Ridge NADP/NTN site in Huntingdon County (Figure 3). When DEP supported deposition monitoring sites are included in the comparison (Table 14), the mean annual concentration at the Allegheny Portage site on Cresson Mountain in Cambria County was actually higher than the highest reported NADP/NTN concentration in Ohio. In fact, mean annual sulfate concentrations at four western Pennsylvania sites (Crooked Creek Lake, Laurel Hill, Allegheny Portage, and Presque Isle) and the Little Pine site in central Pennsylvania were higher in 2006 than recorded at the Leading Ridge NADP/NTN site in Huntingdon County (Table 14).

The highest annual wet sulfate deposition (29.1 kg/ha) in the United States in 2006 was recorded at the Kane NADP/NTN site in Elk County (Figure 4). The second highest sulfate deposition (28 kg/ha) was measured at a site in southeastern Ohio. However, annual wet sulfate deposition at the Crooked Creek Lake and Allegheny Portage sites exceeded 32 kg/ha in 2006, the highest amount recorded in the United States. Although precipitation differences across the region was a contributing factor to the relatively high deposition at these sites, higher sulfate concentrations especially during the growing season (Table 14) was the primary reason for the high annual sulfate deposition at these sites and across the region in general. The volume-weight mean growing season concentration at the Allegheny Portage site (3.035 mg/L) was the highest concentration reported at the site since 2001.

Nitrate (NO_3^-). Nitrate concentrations have decreased approximately 34% (11.7 μeq/L) since 1983 (Table 13). The statewide mean annual nitrate concentration in 2006 was 1.274 mg/L (Table 16) which was the second lowest (by 0.001 mg/L) mean concentration recorded the past 24 years. Growing and dormant season mean nitrate concentrations in 2006 were 1.155g/L and 1.491g/L, respectively (Table 16). Regional differences were also evident in 2006. Regardless of season, the highest nitrate concentrations occurred in the western portion of the state and decreased to the lowest levels in eastern Pennsylvania (Table 16). Reductions in nitrate concentrations since 1983 have resulted in a 6.5 kg/ha (29.1%) reduction in wet nitrate deposition across the state (Table 15). Annual nitrate deposition to the state in 2006 was 15.3 kg/ha, the second lowest amount reported to date. Approximately 58% of the nitrate deposition fell during the growing season (Table 16). Although wet nitrate deposition was highest in western Pennsylvania (18.0 kg/ha), differences in deposition in central and eastern Pennsylvania were much smaller (Table 16). The measured reductions in nitrate concentrations and wet

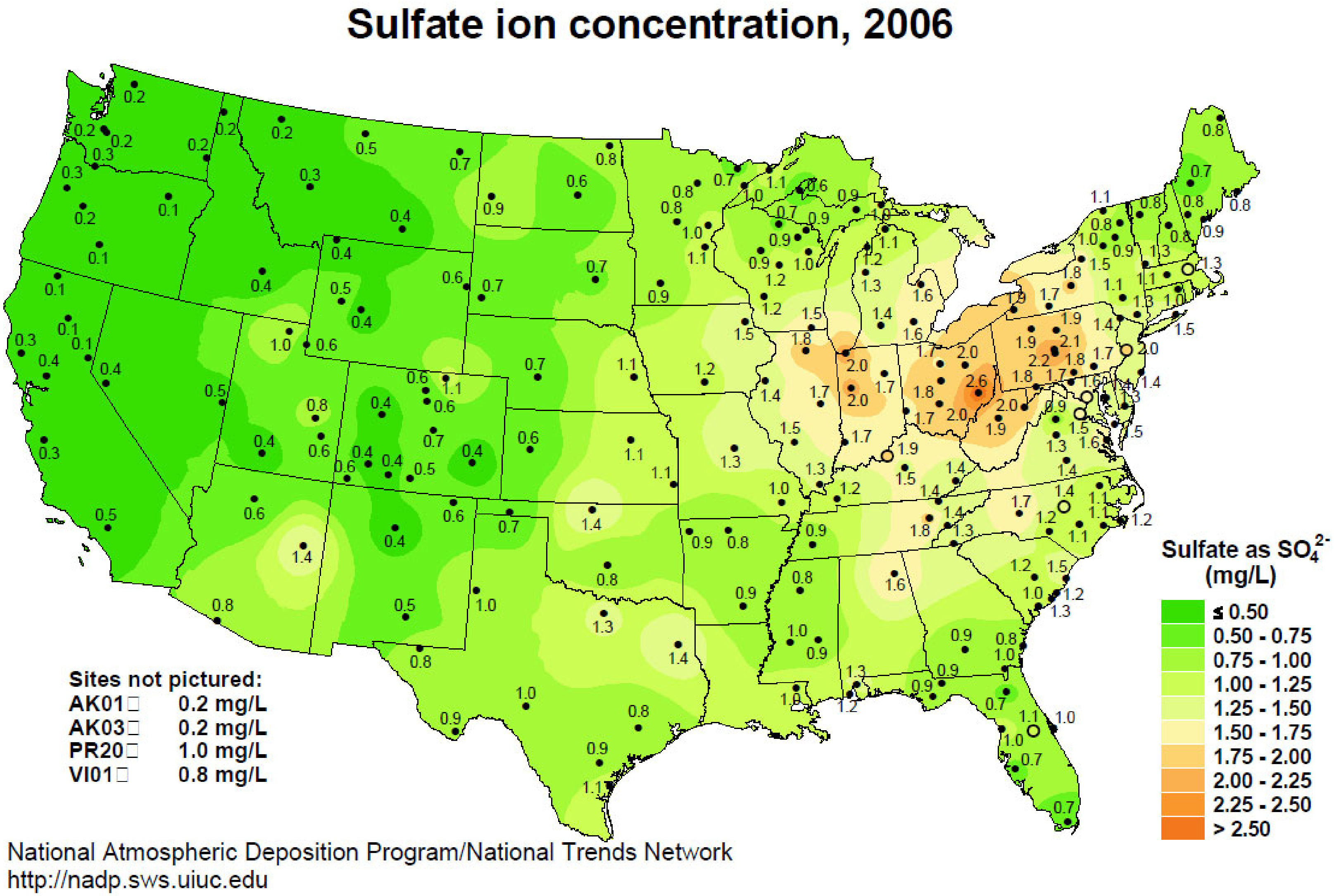


Figure 3. Mean annual sulfate ion concentrations in precipitation collected in the USA in 2006 by the National Atmospheric Deposition Program/National Trends Network.

