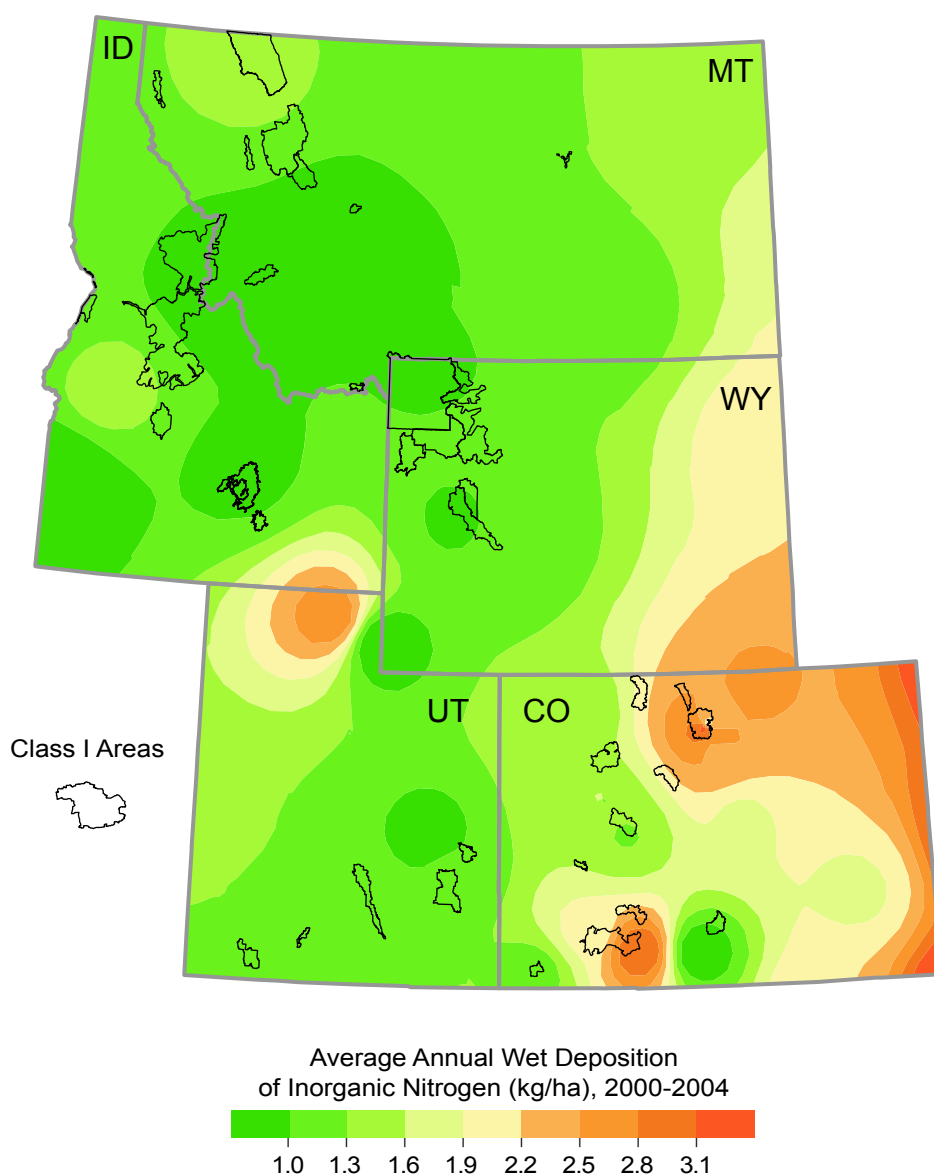


National Atmospheric Deposition Program 2004 Annual Summary



2004 Highlights

In 2004, scientists, students, educators, and others logged more than 300,000 sessions on the National Atmospheric Deposition Program (NADP) Web site (see the back cover for the address). This site had more than 75,000 unique visitors, nearly double the number in 2000, and there are now more than 28,000 registered users. The site receives more than a million hits annually. Records show that 61 percent of users study atmospheric deposition or its effects on aquatic and terrestrial ecosystems and cultural resources, and 39 percent use NADP data for educational purposes.

