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# Atmospheric Deposition in Pennsylvania: Spatial and Temporal Variations 2009



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### About the Report

- This report was prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, within Penn State Institutes of Energy & the Environment.
- The work presented here, detailing monitoring of wet atmospheric deposition at a network of sites across Pennsylvania, was sponsored by the Pennsylvania Department of Environmental Protection.
- The findings are those of the authors and are not necessarily those of The Pennsylvania State University.
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## INTRODUCTION

*Atmospheric deposition* occurs when airborne constituents are transferred to the earth's surface. There are many sources of emissions to the atmosphere, and many pathways where constituents in the atmosphere are transported and deposited to the landscape. Atmospheric deposition can occur as *wet deposition* (via precipitation - in rain, snow, clouds, and fog) and as *dry deposition* (via dry fallout - including particles, aerosols, and gases). Airborne emissions can be transported for short or long distances (e.g., up to hundreds of miles) before being deposited to the landscape. Thus individual emissions sources can affect broad regions, and even relatively undisturbed areas can be blanketed with inputs of pollutants via atmospheric deposition.

*Acidic atmospheric deposition*, commonly referred to as *acid rain*, is the transfer of acids and acid-forming substances from air to the earth's surface (Driscoll et al. 2001). Emissions of gases to the atmosphere from multiple sources can react with water in the atmosphere to form acidic compounds, which in turn can be deposited to the landscape by wet and dry deposition. Acid producing gases are released to the atmosphere through both natural processes (e.g., emissions from volcanoes, lightning, fires, and decaying vegetation) and from anthropogenic processes (e.g., largely attributed to the combustion of fossil fuels). There are numerous airborne gases that produce acids when they react with water in the atmosphere. For example, carbon dioxide reacts with water in the atmosphere to form carbonic acid. Even under natural background conditions, precipitation is typically acidic due to the ubiquitous presence of carbonic acid in the atmosphere, with pH generally cited as being around 5.6. Oxides of nitrogen and sulfur, which are emitted to the atmosphere primarily by fossil fuel combustion, are criteria air pollutants regulated by the US Environmental Protection Agency. These gases react with water in the atmosphere to produce nitric and sulfuric acids, which are considered to be the primary precursors of acid rain. Precipitation is considered to be problematic when pH values drop below about 5.0. The northeastern USA receives precipitation with mean pH that ranges from about 4.3 in Pennsylvania and New York to 4.8 in Maine and the upper Midwest (Kahl et al. 2004). Because acids and other chemical constituents tend to accumulate in the atmosphere during dry periods between storms, the most acidic rain typically falls at the beginning of a storm, and as the rain continues, acids are washed out of the atmosphere. Precipitation plays an important role in biogeochemical cycling by cleansing the atmosphere of many pollutants and delivering dissolved substances to aquatic and terrestrial ecosystems of the landscape.

Atmospheric deposition is among the most ubiquitous non-point sources of chemical inputs to ecosystems. It can affect water quality and human health and impact aquatic, terrestrial, cultural, and material resources. Long-term effects of atmospheric deposition in the northeastern USA (including Pennsylvania) were recently summarized by Driscoll et al. (2001, 2003) and Kahl et al. (2004). The studies highlight the need to quantify the spatial and temporal variation of inputs to the landscape by atmospheric deposition in order to understand potential and realized effects. Atmospheric deposition is of particular interest to scientists, land managers and policy makers in Pennsylvania. Rates of acidic deposition (e.g., nitrogen, sulfur, hydrogen ion) have been elevated for decades (USEPA 2009) and are among the highest in the nation (see Figures 3 & 4). Though emissions from within Pennsylvania are significant, atmospheric pollution is also attributed to the state's geographic setting downwind of major stationary emissions sources in the heavily industrialized Midwestern USA (USEPA 2009). Although significant progress has

been made in reducing acid rain in Pennsylvania and across the Northeast and Mid-Atlantic regions (see Tables 12 and 13), additional reductions in sulfur dioxide and nitrogen oxides emissions are likely necessary to protect acid sensitive aquatic and terrestrial ecosystems and cultural and material resources in the Commonwealth (Driscoll et al. 2001). Climatic variability and change may also change the magnitude and patterns of atmospheric deposition in new ways.

Because of the importance of precipitation in providing water and its dissolved substances to the landscape, 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. Today, work continues to determine the magnitude and distribution of wet atmospheric deposition in Pennsylvania and to consider their potential environmental impacts. The monitoring effort provides an important long term record of precipitation chemistry across Pennsylvania.

The detailed study of the spatial and temporal chemistry of wet deposition (precipitation) and dry deposition serves many functions: (1) it provides basic baseline data needed for quantifying status and trends of atmospheric deposition; (2) it provides basic data needed for quantifying how deposition is related to the frequency of precipitation events and variability of climate; (3) it provides data needed for evaluating possible impacts of pollutants on aquatic and terrestrial ecosystems, cultural and material resources, and human health; (4) it provides for comparisons of both beneficial and detrimental substances associated with atmospheric deposition; and (5) it provides quantitative means of evaluating the effectiveness of present and future air pollution control legislation. This report represents a summary of precipitation chemistry and wet deposition data collected at a network of 17 atmospheric deposition monitoring sites in Pennsylvania in 2009. Precipitation was sampled from each site weekly. Samples were analyzed for ions that are typically associated with acidity (pH, sulfate, nitrate, ammonium), base cations (calcium, magnesium, sodium, potassium), and salinity (chloride and specific conductance).

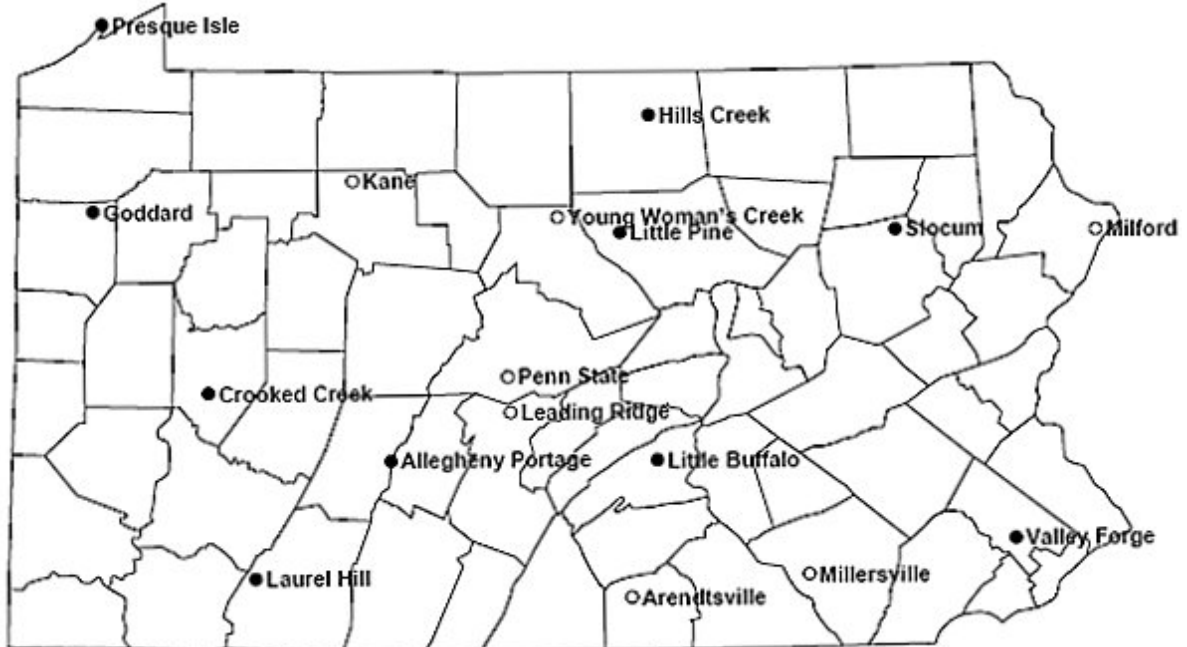
## **NETWORK DESIGN AND OPERATION**

### **Monitoring Site Locations**

Seventeen atmospheric deposition-monitoring sites were in operation in Pennsylvania during 2009 (Figure 1, with details of the locations shown in Table 1). Support for observation and measurement at 11 of these sites was provided by the Pennsylvania Department of Environmental Protection, Bureau of Air Quality Control. These 11 sites include: Presque Isle, Goddard, Crooked Creek, Laurel Hill, Allegheny Portage, Hills Creek, Little Pine, Little Buffalo, Millersville, Slocum, and Valley Forge. Support for another 6 sites was provided by other agencies, including: the U.S. Forest Service (Kane, Milford), the Pennsylvania Agricultural Experiment Station (Leading Ridge), the National Oceanic and Atmospheric Administration (Penn State), the US Geological Survey (Young Woman's Creek), and the US Environmental Protection Agency (Arendtsville). These latter 6 sites plus the Millersville site all participate in, and report data to, the National Atmospheric Deposition Program's National Trends Network.

**Figure 1.** Pennsylvania Wet Atmospheric Deposition Monitoring Network in 2009.

Precipitation chemistry is measured weekly at these 17 sites. PA-Sites (11) denoted with filled circles are part of the state network only; while sites (6) denoted with open circles are also part of a national monitoring network.



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

Site Name	Latitude	Longitude	County	Elev (m)	Start Date
<b>Western Pennsylvania</b>					
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
<b>Central Pennsylvania</b>					
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
<b>Eastern Pennsylvania</b>					
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

### **Consistency with National Network**

To ensure comparability and consistency of data across Pennsylvania and the nation, we operate all of the sites in the Pennsylvania network according to the same protocols of the National Atmospheric Deposition Program's National Trends Network (NADP/NTN), online at <http://nadp.sws.uiuc.edu> (NADP 2009; Dossett and Bowersox 1999). Owing to the vast heterogeneity of Pennsylvania – which spans large gradients in physiographic provinces, terrain, climate, and land use, the sparse number of sampling sites in the national network alone are not sufficient to characterize the spatial and temporal variability of wet atmospheric deposition across the state. The Pennsylvania Department of Protection supports the monitoring at an additional 11 sites, greatly enhancing the network of monitoring observations in the state. The combined dataset characterizes the variation of precipitation chemistry and wet atmospheric deposition over space and time, and allows analyses of long term status and trends.

### **Field Instrumentation**

To measure *chemistry* of precipitation, each site is equipped with an Aerochem Metrics brand wet/dry precipitation collector. This instrument consists of a two-container system with a movable lid designed to expose a wet container and cover a 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. This design ensures that the wet container is exposed only during periods of precipitation, and this sample is used for our analyses of wet deposition and precipitation chemistry. The wet container is rigorously pre-cleaned (by the analytical labs described below) and is replaced weekly.

To measure *volume* of precipitation, each site is instrumented with several recording and non-recording precipitation gages, all of which have wind screens to maximize precipitation catch. A standard Belfort recording 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 a precipitation event recorder mounted on the recording rain gage. A standard Taylor non-recording rain gage was used to determine the total amount of precipitation. All of the monitoring sites in the Pennsylvania network meet the criteria for use in the NADP/NTN national network, meeting their standards for site selection, installation, and maintenance. During 2009, we began comparisons of our aging recording gages (Belfort brand with strip chart recorders) with new recording gages (ETI, Ott brands with digital recorders) that have been approved for use in NADP/NTN. We are comparing the precipitation catch efficiency of old versus new models at one of our field sites (Leading Ridge) and in the laboratory. We aim to replace all of the recording rain gages with new, state of the art gages in 2010-2011. All of the precipitation data used for deposition calculations in 2009 are from the traditional instruments.