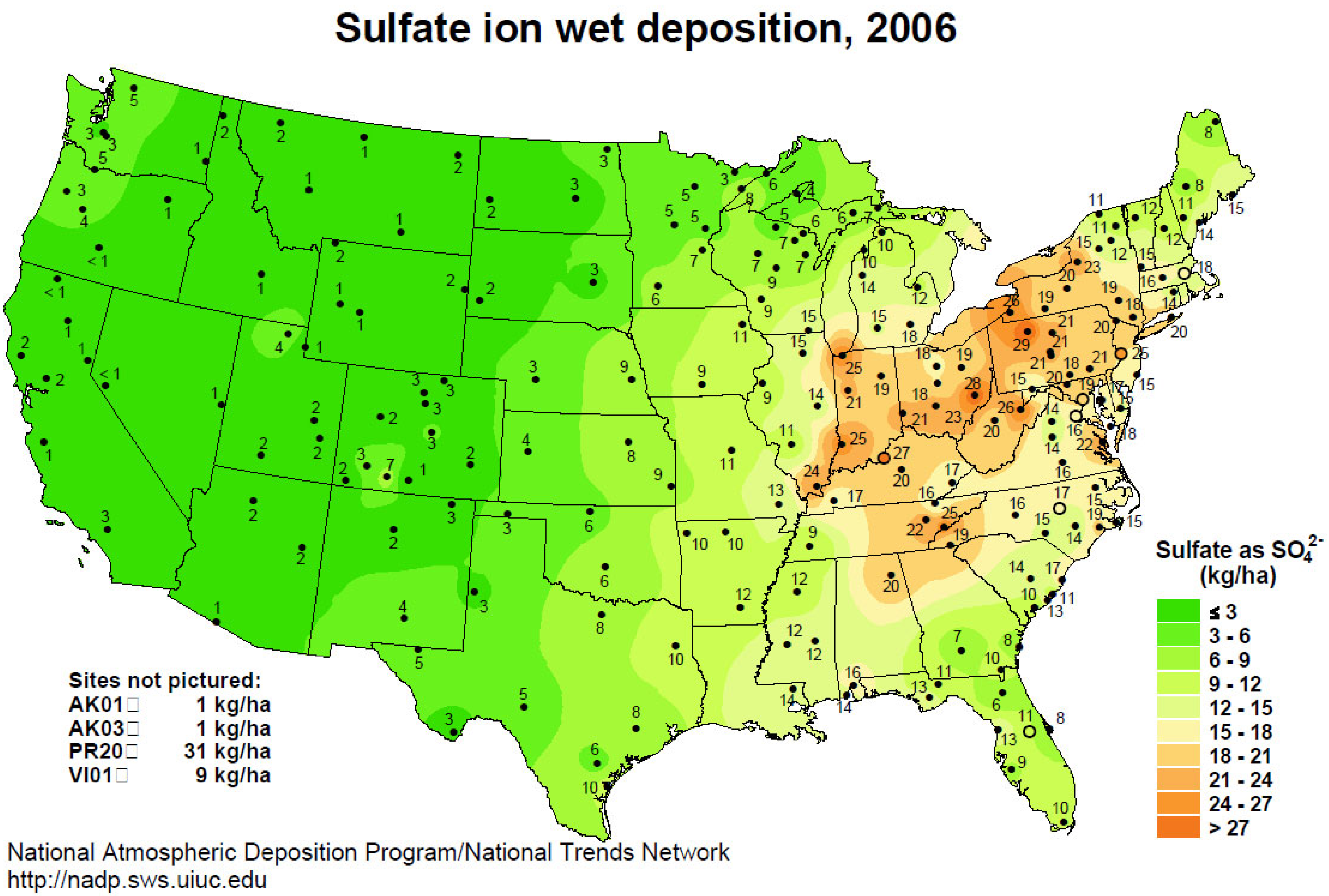


Figure 4. Annual sulfate ion wet deposition in the USA in 2006 based on precipitation collected by the National Atmospheric Deposition Program/National Trends Network.

Table 16. Annual and seasonal nitrate ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

	Volume Weighted Mean Concentrations (mg/L)			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
Region/Site	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	1.387	1.258	1.726	18.63	12.16	6.46	52.61	38.08	14.53	0.22	0.00	0.22
CROOKCRK	1.272	1.154	1.519	17.60	11.25	6.36	48.75	33.05	15.70	6.09	5.31	0.78
LAURHILL	1.441	1.293	1.643	16.83	9.05	7.79	43.91	25.33	18.58	2.29	2.21	0.08
ALLEPORT	1.408	1.233	1.720	17.23	9.34	7.89	44.79	28.66	16.13	3.11	1.17	1.94
PRESQISL	1.852	1.798	1.950	21.18	13.15	8.02	44.74	28.79	15.95	0.26	0.01	0.25
KANE	1.039	0.906	1.399	16.32	9.62	6.70	56.10	40.97	15.13	4.54	0.80	3.74
Region Mean	1.400	1.274	1.659	17.97	10.76	7.20	48.48	32.48	16.00	2.75	1.58	1.17
Central Pennsylvania												
LITTPINE	1.615	1.248	2.250	16.41	8.16	8.25	39.17	24.82	14.35	1.01	0.93	0.08
HILLSCRK	1.094	1.024	1.253	11.65	7.54	4.11	41.13	28.43	12.70	0.80	0.59	0.21
LITTBUFF	1.354	1.289	1.457	15.58	9.00	6.58	39.41	24.15	15.26	5.87	3.35	2.52
PSUNADP	1.240	1.065	1.537	12.53	6.71	5.81	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	1.332	1.124	1.664	12.85	6.46	6.39	35.36	21.72	13.64	2.41	0.93	1.48
YOWOCRK	1.183	1.037	1.442	13.18	7.51	5.67	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	0.985	0.898	1.111	10.05	5.24	4.81	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	1.258	1.098	1.530	13.18	7.23	5.95	38.90	24.54	14.36	2.37	1.35	1.02
Eastern Pennsylvania												
SLOCUM	1.304	1.219	1.439	17.47	10.51	6.96	39.30	24.10	15.20	13.70	9.86	3.84
VALLFORG	1.242	1.240	1.247	17.37	11.10	6.27	52.84	33.28	19.56	2.20	1.96	0.24
MILLERSV	0.901	0.924	0.861	11.11	6.79	4.31	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	1.009	0.926	1.126	13.58	7.43	6.15	50.71	29.63	21.08	2.38	1.95	0.43
Region Mean	1.114	1.077	1.168	14.88	8.96	5.92	46.50	28.53	17.97	5.94	3.90	2.05
State Mean	1.274	1.155	1.491	15.27	8.88	6.38	44.07	28.28	15.79	3.35	2.03	1.31