Educators included NADP maps and other information in textbooks, and the NADP Web site was used in public education and outreach materials. For example:

- Color-contour maps from the NADP National Trends Network (NTN) appeared in two new college textbooks: *Environment, The Science Behind the Stories* and *Chemistry in Context, Applying Chemistry to Society*.
- “Measuring the pH of Rainwater,” the American Chemical Society’s Earth Day 2004 activity, introduced students nationwide to a special NADP-hosted Web site. Students learned about collecting rain samples and measuring pH, and reported their own sample measurements (see figure on page 3).

Government agencies continued to use NADP data to assess the nation’s air quality and evaluate policy decisions. For example:

- The United States-Canada International Joint Commission, published *The United States - Canada Air Quality Agreement, Progress Report 2004*, which used NADP Atmospheric Integrated Research Monitoring Network (AIRMoN) and NTN data in maps

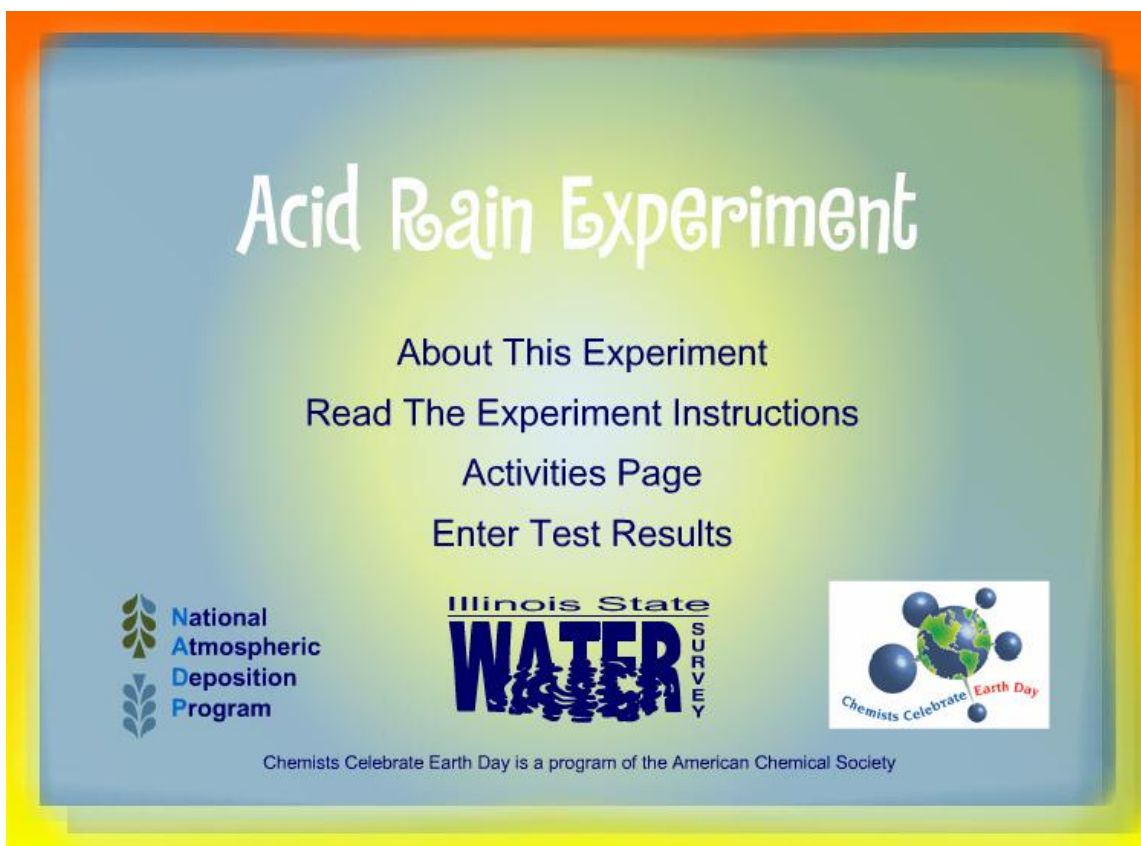
showing 1990-2002 sulfate and nitrate deposition changes.

- In its report, *Air Quality Management in the United States*, the National Research Council cited all three NADP networks, the NTN, AIRMoN, and Mercury Deposition Network (MDN) as essential parts of the U.S. air-quality management system and displayed selected maps showing NADP data applications in assessing benefits of air-quality management.

The NADP was involved in a field of emerging scientific interest: tracking atmospheric transport/deposition of bioaerosols. These fine particles are of biological origin.