### **Field Analyses**

Precipitation samples were collected following standard operating procedures established by the NADP/NTN (Dossett and Bowersox 1999) to ensure compatibility of data. Field personnel collect samples from each monitoring site weekly, on Tuesday mornings (or as near to that as possible). The "wet" sample containers were shipped to the laboratory each week regardless of whether precipitation occurred. Back in the preparation lab, operators weigh the collection

bucket to determine the “field” sample volume, and measure the “field” pH and conductivity of the sample, and transfer the remaining sample from the collection bucket to a 1000 mL polyethylene bottle for shipping to the analytical lab. Samples are shipped overnight or taken directly to the water quality lab of Penn State Institutes of Energy & the Environment (for PA-only sites) or to the Central Analytical Lab of the Illinois State Water Survey (for NADP/NTN sites). 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.

**Laboratory Analyses**

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. 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.

Precipitation samples were analyzed for the following parameters provided a sufficient volume was present: pH (H<sup>+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), chloride (CL<sup>-</sup>), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), potassium (K<sup>+</sup>), sodium (Na<sup>+</sup>), and specific conductance. In the event that insufficient volume was present for complete analysis, the priority on analyses was as listed. Specific analytical techniques and laboratory equipment used for the PA network (not NADP/NTN) sites are listed in below (Table 2).

**Table 2.** Analytical methods used to measure concentrations in precipitation samples.

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 assurance (QA) and quality control (QC) procedures 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.

### ***Field Measurements***

Precipitation samples were collected following procedures established under the NADP/NTN and discussed in detail in the NADP/NTN Site Operation Manual (Dossett and Bowersox 1999). Calibrations of the recording rain gages 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 entered into each site's permanent record. Information on site operations is used in screening precipitation chemistry data to eliminate contaminated samples.

### ***Analytical Laboratory***

Quality assurance for the analytical measurements 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  $\pm 100$  percent of the detection limit, of  $\pm 20$  percent at ten times the detection limit, and  $\pm 10$  percent at 100 times the detection limit. Analytical Instruments (see Table 2) 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

Ion	Detection Limit	
Na <sup>+</sup>	0.005 mg/L	
K <sup>+</sup>	0.005 mg/L	
Ca <sup>2+</sup>	0.005 mg/L	
Mg <sup>2+</sup>	0.005 mg/L	
NH <sub>4</sub> <sup>+</sup>	0.005 mg/L	
SO <sub>4</sub> <sup>2-</sup>	0.2 mg/L	
NO <sub>3</sub> <sup>-</sup>	0.005 mg/L	
Cl <sup>-</sup>	0.02 mg/L	
	Accuracy	Precision
pH < 5.0	$\pm 0.05$	$\pm 0.03$
pH > 5.0	$\pm 0.05$	$\pm 0.01$
Specific Conductance		
10-100 $\mu$ S/cm	$\pm 5\%$	$\pm 3\%$
>100 $\mu$ S/cm	$\pm 2\%$	$\pm 1\%$

**Table 3.** Minimum lab detection limits

standard (comparing stock standards to reference standards) 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.

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  $\pm 5\%$  for all parameters, except nitrate and ammonium that must not differ by more than  $\pm 10\%$  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  $\pm 5\%$  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.

**External Audits:** The water quality laboratory participates in an inter-laboratory comparison study sponsored by the National Water Research Institute of Canada at least once per year. This proficiency testing program allows comparison of lab performance, by analyzing "blind" samples of rain and other soft waters.

**Data Management:** All analytical results and field measurements are entered into a computer database by the Lab Manager. 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.

## DATA REDUCTION

### Precipitation-Weighted Means

Seasonal and annual precipitation-weighted mean concentrations discussed in this report were calculated according to the formula below, where the precipitation-weighted mean concentration,  $C_w$ , for a given ion was calculated from the  $n$  valid samples in the season or year under consideration. Individual sample concentrations,  $C_i$ , were weighted by the measured precipitation,  $P_i$ , 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.

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

### 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 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 2009. 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 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.

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

State (ID No.)	Location
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 (NY68)	Biscuit Brook
New York (NY99)	West Point
Ohio (OH15)	Lykens
Ohio (OH17)	Delaware
Ohio (OH49)	Caldwell
Ohio (OH54)	Deer Creek State Park
Ohio (OH71)	Wooster
Virginia (VA00)	Charlottesville
Virginia (VA10)	Mason Neck
Virginia (VA27)	James Madison University
Virginia (VA28)	Shenandoah National Park
West Virginia (WV05)	Cedar Creek State Park
West Virginia (WV28)	Parsons

### **Concentration and Deposition Trend Statistics**

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 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 2009 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 associated with  $b_y$ .

### **Units**

The standard units used in this report are mg/L (milligrams per liter) or  $\mu\text{eq/L}$  (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.

**Table 5.** Conversion factors for concentration and deposition units.

From	To	Multiply by
$\text{mg/m}^2$	lb/ac	0.00892
$\text{mg/m}^2$	kg/ha	$10^{-2}$
mg/L	$\text{g/m}^2$	$10^{-2} \times \text{cm rainfall}$
mg/L	kg/ha	$10^{-1} \times \text{cm rainfall}$
mg/L	lb/ac	$0.0892 \times \text{cm rainfall}$

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

Ion	Ion as	Factor From mg/L to $\mu\text{moles/L}$	Factor From mg/L to $\mu\text{eq/L}$
		Multiply by	Multiply by
Hydrogen	$\text{H}^+$	1000	1000
Calcium	$\text{Ca}^{2+}$	24.950	49.900
Magnesium	$\text{Mg}^{2+}$	41.144	82.287
Potassium	$\text{K}^+$	25.577	25.577
Sodium	$\text{Na}^+$	43.498	43.498
Ammonium	$\text{NH}_4^+$	55.473	55.438
Sulfate	$\text{SO}_4^{2-}$	10.410	20.821
Nitrate	$\text{NO}_3^-$	16.128	16.128
Chloride	$\text{Cl}^-$	28.206	28.216

### **Summary Periods**

For this report, the *annual period* (defined by the weekly sampling on Tuesdays) started on 12/31/2008 and ended on 12/29/2009. The *growing season* or *warm period* represents the period when precipitation was primarily as rain, and includes samples collected from April to October. The *dormant season* or *cold period* represents the period when precipitation was primarily as snow or ice and includes samples collected from January – March and November-December. These periods are adjusted to accommodate the weekly-on-Tuesday collection period. In 2009, the warm period was defined specifically as: 4/1/2009-11/3/2009, and the cold period was defined specifically as 12/31/2008-3/31/2009 and 11/4/2009-12/29/2009.

## **NETWORK PERFORMANCE IN 2009**

### **Catch Efficiency**

The precipitation catch efficiency of the Aerochem Metrics precipitation samplers and the handling protocols of site operators were very good in 2009. 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 0.68 at the Allegheny-Portage site in Cambria County to 0.97 at the Milford sites (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 0.89 with 10 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 most sites (all but two), the sampler was more efficient during the warm period when precipitation was dominated by rain than during the cold period when precipitation frequently occurred as snow or ice. The network mean ratio during the warm period was 0.92 compared to 0.84 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 condition, such as electrical failures. 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.** Catch efficiency of the Aerochem Metrics precipitation samplers in 2009.

Monitoring Site	Ratio of Bucket Volume to Non-recording Raingage Amount <sup>1</sup>		
	Annual	Warm Period <sup>2</sup>	Cold Period <sup>3</sup>
<u>Western Pennsylvania</u>			
Laurel Hill State Park	0.92	0.93	0.89
M. K. Goddard State Park	0.88	0.91	0.82
Crooked Creek Lake	0.82	0.83	0.78
Allegheny Portage N.H.S.	0.68	0.81	0.43
Presque Isle State Park	0.84	0.89	0.76
Kane - NADP	0.90	0.92	0.84
<u>Central Pennsylvania</u>			
Little Buffalo State Park	0.92	0.93	0.90
Hills Creek State Park	0.85	0.89	0.76
Little Pine State Park	0.89	0.89	0.90
Young Woman's Creek - NADP	0.95	0.96	0.95
Leading Ridge - NADP	0.96	0.97	0.93
Penn. State Univ. - NADP	0.93	0.93	0.92
Arendtsville - NADP	0.93	0.95	0.89
<u>Eastern Pennsylvania</u>			
Valley Forge National Park	0.88	0.93	0.73
Slocum State Park	0.93	0.92	0.97
Millersville - NADP	0.95	0.95	0.92
Milford - NADP	0.97	0.99	0.92
<b>State Mean</b>	<b>0.89</b>	<b>0.92</b>	<b>0.84</b>

<sup>1</sup> 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 rain gage

<sup>2</sup> Warm Period April through October represents period when precipitation was primarily rain

<sup>3</sup> Cold Period: January-April and November-December represents period when precipitation was predominantly snow.

### **Sampling Frequency**

The number of measurements by site and parameter is given in Table 8. There were 884 weekly sampling periods during 2009, but since 44 of these sampling periods were without any recorded precipitation, the maximum number of potential samples available for analysis of precipitation chemistry was 840. Of these, 718 samples (85%) contained sufficient volume for complete analysis. For the sampling periods with precipitation but no analyses, many involved trace precipitation volumes of 0.05 inch or less. Another primary reason for not analyzing a precipitation sample is contamination. Samples are flagged as being contaminated if they have various forms of materials in them, most frequently bird droppings or vegetation. Occasionally, the wet/dry sampler malfunctions and the wet container is exposed during dry periods, where a sample is flagged as potentially contaminated from improper exposure.

### **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 that *actually occurred* at each site. This comparison is given in Table 9 for each precipitation quality parameter. On average in 2009, about 93% of the mean annual precipitation in Pennsylvania was analyzed for various chemical constituents (for example, 6.59% of precipitation was not analyzed for pH, and 6.85% of precipitation was not analyzed for chloride). There is a lot of variability around the mean from site to site, and the network-wide average is distorted, for example, by the approximately 28% of the annual precipitation that was lost at Young Womans Creek, in contrast to less than 1% of the annual precipitation that was lost at Laurel Hill. Sample contamination accounts for nearly all of the precipitation losses, though occasional power outages can also contribute.

### **Quality Assurance with Cation-Anion Balances**

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 2009 is shown in Table 10. Of the 718 precipitation samples that had sufficient volume for complete chemistry analyses, 48 samples (6.7%) did not meet the specified cation/anion criterion. Very dilute samples, which have very low concentrations of dissolved constituents as evidenced by their low ionic strength and low specific conductance, are more likely to be flagged than higher concentration samples. Of the 48 samples that were flagged, 19 % (9 samples) of them were from storms ( $<0.3$  inch), while another 6% (3 samples) were from storms that fell into the 0.3 inch to 0.5 inch range. Collectively, this group of 12 low-volume samples represented only 0.5% of the total volume of precipitation measured in 2009 (Table 10). Another 31% of the "flagged" samples were from storms ranging in size from 0.5 inch to 1.0 inch. These 15 samples represented another 1.8% of the total volume of precipitation measured in 2009. Overall, the analyses of samples from 92% of the precipitation collected in the state met the cation/anion criterion in 2009. 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 or organics, may be present, and if present may affect the ionic strength and subsequently the cation/anion balance.