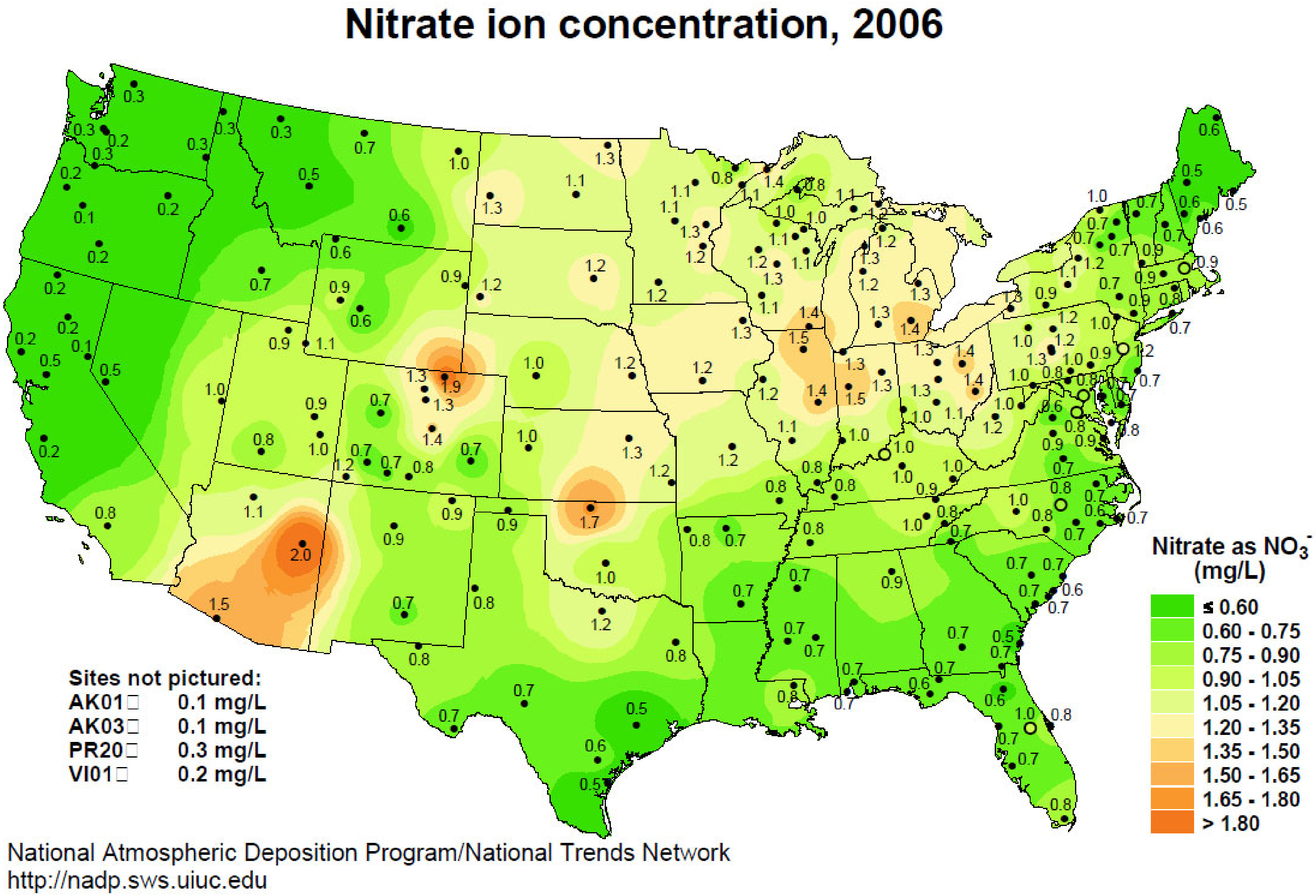
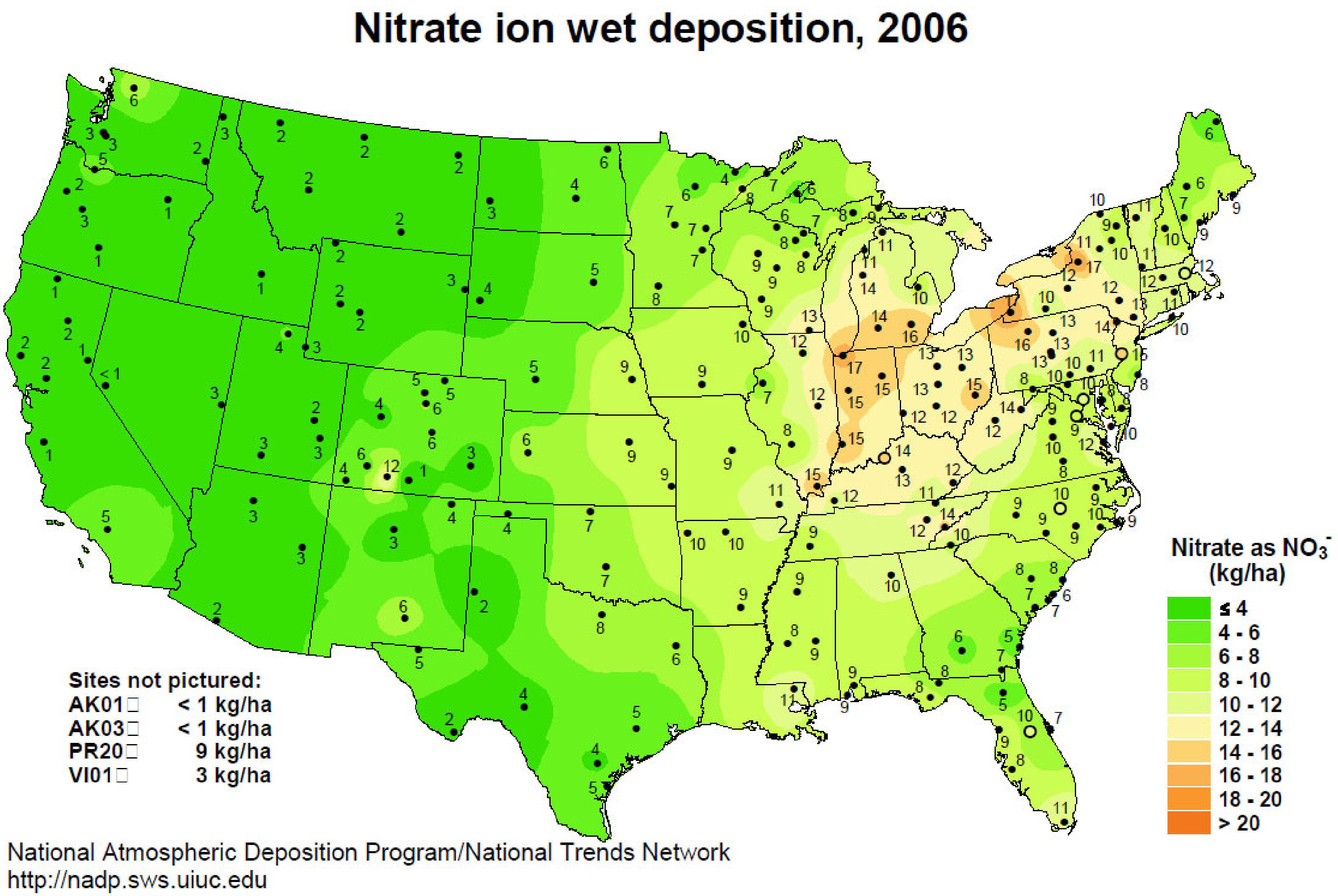


Figure 5. Mean annual nitrate ion concentrations in precipitation collected in the USA in 2006 by the National Atmospheric Deposition Program/National Trends Network.