- During the growing season, filters from NTN samples were sent to the Cereal Disease Laboratory, a U.S. Department of Agriculture facility. There scientists used microbiological tests to demonstrate the presence of wheat stem rust (*Puccinia graminis*) DNA in some Midwestern rain samples. Airborne spores captured by rainfall transmit the fungal disease.

[About the cover: Pictured is the 5-year (2000-2004) average annual wet deposition of inorganic nitrogen from nitrate and ammonium in five Rocky Mountain states. This map illustrates deposition fluxes in that region. The Class I areas, indicated on the map, are national parks and wilderness areas in which the Clean Air Act seeks to preserve, protect, and enhance air quality. The map is based on measurements in a broader area at NTN sites meeting NADP data completeness criteria (<http://nadp.sws.uiuc.edu/documentation/completeness.asp>). Compare this map with the one on page 11 for a national perspective. Except for the criterion requiring precipitation depth measurements at least 90 percent of the time, criteria were relaxed from 75 percent to 60 percent to include sites with high proportions of snow. The NADP collector has a poor snow-capture efficiency; and 23 NTN sites (59 percent) in the five states are above 2000 meters and generally receive more than half of their precipitation as snow. Data from 33 NTN sites in the five states met these relaxed criteria.]



As part of Earth Day 2004, students learned about rainwater pH on a special NADP-hosted Web site.

NADP Background

In 1977, U.S. State Agricultural Experiment Stations (SAES) organized a project, later titled NADP, to measure atmospheric deposition and study its effects on the environment. Sites in the NADP precipitation chemistry network began operations in 1978 with the goal of providing data on the amounts, trends, and geographic distributions of acids, nutrients, and base cations in precipitation. The network grew rapidly in the early 1980s. Much of this expansion was funded by the National Acid Precipitation Assessment Program (NAPAP), established in 1981 to improve understanding of the causes and effects of acidic precipitation. Reflecting the federal NAPAP role in the NADP, the network name was changed to NADP/NTN. Today, the NADP is SAES National Research Support Project - 3. The network has more than 250 sites and is designated NTN.

A second network (AIRMoN) joined the NADP in 1992, and had eight sites at the end of 2004. Although measuring the same chemicals as NTN, AIRMoN sampling is daily rather than weekly. These higher resolution samples enhance researchers' ability to evaluate how emissions affect precipitation chemistry using computer simulations of atmospheric transport and pollutant removal. This network also evaluates alternative sampling and preservation methods.

The MDN joined the NADP in 1996, and had 89 sites at the end of 2004. All MDN samples are analyzed for total mercury, and some for the more toxic methyl mercury. Forty-five states have advisories warning people to limit consumption of fish and wildlife from all or designated water bodies because of mercury contamination (see <http://www.epa.gov/ost/fish>). Researchers use MDN data to evaluate the role of precipitation as a source of mercury in these water bodies.

National Trends Network

The NTN is the only network providing a long-term record of precipitation chemistry across the United States. Sites predominantly are located away from urban areas and point sources of pollution. Each site has a precipitation chemistry collector and gage. The automated collector ensures that the sample is exposed only during precipitation (wet-only-sampling).

Site operators collect samples weekly on Tuesday morning, using only containers cleaned at the Central Analytical Laboratory (CAL) at the Illinois State Water Survey (ISWS). They weigh the collection bucket to determine sample volume and transfer the sample from the collection bucket to a shipping bottle. For volumes less than 70 milliliters (mL), operators send the samples to the CAL for analysis, and data entry, verification, and screening. For samples of 70 mL or more, they first measure pH and conductance on a 16 mL aliquot before sending the remainder to the CAL.

The CAL measures conductance and calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), and free acidity (H^+ as pH). The CAL also measures orthophosphate, but only for quality assurance as an indicator of sample contamination.

The CAL reviews field and laboratory data for completeness and accuracy, and flags samples that were mishandled, compromised by precipitation collector failures, or grossly contaminated. The CAL delivers all data and information to the NADP Program Office, which applies a final set of checks and resolves remaining discrepancies. Data then are made available on the NADP Web site.

Effective January 2005, the NADP discontinued support of NTN site operator measurements of pH and conductance (<http://nadp.sws.uiuc.edu/lib/brochures/FieldChem.pdf>). The pH maps on

the next page include measurements from 2004, the final year of field chemistry measurements.