Table 8. Number of precipitation quality measurements in Pennsylvania in 2009 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 <sub>4</sub>	NO <sub>3</sub>	Cl	NH <sub>4</sub>	Ca	Mg	K	Na	Sum				
<u>Western Pennsylvania</u>																
M. K. Goddard	52	49	48	47	47	47	47	47	47	47	47	473	47	2	3	2
Crooked Creek	52	49	49	48	48	48	48	47	47	47	47	478	47	2	3	2
Laurel Hill	52	49	49	49	49	49	49	49	49	49	49	490	49	0	3	2
Allegheny Portage	52	47	46	44	44	44	43	43	43	43	43	440	43	4	5	1
Presque Isle	52	46	46	45	45	45	45	45	45	45	45	452	45	1	6	2
Kane-NADP	52	47	47	47	47	47	47	47	47	47	47	470	47	0	5	4
<u>Central Pennsylvania</u>																
Little Pine	52	48	44	43	43	43	43	43	43	43	43	436	43	5	4	2
Hills Creek	52	47	45	43	43	43	43	43	43	43	43	436	43	4	5	3
Little Buffalo	52	44	43	42	42	42	42	42	42	42	42	423	42	2	8	3
Penn State-NADP	52	41	41	41	41	41	41	41	41	41	41	410	41	0	11	1
Leading Ridge-NADP	52	42	42	42	42	42	42	42	42	42	42	420	42	0	10	3
Y. Woman Creek-NAD	52	32	32	32	32	32	32	32	32	32	32	320	32	0	20	5
Arendtsville-NADP	52	39	39	39	39	39	39	39	39	39	39	390	39	0	13	3
<u>Eastern Pennsylvania</u>																
Slocum	52	43	42	41	41	41	41	41	41	41	41	413	41	2	9	3
Valley Forge	52	44	43	42	42	42	42	42	42	42	42	423	42	2	8	4
Millersville-NADP	52	37	37	37	37	37	37	37	37	37	37	370	37	0	15	1
Milford-NADP	52	38	38	38	38	38	38	38	38	38	38	380	38	0	14	3
State Sum	884	742	731	720	720	720	719	718	718	718	718	7224	718	24	142	44

Table 9. Annual and seasonal distribution of precipitation in Pennsylvania during 2009 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 <sub>4</sub>	NO <sub>3</sub>	NH <sub>4</sub>	Cl	Cond	Ca	Mg	Na	K
<u>Western Pennsylvania</u>													
M. K. Goddard	43.09	25.88	17.21	0.19	0.35	0.35	0.35	0.35	0.23	0.35	0.35	0.35	0.35
Crooked Creek	42.98	25.48	17.50	0.23	0.26	0.26	0.26	0.26	0.23	0.42	0.42	0.42	0.42
Laurel Hill	49.44	28.98	20.46	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Allegheny Portage	42.61	24.25	18.36	0.73	3.59	3.59	3.73	3.59	1.10	3.73	3.73	3.73	3.73
Presque Isle	42.12	24.24	17.88	1.28	1.54	1.54	1.54	1.54	1.28	1.54	1.54	1.54	1.54
Kane-NADP	47.19	29.84	17.35	1.34	1.34	1.34	1.34	1.34	1.34	1.34	1.34	1.34	1.34
<u>Central Pennsylvania</u>													
Little Pine	37.27	24.10	13.17	5.23	5.66	5.66	5.66	5.66	5.58	5.66	5.66	5.66	5.66
Hills Creek	33.67	22.65	11.02	0.48	0.86	0.86	0.86	0.86	0.56	0.86	0.86	0.86	0.86
Little Buffalo	48.21	33.18	15.03	6.24	6.39	6.39	6.39	6.39	6.31	6.39	6.39	6.39	6.39
Penn State-NADP	40.45	27.22	13.23	9.68	9.68	9.68	9.68	9.68	9.68	9.68	9.68	9.68	9.68
Leading Ridge-NADP	37.41	25.04	12.37	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16	10.16
Arendtsville-NADP	48.97	31.46	17.51	10.45	10.45	10.45	10.45	10.45	10.45	10.45	10.45	10.45	10.45
Y. Woman Creek-NADP	38.70	24.89	13.81	28.83	28.83	28.83	28.83	28.83	28.83	28.83	28.83	28.83	28.83
<u>Eastern Pennsylvania</u>													
Slocum	39.27	28.63	10.64	10.54	10.64	10.64	10.64	10.64	10.57	10.64	10.64	10.64	10.64
Valley Forge	52.76	35.30	17.46	0.47	0.59	0.59	0.59	0.59	0.57	0.59	0.59	0.59	0.59
Milford-NADP	46.14	29.24	16.90	14.53	14.53	14.53	14.53	14.53	14.53	14.53	14.53	14.53	14.53
Millersville-NADP	46.41	31.77	14.64	11.63	11.63	11.63	11.63	11.63	11.63	11.63	11.63	11.63	11.63
<u>State Mean</u>	43.33	27.77	15.56	6.59	6.85	6.85	6.86	6.85	6.65	6.87	6.87	6.87	6.87

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 2009. 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 <sub>i</sub> /v <sub>t</sub> )	Vol. of flagged precip. by interval as a % of total precip. vol. (100.0*x <sub>i</sub> /v <sub>t</sub> )	Distribution of flagged precip. vol. by interval (%) (100.0*x <sub>i</sub> /x <sub>t</sub> )	Percent of precip. vol. that was flagged by interval (%) (100.0*x <sub>i</sub> /v <sub>i</sub> )
<b>Precipitation (Inches)</b>						
0.0 - 0.3	136	6.6 ( 9)	3.3	0.3	3.5	8.5
0.3 - 0.5	99	3.0 ( 3)	5.7	0.2	2.4	3.3
0.5 - 1.0	209	7.2 (15)	22.6	1.8	22.2	7.8
1.0 - 1.5	128	5.5 ( 7)	22.8	1.2	15.2	5.3
1.5 - 2.0	75	9.3 ( 7)	18.8	1.8	23.1	9.7
2.0 - 2.5	39	10.3 ( 4)	12.6	1.4	17.2	10.8
2.5+	32	9.4 ( 3)	14.3	1.3	16.5	9.1
<b>Specific Conductance (µS/cm)</b>						
0 - 16	383	10.2 (39)	68.5	6.8	86.0	9.9
16 - 32	271	3.0 ( 8)	28.2	1.0	13.1	3.7
32 - 48	54	1.9 ( 1)	3.0	0.1	1.0	2.5
48 - 64	9	0.0 ( 0)	0.3	0.0	0.0	0.0
64 - 80	1	0.0 ( 0)	0.0	0.0	0.0	0.0
80+	0	0.0 ( 0)	0.0	0.0	0.0	0.0
<b>Total Ionic Strength</b>						
0 - 100	297	9.1 (27)	57.3	5.5	70.0	9.7
100 - 200	302	6.3 (19)	36.4	2.2	27.8	6.0
200 - 300	82	2.4 ( 2)	4.9	0.2	2.3	3.7
300 - 400	27	0.0 ( 0)	1.1	0.0	0.0	0.0
400 - 500	7	0.0 ( 0)	0.2	0.0	0.0	0.0
500+	3	0.0 ( 0)	0.1	0.0	0.0	0.0

v<sub>i</sub> = volume of precipitation samples for the given interval, summed over all sites.

v<sub>t</sub> = total volume of precipitation samples for 2009, summed over all intervals and sites.

x<sub>i</sub> = volume of flagged precipitation samples for the given interval, summed over all sites.

x<sub>t</sub> = total volume of flagged precipitation samples for 2009, summed over all intervals and sites.

**Quality Assurance with Inter-laboratory Comparison Samples**

The water quality laboratory at Penn State Institutes of Energy & the Environment participates in an inter-laboratory comparison study sponsored by the National Water Research Institute of Canada at least once per year. Below are results for various constituents of water samples, conducted on 20 different rain and soft water samples in 2009 (Table 11). For each of these audit samples, 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. Overall, the Penn State lab compared favorably with other labs participating in this proficiency testing program, and performed acceptably on samples that are in the concentration ranges typical of precipitation samples from the Pennsylvania Atmospheric Deposition Monitoring Network.

**Table 11.** Results of proficiency testing via inter-lab comparisons of 20 rain and soft water audit samples analyzed during 2009.

11a) Proficiency Testing Study from December 2008 to March 2009

Audit Sample	pH <sup>1</sup>	Sulfate <sup>2</sup>	Nitrate <sup>3</sup>	Chloride <sup>4</sup>	Potassium <sup>5</sup>
	Reported - mean	Reported - mean	Reported - mean	Reported - mean	Reported - mean
1	6.42-6.50	1.94-1.90	<0.01-0.002	5.01-4.70	0.32-0.29
2	6.11-6.13	6.15-6.05	0.96-0.948	0.40-0.390	0.15-0.164
3	6.77-6.81	2.13-2.10	0.24-0.220	6.73-6.20	0.44-0.392
4	4.75-4.78	1.95-1.92	0.46-0.460	0.21-0.180	0.05-0.050
5	6.98-6.98	6.72-6.50	1.02-1.005	0.64-0.632	.019-0.214
6	4.86-4.89	1.36-1.30	0.24-0.228	0.18-0.150	0.02-0.037
7	6.43-6.42	5.38-5.27	0.69-0.672	0.25-0.230	0.18-0.200
8	7.01-7.02	3.12-3.01	0.11-0.077	1.69-1.63	0.22-0.218
9	4.98-5.03	1.12-1.04	0.44-0.436	0.14-0.101	0.02-0.036
10	4.55-4.59	3.20-3.15	1.36-1.30	0.32-0.317	0.08-0.108

pH- All values within range of expected values. No analytical bias.  
 Sulfate- All values within range of expected values. Possible high analytical bias indicated.  
 Nitrate- Sample #8 flagged high. Possible high analytical bias indicated.  
 Chloride- Samples #1, #3, #9 flagged high. High analytical bias indicated.  
 Potassium- Sample #10 flagged low. No analytical bias.

Audit Sample	Calcium <sup>6</sup>	Magnesium <sup>7</sup>	Sodium <sup>8</sup>	Ammonium <sup>9</sup>	
	Reported - mean	Reported - mean	Reported - mean	Reported - mean	
1	1.12-1.40	0.45-0.493	2.81-3.11	0.01-0.017	
2	2.53-2.72	0.86-0.929	0.14-0.150	<0.01-0.006	
3	2.81-3.00	0.62-0.676	3.53-4.00	<0.01-0.004	
4	0.41-0.601	0.15-0.150	0.06-0.070	0.18-0.197	
5	4.87-5.22	0.86-0.930	0.57-0.624	0.28-0.302	
6	0.11-0.156	0.03-0.031	0.05-0.066	0.25-0.278	
7	2.98-2.99	0.45-0.480	0.48-0.553	<0.01-0.003	
8	3.68-3.41	0.72-0.731	1.47-1.59	<0.01-0.009	
9	0.54-0.614	0.16-0.152	0.02-0.023	0.04-0.023	
10	1.61-1.83	0.42-0.458	0.05-0.061	0.06-0.074	

Calcium- Samples #1, #4, #6, #9, #10 flagged low. Possible low analytical bias indicated.  
 Magnesium- Sample #1 flagged low. No analytical bias.  
 Sodium- Samples #1, #3, #7 flagged low. Low analytical bias indicated.  
 Ammonium- Sample #9 flagged high. No analytical bias.