Sites not pictured:

AK01	< 1 kg/ha
AK03	< 1 kg/ha
PR20	9 kg/ha
VI01	3 kg/ha

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

Figure 6. Annual nitrate ion wet deposition in the USA in 2006 based on precipitation collected by the National Atmospheric Deposition Program/National Trends Network.

depositions can be attributed to reductions in nitrogen oxides emissions in Pennsylvania and in upwind states (EPA, 2007; Lynch et al., 2007). Although nitrate concentrations in Pennsylvania are fairly comparable to those in neighboring states (Figure 5), wet nitrate deposition in the western third of the Commonwealth (see Table 16) continues to be higher than in most regions in the United States (Figure 6). Nitrate deposition at the Presque Isle site near Erie was 21.2 kg/ha in 2006, which is higher than any of the deposition estimates at the NADP/NTN sites shown in Figure 6. In fact, nitrate deposition across all of western Pennsylvania in 2006 was higher than any of the NADP/NTN sites in the United States. (Table 16, Figure 6).

Ammonium (NH_4^+). Ammonium concentrations and wet depositions have generally increased across the state since 1983, although the increases are not generally statistically significant (Tables 13 and 15). The highest ammonium concentrations and wet depositions in 2006 were measured at the Millersville (0.427 mg/L) site in Lancaster County, the Presque Isle State Park (0.424 mg/L) site near Erie, the Allegheny Portage (0.438 mg/L) site in Cambria County and the Little Pine (0.443 mg/L) site in Lycoming County (Table 17). The Millersville site is located on an active farm in Lancaster County and the likely source of ammonium is from ammonia emissions from agricultural activities. The relatively high ammonium concentrations near Erie are likely from the decomposition of plant material in the shallow waters of Lake Erie which releases ammonia to the atmosphere. Ammonia emissions from urban sources in the city of Erie may also be a contributing source. Ammonia emissions from utility sources are likely influencing the Allegheny Portage site. Why high ammonium concentrations were observed at Little Pine in 2006 is not readily apparent, although the site is located in a field, part of which is managed as a cover crop for wildlife.

Ammonium concentrations at the Millersville site are similar to concentrations reported at many NADP/NTN sites located in agricultural regions of the mid-west, in southeastern United States, and around the Great Lakes (Figure 7). In fact, the 2006 mean annual ammonium concentration at Millersville was the highest concentration of any site east of the Ohio River and comparable to many sites located in the Mid-west and around the Great Lakes (Figure 7). Ammonium deposition in Pennsylvania in 2006 averaged 4.06 kg/ha across the state (Table 17). The highest annual wet depositions were measured at Millersville (5.3 kg/ha) and at Allegheny Portage (5.3 kg/ha). The annual ammonium deposition at Millersville was the highest amount recorded along the East Coast in 2006 and the fourth highest amount reported among all NADP/NTN sites; the other sites are located in the Mid-west, primarily in Indiana (Figure 8).

Cations (Ca^{2+}, Mg^{2+}, K^+, Na^+). Base cation (calcium, magnesium, sodium, and potassium) concentrations occur in precipitation at very low concentrations (Tables 18-21) with annual means ranging from around 0.10 mg/L for calcium to around 0.02 mg/L for magnesium. Calcium and magnesium concentrations have generally decreased the past 24 years where as sodium and potassium concentrations have increased (Table 13). These cations are important in that they are a source of acid neutralizing capacity in precipitation and are also essential plant nutrients. Wind blown soil particles are an important source for these cations, although in coastal areas sea sprays can also be an important source.

Table 17. Annual and seasonal ammonium ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

	Volume Weighted Mean Concentrations (mg/L)			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
Region/Site	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	0.375	0.374	0.379	5.04	3.62	1.42	52.61	38.08	14.53	0.22	0.00	0.22
CROOKCRK	0.296	0.298	0.291	4.13	2.91	1.22	48.75	33.05	15.70	6.09	5.31	0.78
LAURHILL	0.330	0.328	0.333	3.87	2.29	1.58	43.91	25.33	18.58	2.29	2.21	0.08
ALLEPORT	0.438	0.481	0.361	5.30	3.65	1.66	44.79	28.66	16.13	3.11	1.17	1.94
PRESQISL	0.424	0.404	0.459	4.84	2.96	1.89	44.74	28.79	15.95	0.26	0.01	0.25
KANE	0.250	0.259	0.228	3.83	2.74	1.09	53.50	38.38	15.13	7.13	3.39	3.74
Region Mean	0.352	0.357	0.342	4.50	3.03	1.48	48.05	32.05	16.00	3.18	2.02	1.17
Central Pennsylvania												
LITTPINE	0.443	0.469	0.399	4.53	3.07	1.46	39.17	24.82	14.35	1.01	0.93	0.08
HILLSCRK	0.262	0.260	0.268	2.79	1.91	0.88	41.13	28.43	12.70	0.80	0.59	0.21
LITTBUFF	0.401	0.427	0.362	4.61	2.98	1.63	39.41	24.15	15.26	5.87	3.35	2.52
PSUNADP	0.303	0.304	0.302	3.06	1.92	1.14	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	0.334	0.316	0.360	3.20	1.82	1.38	32.79	19.15	13.64	4.98	3.50	1.48
YOWOCRK	0.269	0.275	0.258	3.01	1.99	1.02	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	0.322	0.343	0.291	3.26	2.00	1.26	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	0.334	0.342	0.320	3.50	2.24	1.25	38.53	24.17	14.36	2.74	1.72	1.02
Eastern Pennsylvania												
SLOCUM	0.379	0.427	0.301	5.14	3.69	1.46	39.30	24.10	15.20	13.70	9.86	3.84
VALLFORG	0.318	0.337	0.285	4.45	3.02	1.43	52.84	33.28	19.56	2.20	1.96	0.24
MILLERSV	0.427	0.428	0.426	5.28	3.14	2.13	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	0.198	0.217	0.173	2.68	1.74	0.95	50.12	29.04	21.08	2.97	2.54	0.43
Region Mean	0.330	0.352	0.296	4.39	2.90	1.49	46.35	28.38	17.97	6.09	4.05	2.05
State Mean	0.339	0.350	0.322	4.06	2.67	1.39	43.73	27.94	15.79	3.68	2.37	1.31