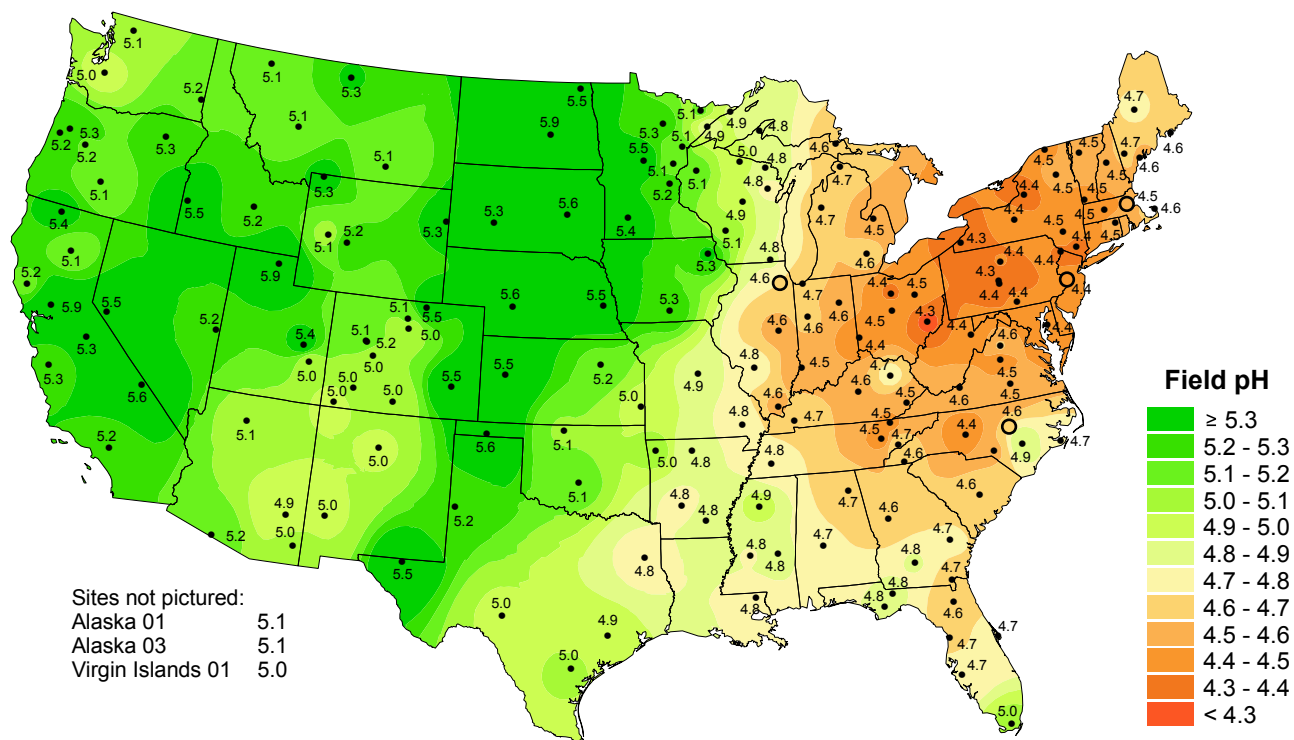
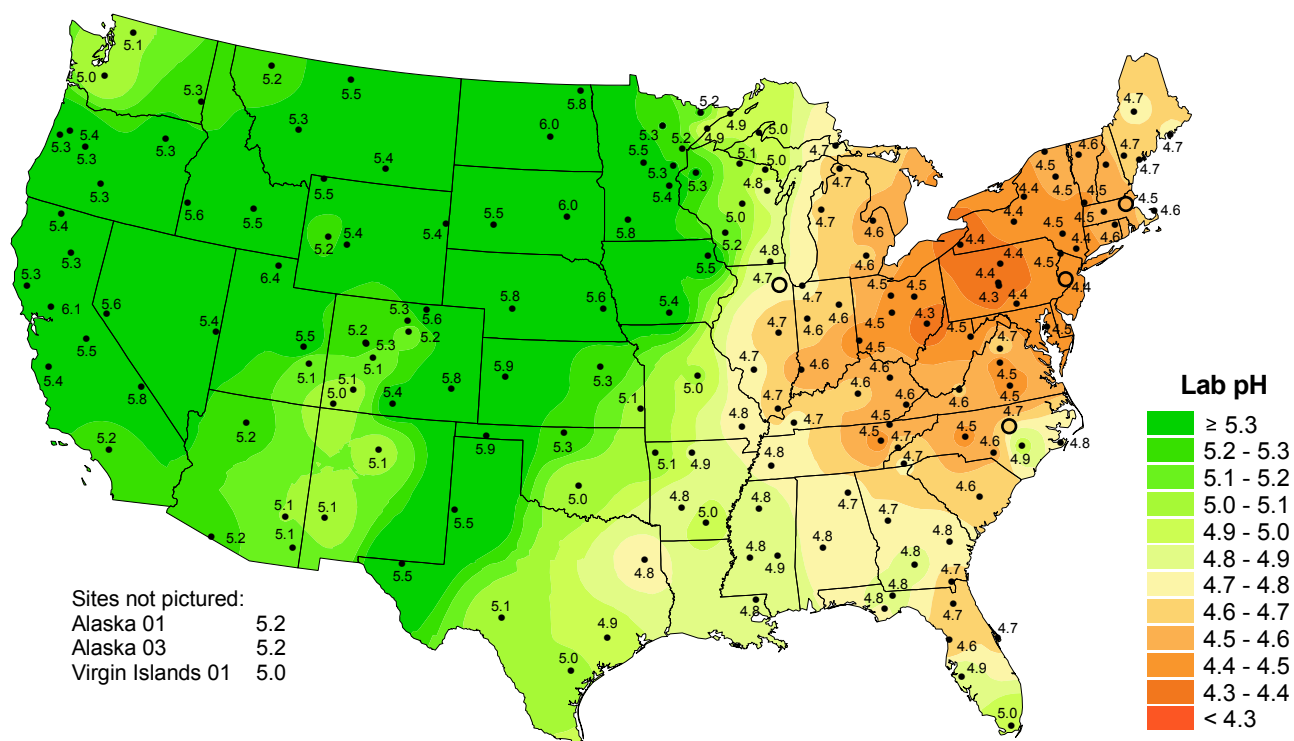
NTN Maps