Table 11b) Proficiency Testing Study from June – September 2009

Audit Sample	pH <sup>1</sup>	Sulfate <sup>2</sup>	Nitrate <sup>3</sup>	Chloride <sup>4</sup>	Potassium <sup>5</sup>
	Reported - mean	Reported - mean	Reported - mean	Reported - mean	Reported - mean
1	5.95-6.08	5.24-5.08	0.19-0.180	0.43-0.455	0.32-0.330
2	4.75-4.82	3.29-3.20	1.55-1.51	0.32-0.310	0.09-0.1020
3	4.49-4.54	5.16-5.09	2.02-1.96	0.50-0.530	0.26-0.280
4	4.42-4.49	5.26-5.15	1.59-1.55	0.30-0.318	0.09-0.106
5	6.92-6.96	7.59-7.39	0.27-0.260	1.11-1.11	0.66-0.637
6	6.24-6.31	7.07-6.84	0.70-0.680	0.46-0.490	0.19-0.206
7	4.96-5.00	1.68-1.64	0.64-0.640	0.15-0.170	0.08-0.0910
8	5.26-5.38	2.33-2.30	0.05-0.032	4.84-4.64	0.24-0.219
9	6.10-6.20	2.01-2.00	0.06-0.036	1.34-1.34	0.11-0.120
10	6.90-6.92	3.35-3.37	0.25-0.234	0.94-0.960	0.37-0.362

pH- No Flags. Caution bias low.  
 Sulfate- No Flags. No analytical bias.  
 Nitrate- Samples #8 and #9 flagged high. Caution bias high.  
 Chloride- No Flags. No analytical bias.  
 Potassium- No Flags. No analytical bias.

Audit Sample	Calcium <sup>6</sup>	Magnesium <sup>7</sup>	Sodium <sup>8</sup>	Ammonium <sup>9</sup>	
	Reported - mean	Reported - mean	Reported - mean	Reported - mean	
1	2.07-2.01	0.33-0.330	0.68-0.734	0.02-0.0280	
2	2.23-2.16	0.64-0.633	0.04-0.0540	0.01-0.03800	
3	3.01-2.90	0.65-0.652	0.13-0.150	0.17-0.218	
4	2.43-2.34	0.66-0.656	0.11-0.1230	0.06-0.096	
5	4.77-4.40	1.23-1.22	1.53-1.54	<0.01-0.005	
6	3.03-2.86	0.84-0.838	0.30-0.334	<0.01-0.003	
7	0.94-0.950	0.22-0.214	0.04-0.0505	0.03-0.0655	
8	0.75-0.744	0.45-0.440	2.83-3.010	0.02-0.0240	
9	0.82-0.879	0.22-0.216	0.89-0.933	0.01-0.02000	
10	2.94-3.08	0.43-0.436	1.46-1.49	<0.01-0.0107	

Calcium- Sample #5 flagged high. No analytical bias.  
 Magnesium- No Flags. No analytical bias.  
 Sodium- Caution bias low.  
 Ammonium- Samples #2, #3, #4, #7 flagged high. Bias low.

## PRECIPITATION CHEMISTRY AND WET DEPOSITION 2009

Wet atmospheric deposition has been monitored at a network of sites across Pennsylvania by the Pennsylvania Department of Environmental Protection (11 sites) and other agencies (6 sites) since the early 1980's. Here, we summarize results of the monitoring network in 2009, for 17 monitoring sites across Pennsylvania (see Figure 1). Of these sites, 7 participate in the national monitoring network (NADP/NTN) and are illustrated in the national scale maps that are shown below (the other 11 state-only sites are not depicted in the nationwide images).

### Hydrogen Ion ( $H^+$ as pH)

The 2009 statewide mean annual pH was 4.63, and seasonal and regional differences in pH were quite small (Table 12). The hydrogen ion concentration (measured as pH) of precipitation in Pennsylvania has declined approximately 58% ( $47 \mu\text{eq/L}$ ) over the last 26 years (Table 13), while hydrogen ion atmospheric deposition rates have declined 56% (Table 14). 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. Despite the decrease in acidity, precipitation in the Commonwealth is still more acidic than nearly all other regions of the United States (Figure 2).

**Figure 2.** Mean annual hydrogen ion concentration (as pH) in precipitation collected in the USA in 2009.

*Note: at the time of this draft report (8/12/2010), official isopleth maps for 2009 from the National Trends Network are not yet available. Preliminary versions were obtained from R. Claybrooke, NADP Program Office, on 8/12/2010. These draft figures will soon be updated and color/contrast will be adjusted).*

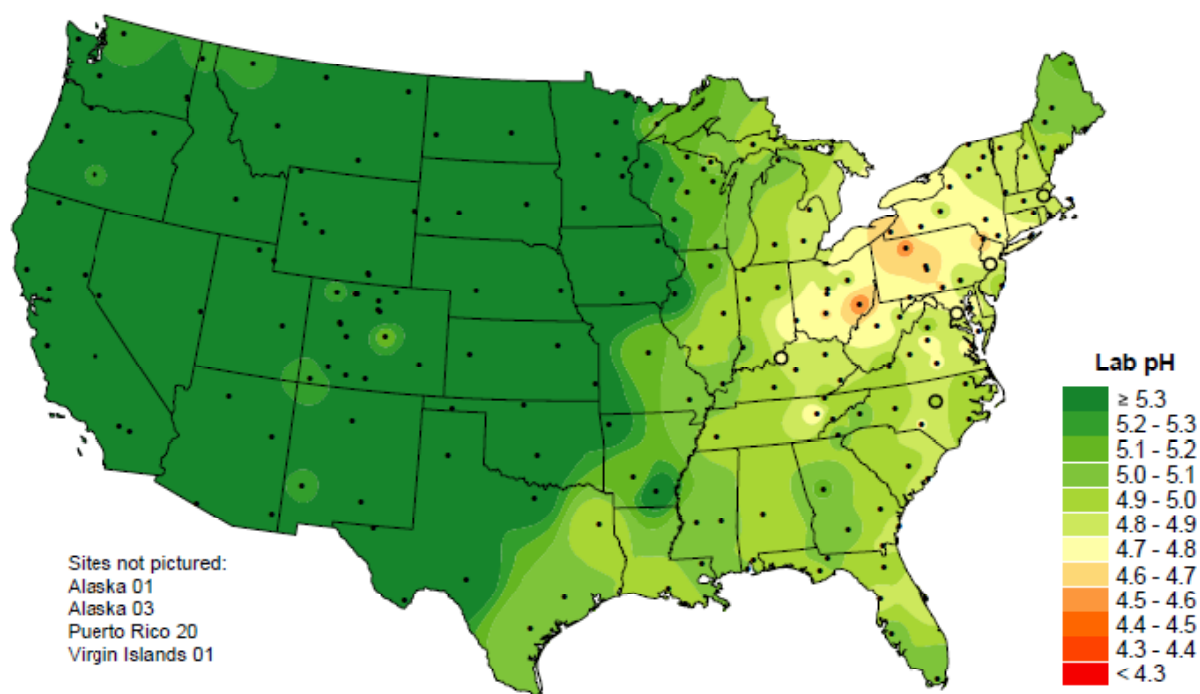


Table 12. Annual and seasonal hydrogen ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

Region/Site	Volume weighted Mean pH			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	4.56	4.54	4.59	0.31	0.19	0.11	43.01	25.88	17.13	0.08	0.00	0.08
CROOKCRK	4.36	4.35	4.39	0.48	0.29	0.18	42.88	25.48	17.40	0.10	0.00	0.10
LAURHILL	4.58	4.61	4.54	0.33	0.18	0.15	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	4.52	4.50	4.55	0.33	0.20	0.13	42.30	24.13	18.17	0.31	0.12	0.19
PRESQISL	4.59	4.68	4.50	0.27	0.13	0.14	41.58	24.06	17.52	0.54	0.18	0.36
KANE	4.58	4.51	4.73	0.32	0.24	0.08	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	4.53	4.53	4.55	0.34	0.21	0.13	44.29	26.39	17.90	0.28	0.05	0.23
Central Pennsylvania												
LITTPINE	4.56	4.59	4.51	0.26	0.16	0.10	35.32	22.15	13.17	1.95	1.95	0.00
HILLSCRK	4.63	4.63	4.61	0.20	0.13	0.07	33.51	22.65	10.86	0.16	0.00	0.16
LITTBUFF	4.68	4.73	4.58	0.26	0.16	0.10	45.20	30.81	14.39	3.01	2.37	0.64
PSUNADP	4.66	4.64	4.70	0.23	0.16	0.07	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	4.68	4.68	4.69	0.20	0.13	0.07	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	4.69	4.72	4.66	0.20	0.12	0.08	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	4.70	4.69	4.72	0.25	0.17	0.09	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	4.66	4.67	4.64	0.23	0.15	0.08	36.51	23.25	13.26	4.16	3.68	0.48
Eastern Pennsylvania												
SLOCUM	4.69	4.72	4.61	0.21	0.14	0.07	35.13	24.78	10.35	4.14	3.85	0.29
VALLFORG	4.68	4.67	4.70	0.28	0.19	0.09	52.51	35.30	17.21	0.25	0.00	0.25
MILLERSV	4.91	4.87	5.05	0.14	0.11	0.03	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	4.67	4.67	4.66	0.25	0.16	0.09	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	4.74	4.73	4.76	0.22	0.15	0.07	42.02	28.32	13.71	4.12	2.92	1.20
State Mean	4.63	4.64	4.64	0.27	0.17	0.10	40.55	25.55	15.00	2.78	2.22	0.56

Table 13. Estimated changes in concentrations of individual ions in precipitation from 1983 to 2009.