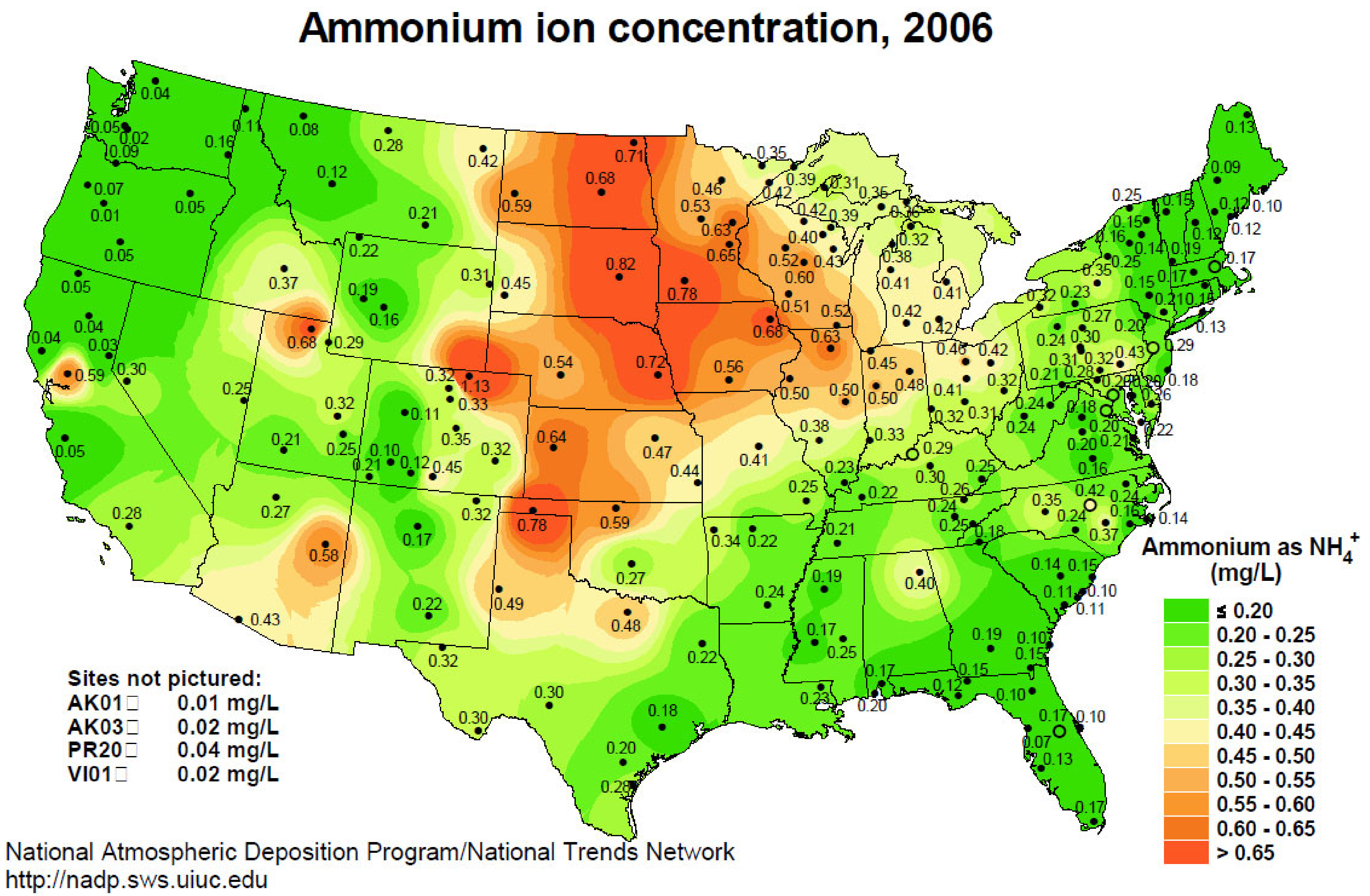


Figure 7. Mean annual ammonium ion concentrations in precipitation collected in the USA in 2006 by the National Atmospheric Deposition Program/National Trends Network.