The NTN maps show spatial variability in the precipitation-weighted average concentration and wet deposition of selected acidic ions, nutrients, and base cations on regional and national scales. Only sites meeting NADP data completeness criteria are included. For the maps on the page 5 and all other 2004 maps, 173 sites and 201 sites, respectively, met these criteria. Black dots mark nonurban sites. Open circles designate urban sites, defined as having at least 400 people per square kilometer (km^2) within a 15-km radius of the site. Concentration or deposition values appear next to each site.

Color contours were created by using nonurban site values to compute an array of regularly spaced grid-point values across the nation. Sites within 500 km of each grid point were used in computations. Color contours and the color fill in the open circle of urban sites represent classes of concentrations or depositions in the legend. (For information about the algorithm used to compute grid-point values, see the NADP Web site.)

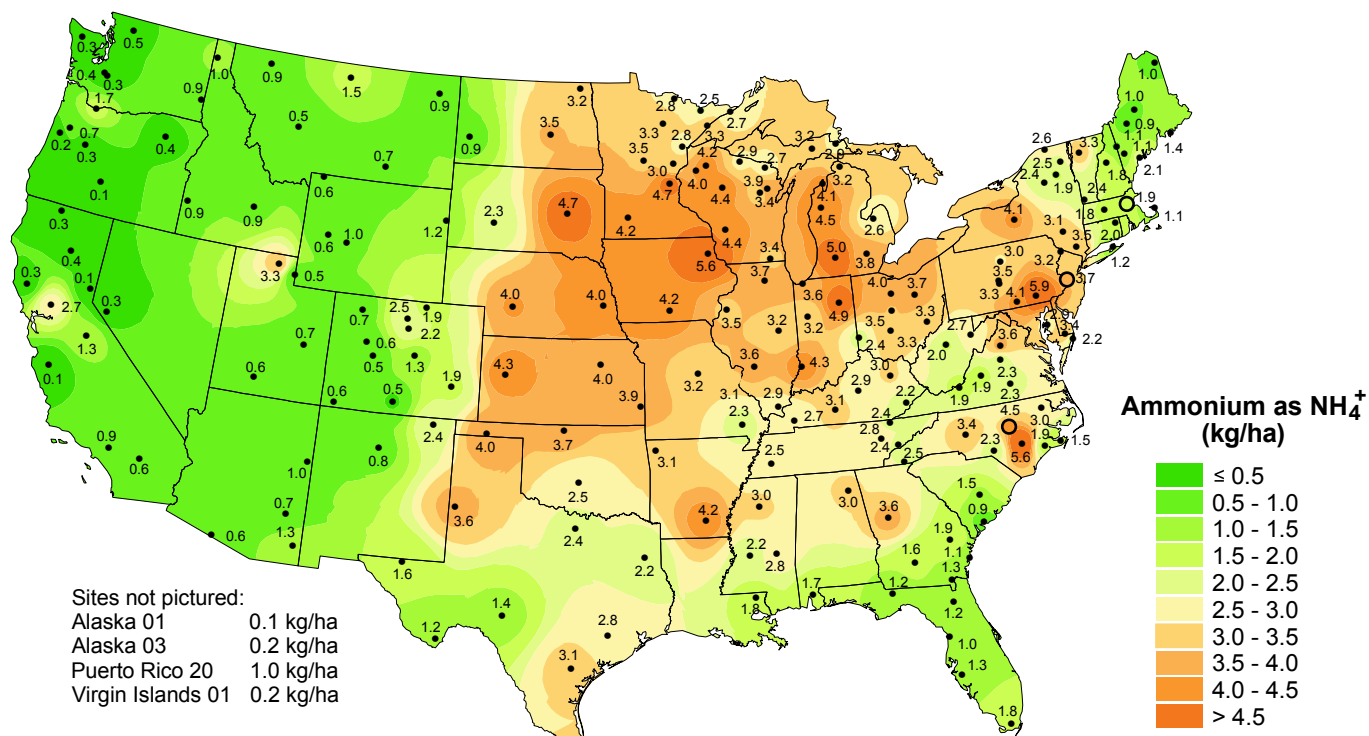
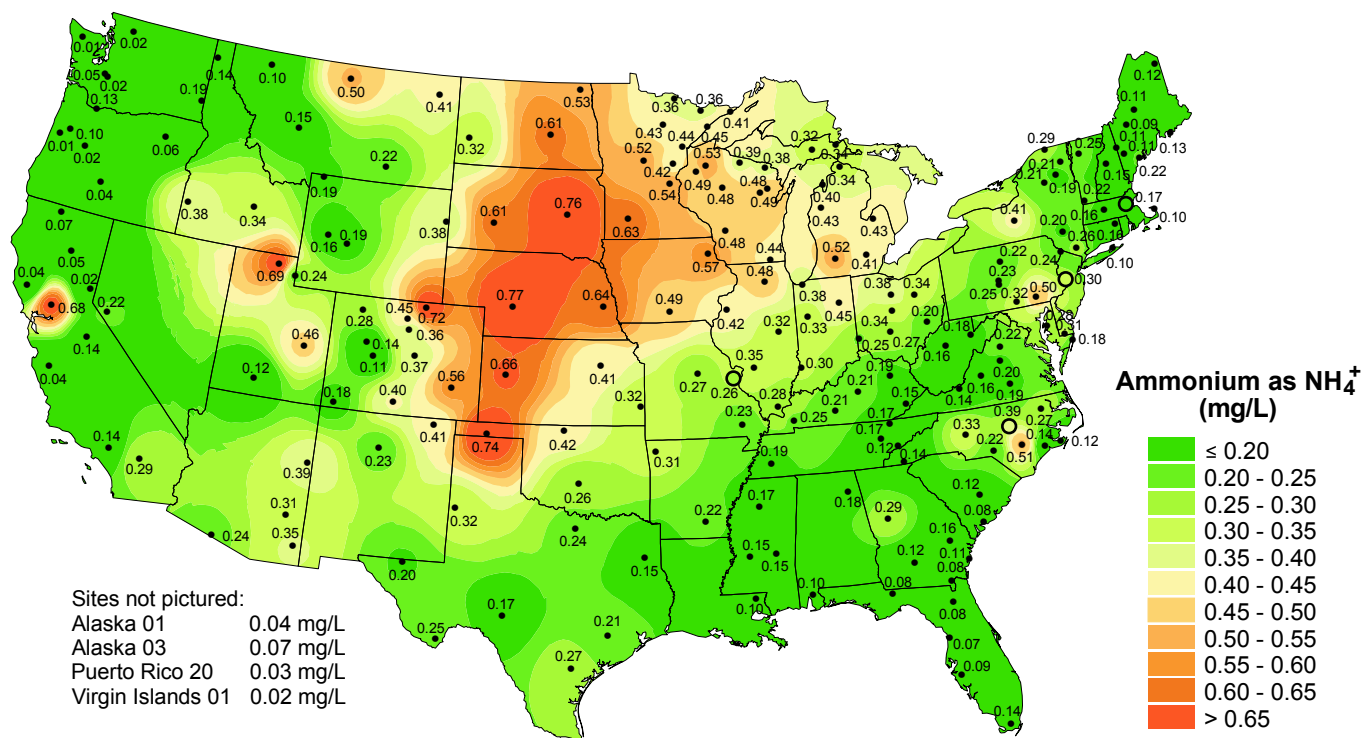
In addition to the pH maps on page 5, concentration and deposition maps for 2004 show NH_4^+ , NO_3^- , SO_4^{2-} , Ca^{2+} , laboratory pH, and inorganic nitrogen wet deposition (N). Also shown is a map of total precipitation for 2004. Maps of Mg^{2+} , Na^+ , K^+ , Cl^- , field pH, and field H^+ deposition are not included but are available from the NADP Web site.