Site	Hydrogen Ion		Sulfate		Nitrate		Chloride	
	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change	Change (ueq/L)	Percent Change
CROOKCRK	-52.303*	-53.38	-31.112*	-40.35	-17.246*	-43.40	-0.930	-12.12
GODDARD	-55.500*	-62.99	-31.941*	-45.23	-17.499*	-44.33	-0.063	-1.21
HILLSCRK	-41.927*	-57.80	-23.877*	-42.91	-14.373*	-43.75	-0.110	-2.47
LAURHILL	-48.150*	-56.52	-26.218*	-39.51	-13.308*	-39.00	0.287	5.57
LITTBUFF	-52.876*	-63.21	-25.572*	-40.31	-13.223*	-36.75	-0.279	-4.18
SLOCUM	-48.147*	-62.17	-25.534*	-43.27	-13.394*	-39.59	-0.191	-3.53
VALLFORG	-44.051*	-62.73	-28.881*	-48.39	-13.304*	-42.19	-0.637	-5.89
LITTPINE	-46.072*	-54.49	-22.323*	-36.31	-15.025*	-39.61	-0.397	-7.59
PSUNADP	-45.258*	-57.99	-31.474*	-47.98	-16.668*	-47.72	-2.082*	-40.81
KANE	-45.718*	-58.15	-33.623*	-49.74	-16.330*	-47.08	-2.422*	-50.89
LEADRIDG	-36.253*	-50.16	-23.908*	-39.02	-12.673*	-37.32	-1.891*	-37.00
MILFORD	-41.767*	-60.72	-31.008*	-55.42	-14.582*	-45.39	-2.286*	-33.48
Mean	-46.502	-58.36	-27.956	-44.04	-14.802	-42.18	-0.917	-16.13

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	-3.279*	-17.69	-1.161	-14.17	-0.910*	-32.39	0.798*	118.57	1.227*	66.17
GODDARD	-0.886	-4.46	-1.205	-14.03	-0.815*	-28.88	0.641*	102.27	1.492*	76.61
HILLSCRK	-0.112	-0.81	0.229	4.75	-0.599*	-29.78	1.148*	232.27	1.861*	133.97
LAURHILL	-0.708	-4.35	1.458	26.29	-0.614*	-28.49	0.886*	121.08	1.770*	104.87
LITTBUFF	4.263*	22.47	-1.427	-21.62	-0.890*	-33.66	1.278*	198.03	1.637*	55.68
SLOCUM	1.313	8.57	0.296	6.42	-0.742*	-33.67	1.021*	152.00	0.958*	34.61
VALLFORG	1.497	9.47	-1.715*	-27.42	-2.763*	-53.33	0.999*	153.77	0.787	10.78
LITTPINE	2.161	13.95	0.687	14.11	-0.071	-3.91	1.019*	206.92	1.700*	97.80
PSUNADP	1.464	11.46	-1.145*	-19.92	-0.700*	-39.59	-0.011	-2.78	-1.040*	-40.61
KANE	-1.485	-10.32	-1.180*	-20.65	-0.740*	-42.30	-0.033	-8.04	-1.110*	-47.63
LEADRIDG	1.364	9.66	-0.367	-6.72	-0.575*	-31.36	-0.094	-15.73	-0.905*	-33.91
MILFORD	1.378	13.72	-0.314	-8.12	-0.748*	-37.75	-0.022	-4.76	-1.264*	-26.33
Mean	0.581	4.31	-0.487	-6.76	-0.847	-32.93	0.636	104.47	0.593	36.00

\* p<0.05

Table 14. Estimated changes in wet deposition of individual ions in precipitation from 1983 to 2009.

Site	Hydrogen Ion		Sulfate		Nitrate		Chloride	
	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change	Change (kg/ha)	Percent Change
CROOKCRK	-0.438*	-44.60	-9.756*	-26.33	-8.093*	-33.45	0.163	6.21
GODDARD	-0.607*	-63.22	-16.554*	-44.66	-11.406*	-43.76	-0.004	-0.21
HILLSCRK	-0.342*	-53.48	-8.841*	-37.07	-6.517*	-37.69	0.123	9.30
LAURHILL	-0.592*	-55.03	-15.202*	-37.74	-9.796*	-36.91	0.312	14.10
LITTBUFF	-0.506*	-59.06	-10.536*	-33.53	-6.663*	-29.51	0.141	5.99
SLOCUM	-0.481*	-59.62	-11.760*	-39.45	-7.575*	-35.53	0.058	2.99
VALLFORG	-0.463*	-59.19	-13.929*	-43.87	-7.207*	-34.70	0.250	6.15
LITTPINE	-0.464*	-53.86	-10.706*	-35.43	-9.036*	-38.78	-0.116	-6.34
PSUNADP	-0.398*	-52.25	-12.537*	-40.55	-8.316*	-40.25	-0.534*	-31.64
KANE	-0.572*	-59.60	-20.432*	-51.47	-12.581*	-48.90	-1.053*	-52.56
LEADRIDG	-0.437*	-55.59	-14.716*	-45.76	-9.279*	-41.90	-0.782*	-42.03
MILFORD	-0.388*	-54.50	-13.256*	-47.75	-7.800*	-37.83	-0.427	-17.91
Mean	-0.474	-55.83	-13.185	-40.30	-8.689	-38.27	-0.156	-8.83

Table 14 (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	-0.091	-2.72	0.061	3.76	-0.062	-18.26	0.399*	146.31	0.425*	103.08
GODDARD	-0.368	-9.12	-0.135	-7.53	-0.105*	-28.11	0.275*	105.00	0.350*	74.34
HILLSCRK	0.223	10.07	0.138	16.55	-0.048	-22.56	0.435*	253.60	0.410*	157.36
LAURHILL	0.045	1.24	0.431*	30.64	-0.078	-23.85	0.464*	132.70	0.541*	111.06
LITTBUFF	1.137*	31.42	-0.180	-13.30	-0.087*	-26.60	0.597*	230.30	0.471*	71.38
SLOCUM	0.449	15.47	0.125	13.18	-0.082*	-29.45	0.459*	168.83	0.279*	44.94
VALLFORG	0.599	18.99	-0.236	-17.74	-0.319*	-48.08	0.508*	187.45	0.366	21.03
LITTPINE	0.486	17.17	0.153	15.69	-0.006	-2.72	0.408*	212.91	0.395*	101.73
PSUNADP	0.487	20.89	-0.101	-9.02	-0.065*	-31.30	-0.004	-2.43	-0.177*	-32.54
KANE	-0.426	-13.40	-0.326*	-23.38	-0.115*	-44.24	-0.015	-7.56	-0.314*	-49.46
LEADRIDG	0.050	1.83	-0.157	-13.43	-0.081*	-34.65	-0.057	-22.50	-0.248*	-39.29
MILFORD	0.395	19.73	0.100	12.83	-0.065*	-26.03	0.047	27.14	-0.152	-13.52
Mean	0.249	9.30	-0.011	0.69	-0.093	-27.99	0.293	119.31	0.196	45.84

\* p<0.05

### **Sulfate (SO<sub>4</sub><sup>2-</sup>)**

The statewide mean annual sulfate concentration in 2009 was 1.4 mg/L, with growing season mean of 1.5 mg/L and dormant season mean of 1.2 mg/L (Table 15). Sulfate concentrations have decreased approximately 44% since 1983 (see Table 13). Despite the dramatic decreases, sulfate concentrations and wet sulfate deposition in Pennsylvania continue to be higher than in most regions in the United States (Figure 3). The state received approximately 15.1 kg/ha of wet sulfate deposition in 2009 (Table 15).

### **Nitrate (NO<sub>3</sub><sup>-</sup>)**

The statewide mean annual nitrate concentration in 2009 was 1.0 mg/L, with growing season mean of 0.88 mg/L and dormant season mean of 1.2 mg/L (Table 16). Nitrate concentrations have decreased approximately 38% since 1983 (see Table 13). Despite the dramatic reductions, nitrate concentrations in precipitation and rates of wet nitrate deposition in Pennsylvania continue to be higher than in most regions in the United States (Figure 4). The state received approximately 10.9 kg/ha of wet nitrate deposition in 2009 (Table 16).

### **Ammonium (NH<sub>4</sub><sup>+</sup>)**

The statewide mean annual ammonium concentration in 2009 was 0.28 mg/L, with growing season mean of 0.29 mg/L and dormant season mean of 0.26 mg/L (Table 17). Ammonium concentrations have decreased approximately 9% since 1983 (see Table 13). Rates of ammonium deposition in Pennsylvania are not as high as the heavily agricultural mid-west, but are nonetheless important (Figure 5). As rates of nitrate deposition have declined, ammonia deposition is becoming more important as a fraction of total atmospheric nitrogen deposition. The state received approximately 3.1 kg/ha of wet ammonia deposition in 2009 (Table 17).

### **Base Cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>)**

Base cation (calcium, magnesium, sodium, and potassium) concentrations occur in precipitation at very low concentrations (Tables 18-21) with annual means ranging from around 0.12 mg/L for calcium to around 0.02 mg/L for magnesium. Calcium and magnesium concentrations have generally decreased the past 25 years where as sodium and potassium concentrations have increased (Table 12). 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 and coastal sea sprays are important sources for these cations.

### **Chloride (Cl<sup>-</sup>)**

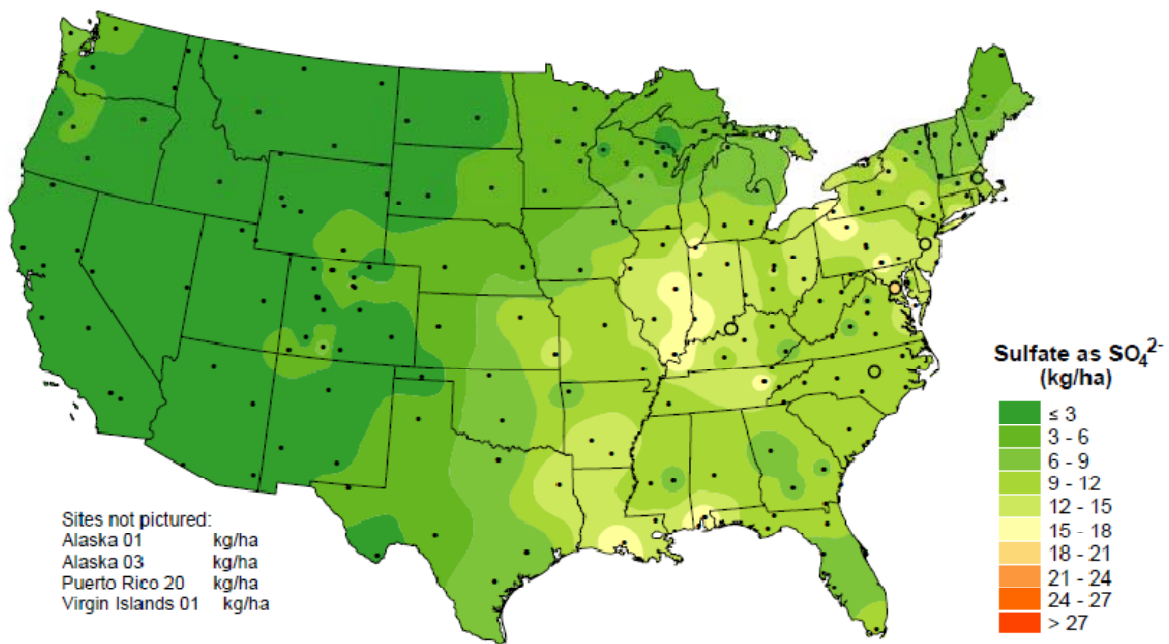
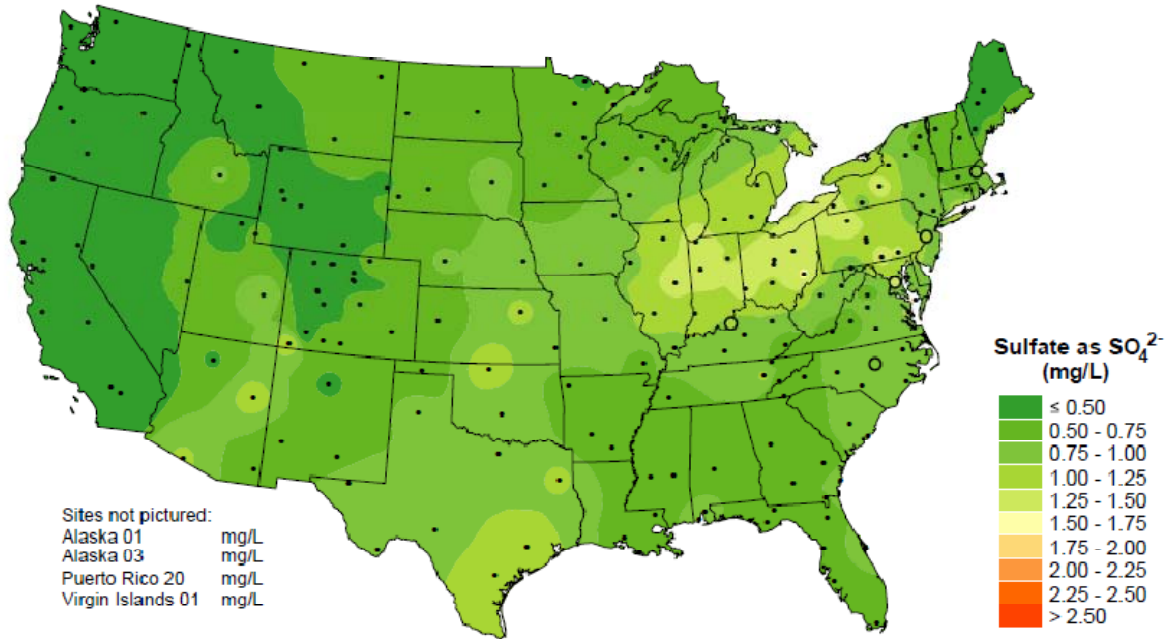
Sea-salts can be an important source of chloride concentrations in south eastern Pennsylvania (Table 22), while coal combustion and the release of hydrochloric acids is an important source in western Pennsylvania. Mean annual chloride concentrations range from 0.08 mg/L to 0.33 mg/L across the state (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 12).