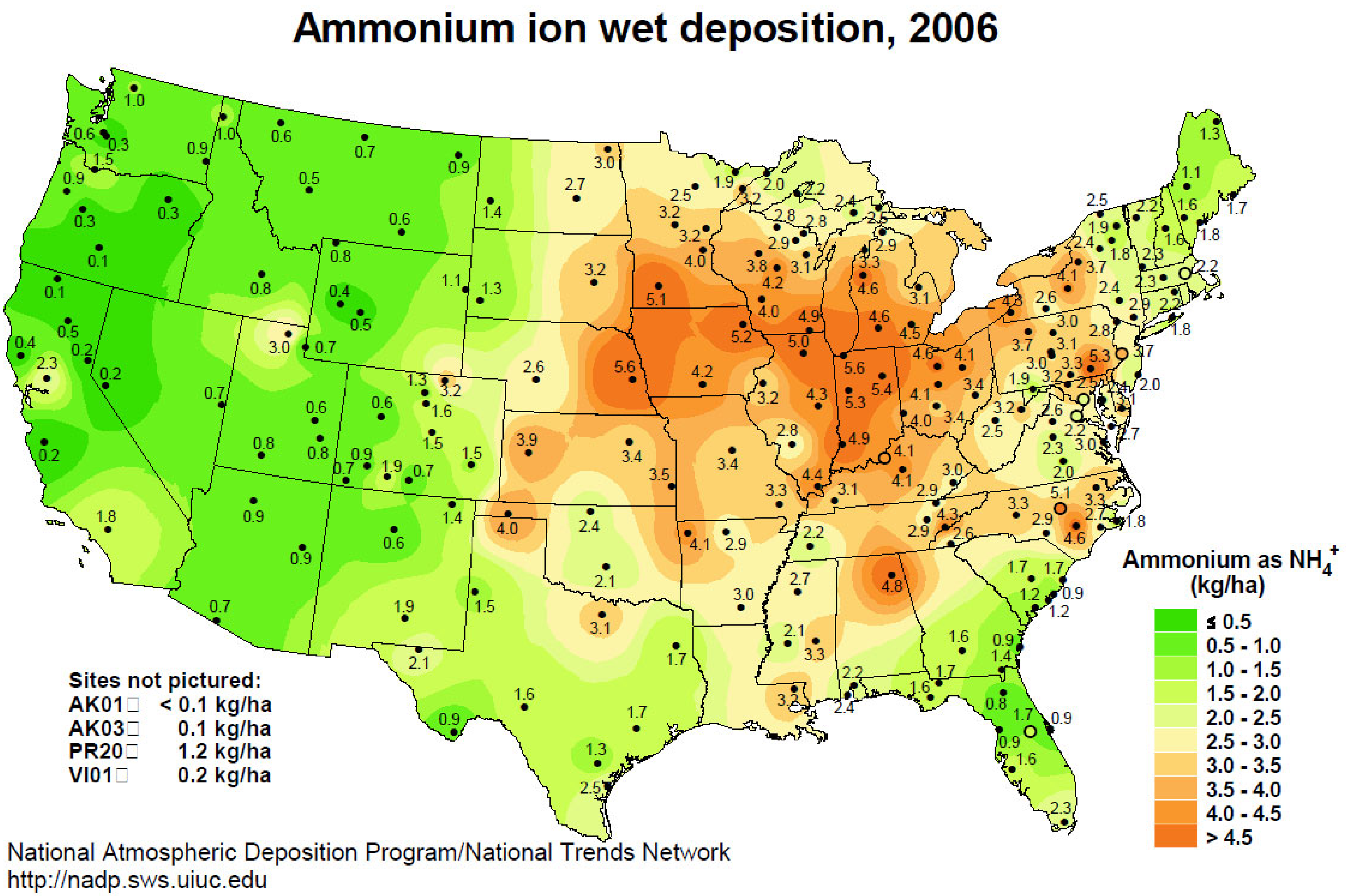


Figure 8. Annual ammonium ion wet deposition in the USA in 2006 based on precipitation collected by the National Atmospheric Deposition Program/National Trends Network.

Table 18. Annual and seasonal calcium ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

	Volume Weighted Mean Concentrations (mg/L)			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
Region/Site	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	0.151	0.126	0.216	2.02	1.21	0.81	52.61	38.08	14.53	0.22	0.00	0.22
CROOKCRK	0.132	0.119	0.160	1.83	1.16	0.67	48.75	33.05	15.70	6.09	5.31	0.78
LAURHILL	0.173	0.140	0.217	2.01	0.98	1.03	43.91	25.33	18.58	2.29	2.21	0.08
ALLEPORT	0.217	0.182	0.279	2.66	1.38	1.28	44.79	28.66	16.13	3.11	1.17	1.94
PRESQISL	0.242	0.179	0.355	2.77	1.31	1.46	44.74	28.79	15.95	0.26	0.01	0.25
KANE	0.092	0.084	0.115	1.44	0.89	0.55	56.10	40.97	15.13	4.54	0.80	3.74
Region Mean	0.168	0.138	0.224	2.12	1.16	0.97	48.48	32.48	16.00	2.75	1.58	1.17
Central Pennsylvania												
LITTPINE	0.146	0.125	0.180	1.48	0.82	0.66	39.17	24.82	14.35	1.01	0.93	0.08
HILLSCRK	0.122	0.127	0.110	1.30	0.94	0.36	41.13	28.43	12.70	0.80	0.59	0.21
LITTBUFF	0.118	0.124	0.109	1.36	0.87	0.49	39.41	24.15	15.26	5.87	3.35	2.52
PSUNADP	0.116	0.103	0.137	1.17	0.65	0.52	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	0.134	0.098	0.192	1.30	0.57	0.74	35.36	21.72	13.64	2.41	0.93	1.48
YOWOCRK	0.085	0.076	0.101	0.94	0.55	0.40	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	0.080	0.071	0.094	0.82	0.41	0.41	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	0.114	0.104	0.132	1.20	0.69	0.51	38.90	24.54	14.36	2.37	1.35	1.02
Eastern Pennsylvania												
SLOCUM	0.126	0.117	0.140	1.69	1.01	0.68	39.30	24.10	15.20	13.70	9.86	3.84
VALLFORG	0.124	0.110	0.148	1.73	0.99	0.75	52.84	33.28	19.56	2.20	1.96	0.24
MILLERSV	0.087	0.092	0.078	1.06	0.67	0.39	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	0.077	0.064	0.094	1.03	0.51	0.52	50.71	29.63	21.08	2.38	1.95	0.43
Region Mean	0.103	0.096	0.115	1.38	0.80	0.58	46.50	28.53	17.97	5.94	3.90	2.05
State Mean	0.131	0.114	0.160	1.57	0.88	0.69	44.07	28.28	15.79	3.35	2.03	1.31

Table 19. Annual and seasonal magnesium ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

Region/Site	Volume Weighted Mean Concentrations (mg/L)			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	0.027	0.024	0.034	0.36	0.23	0.13	52.61	38.08	14.53	0.22	0.00	0.22
CROOKCRK	0.026	0.026	0.027	0.37	0.25	0.11	48.75	33.05	15.70	6.09	5.31	0.78
LAURHILL	0.027	0.024	0.031	0.31	0.17	0.15	43.91	25.33	18.58	2.29	2.21	0.08
ALLEPORT	0.051	0.049	0.056	0.63	0.37	0.26	44.79	28.66	16.13	3.11	1.17	1.94
PRESQISL	0.048	0.036	0.069	0.55	0.27	0.28	44.74	28.79	15.95	0.26	0.01	0.25
KANE	0.012	0.010	0.018	0.19	0.11	0.09	56.10	40.97	15.13	4.54	0.80	3.74
Region Mean	0.032	0.028	0.039	0.40	0.23	0.17	48.48	32.48	16.00	2.75	1.58	1.17
Central Pennsylvania												
LITTPINE	0.028	0.025	0.034	0.29	0.16	0.12	39.17	24.82	14.35	1.01	0.93	0.08
HILLSCRK	0.022	0.022	0.022	0.23	0.16	0.07	41.13	28.43	12.70	0.80	0.59	0.21
LITTBUFF	0.027	0.027	0.027	0.31	0.19	0.12	39.41	24.15	15.26	5.87	3.35	2.52
PSUNADP	0.018	0.016	0.021	0.18	0.10	0.08	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	0.024	0.019	0.031	0.23	0.11	0.12	35.36	21.72	13.64	2.41	0.93	1.48
YOWOCRK	0.012	0.011	0.014	0.14	0.08	0.06	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	0.016	0.011	0.022	0.16	0.07	0.09	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	0.021	0.019	0.024	0.22	0.13	0.09	38.90	24.54	14.36	2.37	1.35	1.02
Eastern Pennsylvania												
SLOCUM	0.028	0.027	0.030	0.38	0.23	0.15	39.30	24.10	15.20	13.70	9.86	3.84
VALLFORG	0.047	0.036	0.067	0.66	0.32	0.34	52.84	33.28	19.56	2.20	1.96	0.24
MILLERSV	0.021	0.018	0.026	0.26	0.13	0.13	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	0.022	0.016	0.030	0.29	0.13	0.16	50.71	29.63	21.08	2.38	1.95	0.43
Region Mean	0.030	0.024	0.038	0.40	0.20	0.19	46.50	28.53	17.97	5.94	3.90	2.05
State Mean	0.027	0.023	0.033	0.33	0.18	0.14	44.07	28.28	15.79	3.35	2.03	1.31

Table 20. Annual and seasonal potassium ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

	Volume Weighted Mean Concentrations (mg/L)			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
Region/Site	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	0.053	0.056	0.045	0.71	0.54	0.17	52.61	38.08	14.53	0.22	0.00	0.22
CROOKCRK	0.069	0.075	0.055	0.97	0.74	0.23	48.75	33.05	15.70	6.09	5.31	0.78
LAURHILL	0.095	0.126	0.052	1.13	0.88	0.25	43.91	25.33	18.58	2.29	2.21	0.08
ALLEPORT	0.127	0.161	0.065	1.52	1.22	0.30	44.79	28.66	16.13	3.11	1.17	1.94
PRESQISL	0.105	0.121	0.076	1.20	0.88	0.31	44.74	28.79	15.95	0.26	0.01	0.25
KANE	0.018	0.017	0.021	0.28	0.18	0.10	56.10	40.97	15.13	4.54	0.80	3.74
Region Mean	0.078	0.093	0.052	0.97	0.74	0.23	48.48	32.48	16.00	2.75	1.58	1.17
Central Pennsylvania												
LITTPINE	0.107	0.141	0.048	1.10	0.92	0.18	39.17	24.82	14.35	1.01	0.93	0.08
HILLSCRK	0.109	0.132	0.058	1.17	0.98	0.19	41.13	28.43	12.70	0.80	0.59	0.21
LITTBUFF	0.078	0.094	0.052	0.90	0.66	0.24	39.41	24.15	15.26	5.87	3.35	2.52
PSUNADP	0.027	0.031	0.021	0.28	0.20	0.08	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	0.053	0.072	0.024	0.51	0.42	0.09	35.36	21.72	13.64	2.41	0.93	1.48
YOWOCRK	0.026	0.032	0.015	0.29	0.23	0.06	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	0.013	0.011	0.015	0.13	0.06	0.06	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	0.059	0.074	0.033	0.62	0.50	0.13	38.90	24.54	14.36	2.37	1.35	1.02
Eastern Pennsylvania												
SLOCUM	0.133	0.151	0.106	1.81	1.30	0.51	39.30	24.10	15.20	13.70	9.86	3.84
VALLFORG	0.094	0.108	0.070	1.32	0.97	0.35	52.84	33.28	19.56	2.20	1.96	0.24
MILLERSV	0.017	0.016	0.017	0.21	0.12	0.09	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	0.030	0.037	0.019	0.40	0.29	0.11	50.71	29.63	21.08	2.38	1.95	0.43
Region Mean	0.068	0.078	0.053	0.93	0.67	0.26	46.50	28.53	17.97	5.94	3.90	2.05
State Mean	0.068	0.081	0.045	0.82	0.62	0.19	44.07	28.28	15.79	3.35	2.03	1.31

Table 21. Annual and seasonal sodium ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

	Volume Weighted Mean Concentrations (mg/L)			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
Region/Site	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	0.091	0.075	0.132	1.23	0.73	0.50	52.61	38.08	14.53	0.22	0.00	0.22
CROOKCRK	0.083	0.073	0.105	1.15	0.71	0.44	48.75	33.05	15.70	6.09	5.31	0.78
LAURHILL	0.107	0.100	0.117	1.25	0.70	0.55	43.91	25.33	18.58	2.29	2.21	0.08
ALLEPORT	0.128	0.088	0.199	1.58	0.67	0.91	44.79	28.66	16.13	3.11	1.17	1.94
PRESQISL	0.100	0.088	0.120	1.14	0.65	0.49	44.74	28.79	15.95	0.26	0.01	0.25
KANE	0.033	0.018	0.074	0.54	0.19	0.35	56.10	40.97	15.13	4.54	0.80	3.74
Region Mean	0.090	0.074	0.124	1.15	0.61	0.54	48.48	32.48	16.00	2.75	1.58	1.17
Central Pennsylvania												
LITTPINE	0.109	0.092	0.138	1.11	0.60	0.51	39.17	24.82	14.35	1.01	0.93	0.08
HILLSCRK	0.127	0.125	0.130	1.35	0.92	0.43	41.13	28.43	12.70	0.80	0.59	0.21
LITTBUFF	0.121	0.088	0.172	1.39	0.61	0.78	39.41	24.15	15.26	5.87	3.35	2.52
PSUNADP	0.044	0.018	0.088	0.44	0.11	0.33	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	0.052	0.021	0.101	0.51	0.12	0.39	35.36	21.72	13.64	2.41	0.93	1.48
YOWOCRK	0.030	0.014	0.058	0.33	0.10	0.23	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	0.073	0.034	0.129	0.75	0.20	0.56	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	0.079	0.056	0.117	0.84	0.38	0.46	38.90	24.54	14.36	2.37	1.35	1.02
Eastern Pennsylvania												
SLOCUM	0.133	0.104	0.179	1.76	0.90	0.87	39.30	24.10	15.20	13.70	9.86	3.84
VALLFORG	0.260	0.171	0.413	3.61	1.53	2.08	52.84	33.28	19.56	2.20	1.96	0.24
MILLERSV	0.108	0.066	0.178	1.38	0.49	0.89	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	0.133	0.075	0.215	1.78	0.60	1.17	50.71	29.63	21.08	2.38	1.95	0.43
Region Mean	0.159	0.104	0.246	2.13	0.88	1.25	46.50	28.53	17.97	5.94	3.90	2.05
State Mean	0.102	0.074	0.150	1.25	0.58	0.68	44.07	28.28	15.79	3.35	2.03	1.31

Table 22. Annual and seasonal chloride ion analyses of precipitation collected at sites throughout Pennsylvania during 2006.