### **Conductance (Cl)**

Conductivity gives a measure of total dissolved solids in precipitation, and is used to aid in our quality assurance program. Mean annual specific conductance ranged from 11-21 uS/cm across the state (Table 23), with a lot of variability over time (e.g. seasonally) and space (site to site).

**Figure 3.** Mean annual sulfate ion concentrations in precipitation, and mean annual atmospheric sulfate deposition for the USA in 2009.

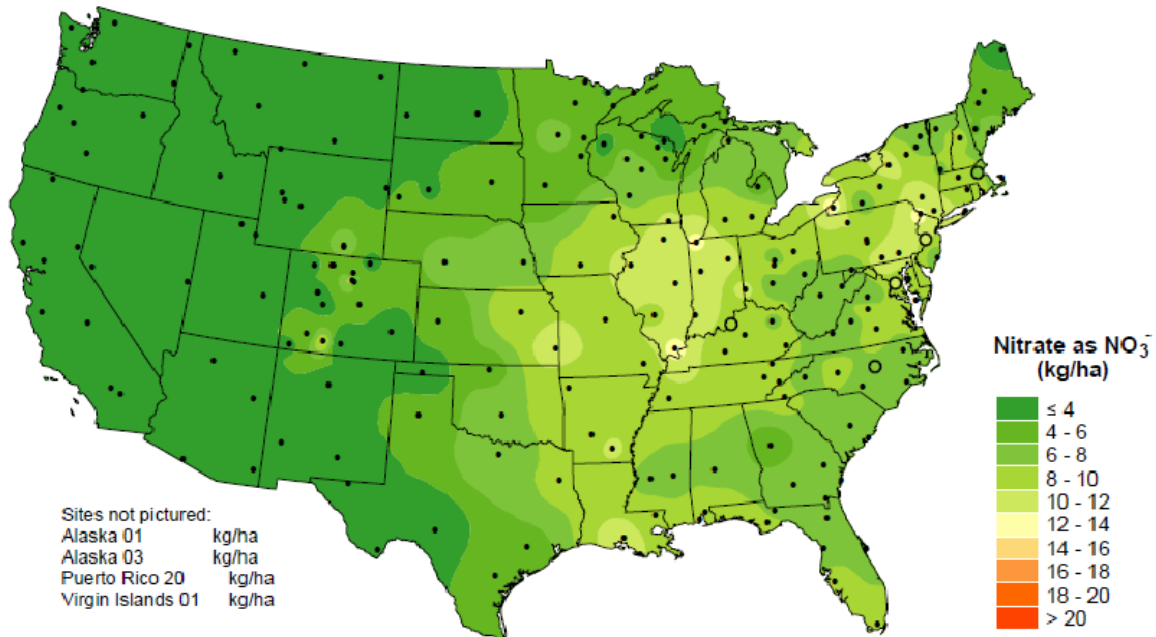
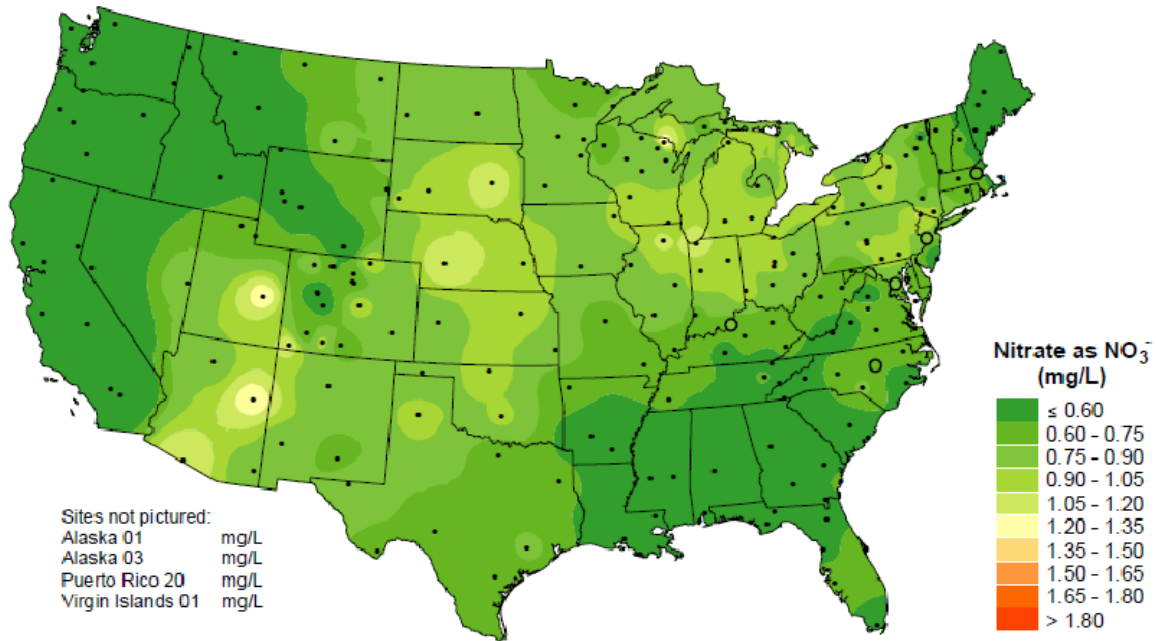
*Note: at the time of this draft report (8/12/2010), official isopleth maps for 2009 from the National Trends Network are not yet available. Preliminary versions were obtained from R. Claybrooke, NADP Program Office, on 8/12/2010. These draft figures will soon be updated and color/contrast will be adjusted.*



National Atmospheric Deposition Program/National Trends Network

**Figure 4.** Annual nitrate ion concentration in precipitation (top) and nitrate ion wet deposition (bottom) for the USA in 2009.

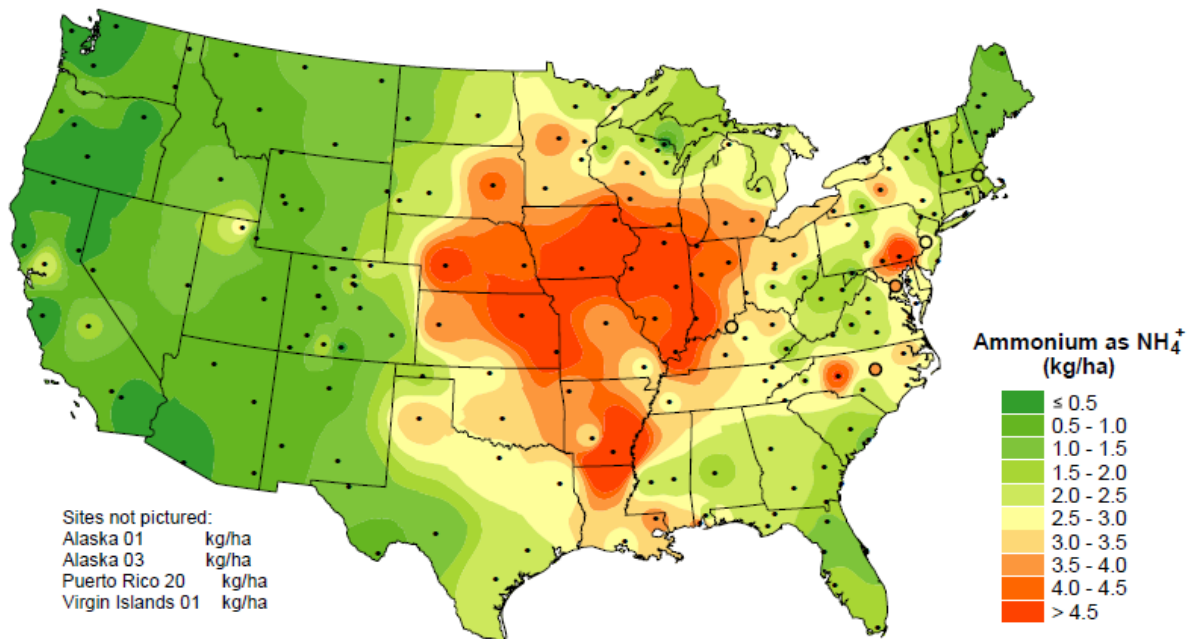
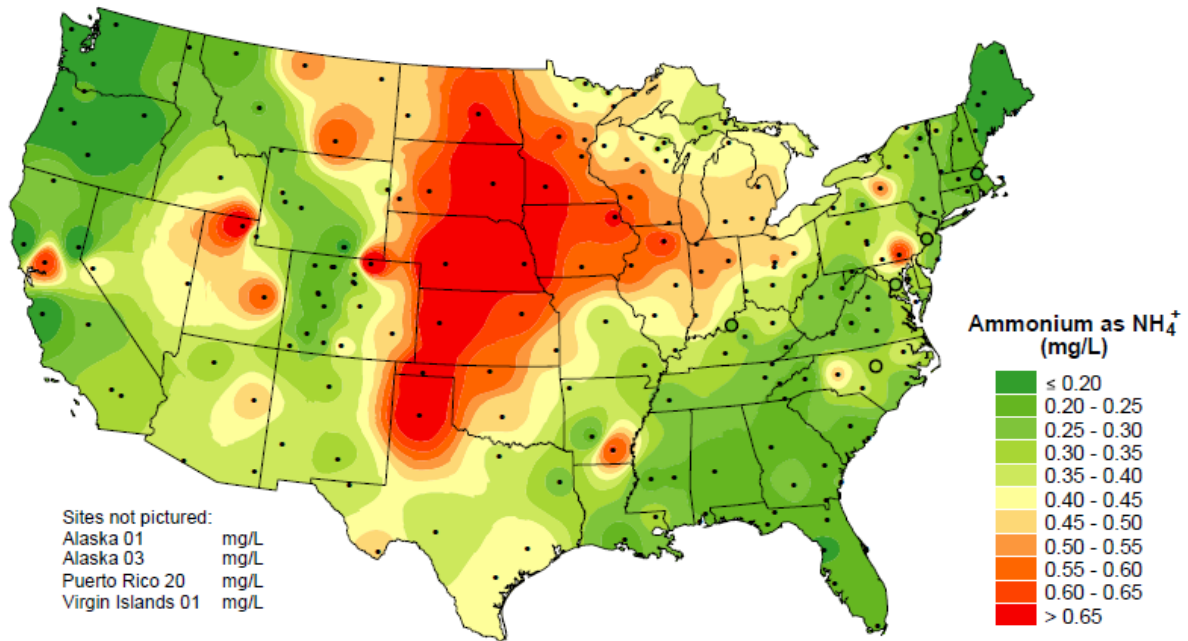
*Note: at the time of this draft report (8/12/2010), official isopleth maps for 2009 from the National Trends Network are not yet available. Preliminary versions were obtained from R. Claybrooke, NADP Program Office, on 8/12/2010. These draft figures will soon be updated and color/contrast will be adjusted.*



National Atmospheric Deposition Program/National Trends Network

**Figure 5.** Annual ammonium ion concentration in precipitation (top) and ammonium ion wet deposition (bottom) for the USA in 2009.

*Note: at the time of this draft report (8/12/2010), official isopleth maps for 2009 from the National Trends Network are not yet available. Preliminary versions were obtained from R. Claybrooke, NADP Program Office, on 8/12/2010. These draft figures will soon be updated and color/contrast will be adjusted.*



National Atmospheric Deposition Program/National Trends Network

Table 15. Annual and seasonal sulfate ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

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	1.587	1.700	1.417	17.37	11.17	6.19	42.94	25.86	17.08	0.15	0.02	0.13
CROOKCRK	2.015	2.201	1.743	21.99	14.24	7.75	42.87	25.48	17.39	0.11	0.00	0.11
LAURHILL	1.405	1.398	1.416	17.65	10.29	7.36	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	1.748	1.755	1.738	18.92	10.81	8.11	41.08	24.13	16.95	1.53	0.12	1.41
PRESQISL	1.449	1.462	1.430	15.50	9.00	6.50	41.47	24.06	17.41	0.65	0.18	0.47
KANE	1.459	1.693	1.043	17.42	12.83	4.59	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	1.611	1.701	1.464	18.14	11.39	6.75	44.06	26.39	17.67	0.51	0.06	0.46
Central Pennsylvania												
LITTPINE	1.401	1.414	1.380	13.27	8.65	4.62	35.16	22.11	13.05	2.11	1.99	0.12
HILLSCRK	1.274	1.293	1.232	10.89	7.44	3.45	33.38	22.64	10.74	0.29	0.01	0.28
LITTBUFF	1.470	1.511	1.382	18.01	12.73	5.28	45.13	30.81	14.32	3.08	2.37	0.71
PSUNADP	1.238	1.365	1.005	12.82	9.44	3.38	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	1.241	1.369	1.016	11.90	8.70	3.19	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	1.238	1.270	1.197	12.23	8.03	4.20	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	1.290	1.395	1.128	16.17	11.15	5.01	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	1.307	1.374	1.191	13.61	9.45	4.16	36.46	23.24	13.21	4.21	3.69	0.52
Eastern Pennsylvania												
SLOCUM	1.266	1.304	1.173	12.65	9.48	3.17	35.09	24.78	10.31	4.18	3.85	0.33
VALLFORG	1.102	1.157	0.989	14.76	10.37	4.39	52.45	35.29	17.16	0.31	0.01	0.30
MILLERSV	1.231	1.315	1.009	14.36	10.61	3.75	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	0.972	1.116	0.760	11.55	8.29	3.26	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	1.143	1.223	0.983	13.33	9.69	3.64	42.00	28.31	13.68	4.15	2.92	1.23
State Mean	1.376	1.454	1.239	15.14	10.19	4.95	40.44	25.55	14.90	2.89	2.23	0.66

Table 16. Annual and seasonal nitrate ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

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	0.994	0.907	1.125	10.88	5.96	4.92	42.94	25.86	17.08	0.15	0.02	0.13
CROOKCRK	1.092	1.027	1.188	11.93	6.65	5.28	42.87	25.48	17.39	0.11	0.00	0.11
LAURHILL	0.946	0.753	1.219	11.88	5.54	6.33	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	1.101	0.946	1.321	11.99	5.83	6.16	41.08	24.13	16.95	1.53	0.12	1.41
PRESQISL	1.321	0.907	1.893	14.18	5.58	8.60	41.47	24.06	17.41	0.65	0.18	0.47
KANE	0.836	0.878	0.761	10.00	6.65	3.35	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	1.048	0.903	1.251	11.81	6.04	5.77	44.06	26.39	17.67	0.51	0.06	0.46
Central Pennsylvania												
LITTPINE	1.011	0.828	1.321	9.49	5.07	4.42	35.16	22.11	13.05	2.11	1.99	0.12
HILLSCRK	0.921	0.814	1.147	7.89	4.68	3.21	33.38	22.64	10.74	0.29	0.01	0.28
LITTBUFF	1.084	0.959	1.351	13.24	8.08	5.16	45.13	30.81	14.32	3.08	2.37	0.71
PSUNADP	0.866	0.789	1.006	8.84	5.46	3.38	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	0.966	0.872	1.131	9.10	5.54	3.55	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	0.854	0.733	1.009	8.17	4.64	3.54	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	0.936	0.878	1.025	11.57	7.01	4.56	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	0.948	0.839	1.141	9.76	5.78	3.97	36.46	23.24	13.21	4.21	3.69	0.52
Eastern Pennsylvania												
SLOCUM	0.937	0.820	1.217	9.25	5.96	3.29	35.09	24.78	10.31	4.18	3.85	0.33
VALLFORG	0.959	0.933	1.012	12.85	8.36	4.49	52.45	35.29	17.16	0.31	0.01	0.30
MILLERSV	0.965	0.976	0.936	11.35	7.87	3.48	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	1.057	1.007	1.131	12.33	7.48	4.86	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	0.979	0.934	1.074	11.45	7.42	4.03	42.00	28.31	13.68	4.15	2.92	1.23
State Mean	0.991	0.884	1.164	10.88	6.26	4.62	40.44	25.55	14.90	2.89	2.23	0.66

Table 17. Annual and seasonal ammonium ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

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	0.274	0.302	0.233	3.00	1.98	1.02	42.94	25.86	17.08	0.15	0.02	0.13
CROOKCRK	0.230	0.251	0.200	2.52	1.63	0.89	42.87	25.48	17.39	0.11	0.00	0.11
LAURHILL	0.223	0.212	0.238	2.80	1.56	1.24	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	0.283	0.288	0.275	3.06	1.78	1.28	41.02	24.07	16.95	1.59	0.18	1.41
PRESQISL	0.299	0.268	0.340	3.20	1.65	1.55	41.47	24.06	17.41	0.65	0.18	0.47
KANE	0.213	0.241	0.163	2.55	1.83	0.72	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	0.254	0.260	0.241	2.85	1.74	1.11	44.05	26.38	17.67	0.52	0.06	0.46
Central Pennsylvania												
LITTPINE	0.256	0.258	0.252	2.42	1.58	0.84	35.16	22.11	13.05	2.11	1.99	0.12
HILLSCRK	0.227	0.225	0.230	1.94	1.30	0.64	33.38	22.64	10.74	0.29	0.01	0.28
LITTBUFF	0.420	0.453	0.351	5.15	3.81	1.34	45.13	30.81	14.32	3.08	2.37	0.71
PSUNADP	0.223	0.241	0.191	2.31	1.67	0.64	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	0.258	0.273	0.232	2.46	1.73	0.73	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	0.246	0.264	0.222	2.45	1.67	0.78	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	0.322	0.332	0.307	4.02	2.65	1.36	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	0.279	0.292	0.255	2.97	2.06	0.91	36.46	23.24	13.21	4.21	3.69	0.52
Eastern Pennsylvania												
SLOCUM	0.296	0.322	0.232	2.97	2.34	0.63	35.09	24.78	10.31	4.18	3.85	0.33
VALLFORG	0.249	0.259	0.230	3.34	2.32	1.02	52.45	35.29	17.16	0.31	0.01	0.30
MILLERSV	0.531	0.533	0.528	6.26	4.30	1.96	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	0.198	0.228	0.155	2.36	1.69	0.66	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	0.319	0.336	0.286	3.73	2.66	1.07	42.00	28.31	13.68	4.15	2.92	1.23
State Mean	0.279	0.291	0.258	3.11	2.09	1.02	40.44	25.54	14.90	2.89	2.23	0.66

Table 18. Annual and seasonal calcium ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

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	0.149	0.124	0.186	1.63	0.82	0.81	42.94	25.86	17.08	0.15	0.02	0.13
CROOKCRK	0.168	0.156	0.184	1.83	1.01	0.82	42.80	25.41	17.39	0.18	0.07	0.11
LAURHILL	0.151	0.135	0.173	1.89	0.99	0.90	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	0.192	0.127	0.283	2.10	0.78	1.32	41.02	24.07	16.95	1.59	0.18	1.41
PRESQISL	0.190	0.193	0.186	2.04	1.19	0.85	41.47	24.06	17.41	0.65	0.18	0.47
KANE	0.085	0.084	0.089	1.03	0.63	0.39	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	0.156	0.137	0.184	1.75	0.90	0.85	44.04	26.37	17.67	0.54	0.08	0.46
Central Pennsylvania												
LITTPINE	0.117	0.099	0.146	1.10	0.61	0.49	35.16	22.11	13.05	2.11	1.99	0.12
HILLSCRK	0.127	0.112	0.159	1.09	0.64	0.44	33.38	22.64	10.74	0.29	0.01	0.28
LITTBUFF	0.122	0.112	0.145	1.50	0.94	0.55	45.13	30.81	14.32	3.08	2.37	0.71
PSUNADP	0.092	0.084	0.108	0.94	0.58	0.36	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	0.109	0.101	0.123	1.03	0.64	0.39	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	0.096	0.081	0.114	0.91	0.51	0.40	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	0.078	0.069	0.093	0.96	0.55	0.41	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	0.106	0.094	0.127	1.07	0.64	0.44	36.46	23.24	13.21	4.21	3.69	0.52
Eastern Pennsylvania												
SLOCUM	0.117	0.100	0.159	1.15	0.72	0.43	35.09	24.78	10.31	4.18	3.85	0.33
VALLFORG	0.108	0.111	0.101	1.45	1.00	0.45	52.45	35.29	17.16	0.31	0.01	0.30
MILLERSV	0.075	0.077	0.072	0.89	0.62	0.27	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	0.073	0.073	0.072	0.85	0.54	0.31	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	0.093	0.090	0.101	1.08	0.72	0.36	42.00	28.31	13.68	4.15	2.92	1.23
State Mean	0.120	0.108	0.141	1.32	0.75	0.56	40.44	25.54	14.90	2.90	2.23	0.66

Table 19. Annual and seasonal magnesium ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