Region/Site	Volume Weighted Mean Concentrations (mg/L)			Total Wet Depositions (kg/ha)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania												
GODDARD	0.157	0.117	0.263	2.12	1.13	0.99	52.61	38.08	14.53	0.22	0.00	0.22
CROOKCRK	0.170	0.131	0.253	2.33	1.27	1.06	48.75	33.05	15.70	6.09	5.31	0.78
LAURHILL	0.199	0.182	0.223	2.33	1.27	1.06	43.91	25.33	18.58	2.29	2.21	0.08
ALLEPORT	0.260	0.178	0.404	3.21	1.35	1.86	44.79	28.66	16.13	3.11	1.17	1.94
PRESQISL	0.170	0.138	0.226	1.94	1.01	0.93	44.74	28.79	15.95	0.26	0.01	0.25
KANE	0.087	0.061	0.155	1.39	0.65	0.74	56.10	40.97	15.13	4.54	0.80	3.74
Region Mean	0.174	0.134	0.254	2.22	1.11	1.11	48.48	32.48	16.00	2.75	1.58	1.17
Central Pennsylvania												
LITTPINE	0.169	0.128	0.241	1.72	0.84	0.88	39.17	24.82	14.35	1.01	0.93	0.08
HILLSCRK	0.217	0.207	0.239	2.31	1.53	0.78	41.13	28.43	12.70	0.80	0.59	0.21
LITTBUFF	0.212	0.149	0.312	2.45	1.04	1.41	39.41	24.15	15.26	5.87	3.35	2.52
PSUNADP	0.123	0.082	0.193	1.25	0.52	0.73	38.82	24.38	14.44	0.90	0.45	0.45
LEADRIDG	0.134	0.084	0.214	1.30	0.48	0.82	35.36	21.72	13.64	2.41	0.93	1.48
YOWOCRK	0.102	0.083	0.134	1.13	0.60	0.53	39.74	25.42	14.32	4.24	3.08	1.16
ARENDTSV	0.161	0.092	0.261	1.67	0.54	1.13	38.66	22.83	15.82	1.35	0.12	1.23
Region Mean	0.160	0.118	0.228	1.69	0.79	0.90	38.90	24.54	14.36	2.37	1.35	1.02
Eastern Pennsylvania												
SLOCUM	0.195	0.156	0.256	2.58	1.34	1.24	39.30	24.10	15.20	13.70	9.86	3.84
VALLFORG	0.447	0.272	0.743	6.17	2.44	3.74	52.84	33.28	19.56	2.20	1.96	0.24
MILLERSV	0.223	0.157	0.335	2.83	1.15	1.68	43.16	27.11	16.05	5.50	1.82	3.68
MILFORD	0.255	0.163	0.386	3.41	1.30	2.11	50.71	29.63	21.08	2.38	1.95	0.43
Region Mean	0.280	0.187	0.430	3.75	1.56	2.19	46.50	28.53	17.97	5.94	3.90	2.05
State Mean	0.193	0.140	0.285	2.36	1.09	1.28	44.07	28.28	15.79	3.35	2.03	1.31

Chloride (Cl^-). Sea-salts are also an important source of chloride concentrations in south eastern Pennsylvania (Table 22), while coal combustion and the release of hydrochloric acids is an important source in western Pennsylvania. Mean annual chloride concentrations range from 0.16 mg/L to 0.45 mg/L across the state (Table 22) with the highest concentrations occurring at the Valley Forge site in Montgomery County. Chloride concentrations have exhibited mixed temporal patterns with some sites increasing slightly while others have decreased (Table 13).

Summary. Although significant progress has been made in reducing "acid rain" in Pennsylvania and across the Northeast and Mid-Atlantic regions, additional reductions in sulfur dioxide and nitrogen oxides emissions may be necessary to protect acid sensitive aquatic and terrestrial ecosystems and cultural and material resources in the Commonwealth, particularly in western Pennsylvania where 2006 sulfate concentrations and wet depositions were higher than any region of the United States. Some of the relatively high wet sulfate deposition in western and central Pennsylvania in 2006 over previous years can be attributed to above average precipitation; however, sulfur dioxide emissions from upwind sources, particularly during the 2006 dormant season was a major contributing factor. 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 but improve visibility. An assessment of source-receptor relationships should be undertaken to identify those sources that would 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 analyses would provide valuable information to determine the location and the level of emissions reductions that would be necessary to achieve adequate protection of all sensitive aquatic and terrestrial ecosystems and cultural and material resources in the Commonwealth.

LITERATURE CITED

Bigelow, D.S. 1984. Instruction manual for NADP/NTN site selection and installation. National Atmospheric Deposition Program, NREL, Colorado State Univ., Fort. Collins, CO.

Bigelow, D.S. and S.R. Dossett. 1988. Instruction manual for NADP/NTN site operation. Natural Atmospheric Deposition Program, NREL, Colorado State Univ., Fort Collins, CO.

Dana, M.T. and Easter, R.C. 1987. Statistical summary and analysis of event precipitation chemistry from the MAP3S network, 1976-1983. Atoms. Environ. 21:113-128.

Coscio, M.R., G.C. Pratt, and S.V. Krupa. 1982. An automatic, refrigerated, sequential precipitation sampler. Atmos. Environ. 16:1939-1944

Environmental Protection Agency. 2007. Acid Rain Program: 2006 Progress Report. Clean Air

Markets Division, Office of Air and Radiation. U.S EPA. EPA-430-R-06-015, 28 pp. This report is available at Http://www.epa.gov/airmarkets.

Hardy, R.L. 1976. Multiquadic equations of topography and other irregular surfaces. Jour. Geophys. Res. 76:1905-1915.

Hirsch, R.M., J.R. Slack, and R.A. Smith. 1982. Techniques of trend analysis for monthly water quality data. Water Resour. Res., 18(1):107-121.

Lynch, J.A., J.W. Grimm, and V.C. Bowersox. 1995. Trends in precipitation chemistry in the United States: A national perspective, 1980-1992. Atmos. Environ., 29(11):1231-1246.

Lynch, J.A., K.S. Horner, J.W. Grimm, E.W. Boyer, H.J. Carrick. 2007. Reductions in Acidic Wet Deposition in Pennsylvania Following Implementation of the Clean Air Act Amendments of 1990: 1995-2006. Annual Technical Assessment Report to The Department of Environmental Protection, Bureau of Air Quality Control. Penn State Institutes of Energy and the Environment. 41 pp. This report is available at http://www.dep.state.pa.us.

National Atmospheric Deposition Program/National Trends Network. 2006. NADP/NTN Annual Data Summary. Precipitation Chemistry in the United States. 2005. The Illinois State Water Survey, Champaign, IL. http://nadp.sws.uiuc.edu.

Peden, M.E. and L.M. Skowron. 1978. Ionic stability of precipitation samples. Atmos. Environ., 12:2343-2349.

Peden, M.E., L.M. Skowron, and F.M. McGork, 1979. Precipitation sample handling, analysis, and storage procedures. Res. Rpt. 4. Illinois State Water Survey, University of Illinois, Urbana, Illinois.

de Pena, R.G., K.C. Walker, L. Lebowitz, and J.G. Micka. 1985. Wet deposition monitoring-effect of sampling period. Atmos. Environ., 19:151-156.

Public Law 101-549, enacted November 15, 1990, amends the U.S. Clean Air Act.

Public Law 101-549, Title IV, Acid Deposition Control, Table A, Affected Sources and Units in Phase I, Clean Air Act Amendments of 1990.

Ridder, T.B., T.A. Buishand, H.F.R. Reijnders, J.J. 't Hart, and J. Slalina. 1985. Effects of storage on the composition of main components in rainwater samples. Atmos. Environ., 19:759-762.

SAS Institute, Inc. 1988. SAS/STAT User's Guide, Release 6.03 Edition. Cary, NC. SAS Institute Inc., 1988. 1028 pp.