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	0.020	0.020	0.019	0.22	0.13	0.08	42.94	25.86	17.08	0.15	0.02	0.13
CROOKCRK	0.023	0.024	0.021	0.25	0.16	0.09	42.80	25.41	17.39	0.18	0.07	0.11
LAURHILL	0.019	0.022	0.015	0.24	0.16	0.08	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	0.037	0.027	0.052	0.40	0.16	0.24	41.02	24.07	16.95	1.59	0.18	1.41
PRESQISL	0.032	0.031	0.033	0.34	0.19	0.15	41.47	24.06	17.41	0.65	0.18	0.47
KANE	0.013	0.013	0.012	0.15	0.10	0.05	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	0.024	0.023	0.025	0.27	0.15	0.12	44.04	26.37	17.67	0.54	0.08	0.46
Central Pennsylvania												
LITTPINE	0.018	0.017	0.020	0.17	0.10	0.07	35.16	22.11	13.05	2.11	1.99	0.12
HILLSCRK	0.018	0.018	0.019	0.16	0.10	0.05	33.38	22.64	10.74	0.29	0.01	0.28
LITTBUFF	0.024	0.026	0.019	0.29	0.22	0.07	45.13	30.81	14.32	3.08	2.37	0.71
PSUNADP	0.014	0.013	0.015	0.14	0.09	0.05	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	0.017	0.017	0.018	0.16	0.11	0.06	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	0.016	0.014	0.018	0.15	0.09	0.06	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	0.016	0.016	0.015	0.20	0.13	0.07	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	0.018	0.017	0.018	0.18	0.12	0.06	36.46	23.24	13.21	4.21	3.69	0.52
Eastern Pennsylvania												
SLOCUM	0.021	0.022	0.019	0.21	0.16	0.05	35.09	24.78	10.31	4.18	3.85	0.33
VALLFORG	0.029	0.029	0.031	0.40	0.26	0.14	52.45	35.29	17.16	0.31	0.01	0.30
MILLERSV	0.018	0.019	0.016	0.21	0.15	0.06	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	0.017	0.018	0.015	0.20	0.14	0.07	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	0.021	0.022	0.020	0.25	0.18	0.08	42.00	28.31	13.68	4.15	2.92	1.23
State Mean	0.021	0.020	0.021	0.23	0.14	0.08	40.44	25.54	14.90	2.90	2.23	0.66

Table 20. Annual and seasonal potassium ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

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	0.030	0.025	0.039	0.33	0.16	0.17	42.94	25.86	17.08	0.15	0.02	0.13
CROOKCRK	0.034	0.030	0.041	0.38	0.20	0.18	42.80	25.41	17.39	0.18	0.07	0.11
LAURHILL	0.050	0.057	0.039	0.62	0.42	0.20	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	0.072	0.058	0.092	0.79	0.36	0.43	41.02	24.07	16.95	1.59	0.18	1.41
PRESQISL	0.050	0.057	0.039	0.53	0.35	0.18	41.47	24.06	17.41	0.65	0.18	0.47
KANE	0.012	0.012	0.013	0.15	0.09	0.06	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	0.041	0.040	0.044	0.47	0.26	0.20	44.04	26.37	17.67	0.54	0.08	0.46
Central Pennsylvania												
LITTPINE	0.045	0.034	0.065	0.42	0.21	0.22	35.16	22.11	13.05	2.11	1.99	0.12
HILLSCRK	0.047	0.051	0.037	0.40	0.30	0.10	33.38	22.64	10.74	0.29	0.01	0.28
LITTBUFF	0.055	0.065	0.036	0.68	0.54	0.14	45.13	30.81	14.32	3.08	2.37	0.71
PSUNADP	0.013	0.011	0.015	0.13	0.08	0.05	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	0.021	0.024	0.015	0.20	0.15	0.05	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	0.034	0.045	0.021	0.36	0.28	0.07	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	0.012	0.012	0.012	0.15	0.10	0.05	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	0.032	0.034	0.029	0.33	0.24	0.10	36.46	23.24	13.21	4.21	3.69	0.52
Eastern Pennsylvania												
SLOCUM	0.058	0.057	0.061	0.58	0.42	0.16	35.09	24.78	10.31	4.18	3.85	0.33
VALLFORG	0.035	0.034	0.038	0.47	0.31	0.17	52.45	35.29	17.16	0.31	0.01	0.30
MILLERSV	0.016	0.017	0.014	0.19	0.13	0.05	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	0.022	0.027	0.013	0.26	0.20	0.06	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	0.033	0.034	0.031	0.37	0.26	0.11	42.00	28.31	13.68	4.15	2.92	1.23
State Mean	0.036	0.036	0.035	0.39	0.25	0.14	40.44	25.54	14.90	2.90	2.23	0.66

Table 21. Annual and seasonal sodium ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

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	0.061	0.042	0.090	0.67	0.28	0.39	42.94	25.86	17.08	0.15	0.02	0.13
CROOKCRK	0.064	0.038	0.101	0.70	0.25	0.45	42.80	25.41	17.39	0.18	0.07	0.11
LAURHILL	0.054	0.043	0.069	0.68	0.32	0.36	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	0.129	0.037	0.260	1.44	0.23	1.21	41.02	24.07	16.95	1.59	0.18	1.41
PRESQISL	0.063	0.026	0.113	0.68	0.16	0.51	41.47	24.06	17.41	0.65	0.18	0.47
KANE	0.034	0.023	0.054	0.41	0.17	0.24	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	0.067	0.035	0.115	0.76	0.23	0.53	44.04	26.37	17.67	0.54	0.08	0.46
Central Pennsylvania												
LITTPINE	0.074	0.038	0.135	0.68	0.23	0.45	35.16	22.11	13.05	2.11	1.99	0.12
HILLSCRK	0.050	0.037	0.077	0.43	0.21	0.21	33.38	22.64	10.74	0.29	0.01	0.28
LITTBUFF	0.084	0.075	0.104	1.02	0.63	0.40	45.13	30.81	14.32	3.08	2.37	0.71
PSUNADP	0.041	0.023	0.074	0.40	0.16	0.25	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	0.046	0.027	0.079	0.42	0.17	0.25	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	0.064	0.037	0.098	0.58	0.23	0.34	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	0.080	0.080	0.080	1.00	0.64	0.36	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	0.063	0.045	0.092	0.65	0.33	0.32	36.46	23.24	13.21	4.21	3.69	0.52
Eastern Pennsylvania												
SLOCUM	0.085	0.073	0.114	0.84	0.53	0.31	35.09	24.78	10.31	4.18	3.85	0.33
VALLFORG	0.167	0.108	0.286	2.24	0.97	1.27	52.45	35.29	17.16	0.31	0.01	0.30
MILLERSV	0.094	0.092	0.100	1.11	0.74	0.37	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	0.105	0.082	0.138	1.20	0.61	0.59	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	0.113	0.089	0.160	1.35	0.71	0.64	42.00	28.31	13.68	4.15	2.92	1.23
State Mean	0.076	0.052	0.116	0.85	0.38	0.47	40.44	25.54	14.90	2.90	2.23	0.66

Table 22. Annual and seasonal chloride ion analyses of precipitation collected at sites throughout Pennsylvania during 2009.

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	0.146	0.110	0.201	1.60	0.72	0.88	42.94	25.86	17.08	0.15	0.02	0.13
CROOKCRK	0.224	0.156	0.325	2.45	1.01	1.45	42.87	25.48	17.39	0.11	0.00	0.11
LAURHILL	0.141	0.113	0.179	1.77	0.84	0.93	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	0.279	0.128	0.495	3.09	0.79	2.31	41.08	24.13	16.95	1.53	0.12	1.41
PRESQISL	0.164	0.104	0.246	1.76	0.64	1.12	41.47	24.06	17.41	0.65	0.18	0.47
KANE	0.078	0.065	0.101	0.94	0.49	0.45	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	0.172	0.113	0.258	1.94	0.75	1.19	44.06	26.39	17.67	0.51	0.06	0.46
Central Pennsylvania												
LITTPINE	0.149	0.118	0.201	1.39	0.72	0.67	35.16	22.11	13.05	2.11	1.99	0.12
HILLSCRK	0.129	0.103	0.185	1.11	0.59	0.52	33.38	22.64	10.74	0.29	0.01	0.28
LITTBUFF	0.195	0.173	0.242	2.38	1.46	0.93	45.13	30.81	14.32	3.08	2.37	0.71
PSUNADP	0.102	0.070	0.159	1.02	0.49	0.53	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	0.108	0.077	0.161	1.00	0.49	0.51	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	0.122	0.083	0.171	1.13	0.53	0.60	27.54	15.45	12.09	11.16	9.44	1.72
ARENDSV	0.166	0.169	0.161	2.06	1.35	0.72	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	0.139	0.113	0.183	1.44	0.80	0.64	36.46	23.24	13.21	4.21	3.69	0.52
Eastern Pennsylvania												
SLOCUM	0.200	0.181	0.246	1.98	1.32	0.67	35.09	24.78	10.31	4.18	3.85	0.33
VALLFORG	0.334	0.235	0.538	4.49	2.11	2.39	52.45	35.29	17.16	0.31	0.01	0.30
MILLERSV	0.186	0.182	0.195	2.19	1.47	0.72	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	0.190	0.162	0.231	2.19	1.20	0.99	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	0.227	0.190	0.303	2.72	1.52	1.19	42.00	28.31	13.68	4.15	2.92	1.23
State Mean	0.171	0.131	0.238	1.92	0.95	0.96	40.44	25.55	14.90	2.89	2.23	0.66

Table 23. Annual and seasonal specific conductance analyses of precipitation collected at sites throughout Pennsylvania during 2009.

Region/Site	Volume Weighted Mean Conductance (us/cm)			Precipitation Analyzed (Inches)			Precipitation Not Analyzed (Inches)		
	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.	Annual	Grow.	Dorm.
Western Pennsylvania									
GODDARD	14.96	15.52	14.11	42.99	25.86	17.13	0.10	0.02	0.08
CROOKCRK	20.84	21.58	19.76	42.88	25.48	17.40	0.10	0.00	0.10
LAURHILL	13.56	12.71	14.77	49.43	28.97	20.46	0.01	0.01	0.00
ALLEPORT	17.60	16.15	19.54	42.14	24.13	18.01	0.47	0.12	0.35
PRESQISL	14.85	12.34	18.31	41.58	24.06	17.52	0.54	0.18	0.36
KANE	14.89	17.00	11.12	46.55	29.84	16.71	0.63	0.00	0.63
Region Mean	16.12	15.88	16.27	44.26	26.39	17.87	0.31	0.06	0.25
Central Pennsylvania									
LITTPINE	14.63	14.02	15.68	35.19	22.14	13.05	2.08	1.96	0.12
HILLSCRK	12.62	12.16	13.56	33.48	22.64	10.84	0.19	0.01	0.18
LITTBUFF	13.44	12.66	15.10	45.17	30.81	14.36	3.04	2.37	0.67
PSUNADP	13.16	13.51	12.53	36.54	23.60	12.94	3.92	3.62	0.30
LEADRIDG	13.13	13.40	12.65	33.61	21.46	12.15	3.80	3.58	0.22
YOWOCRK	12.64	12.12	13.30	27.54	15.45	12.09	11.16	9.44	1.72
ARENDTSV	13.32	13.73	12.67	43.85	26.64	17.21	5.12	4.82	0.30
Region Mean	13.28	13.09	13.64	36.48	23.25	13.23	4.19	3.69	0.50
Eastern Pennsylvania									
SLOCUM	12.09	11.59	13.28	35.12	24.78	10.34	4.15	3.85	0.30
VALLFORG	12.09	12.27	11.73	52.46	35.30	17.16	0.30	0.00	0.30
MILLERSV	11.24	11.87	9.57	41.01	29.70	11.31	5.39	2.07	3.33
MILFORD	13.18	13.65	12.49	39.44	23.48	15.96	6.70	5.76	0.94
Region Mean	12.15	12.35	11.77	42.01	28.32	13.69	4.14	2.92	1.22
State Mean	14.01	13.90	14.13	40.53	25.55	14.98	2.81	2.22	0.58

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