Explanation of NTN Color Contours: Refer to the figures on the next page, which have 12 pH classes or contours. The lightest green color in the legend represents 4.8 - 4.9 average annual pH. The pH values in the area covered by this contour are greater than 4.8 and less than or equal to 4.9.



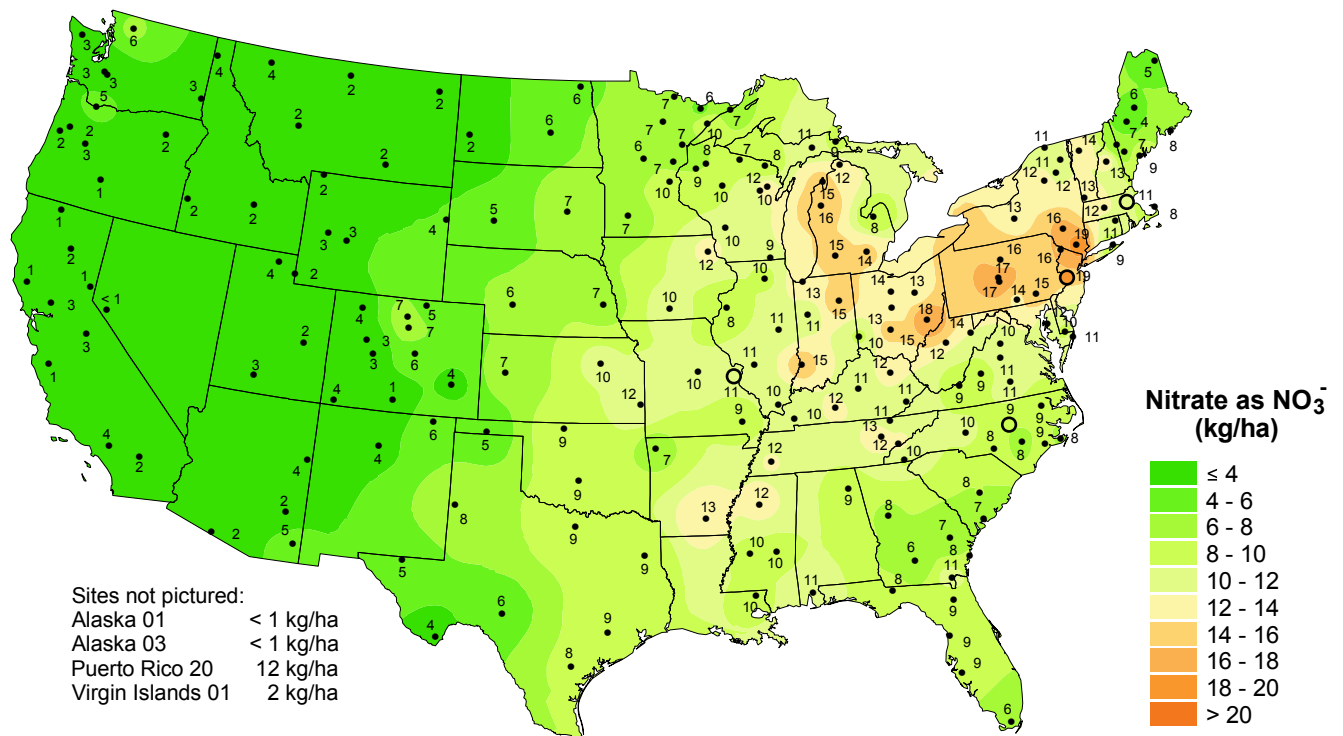
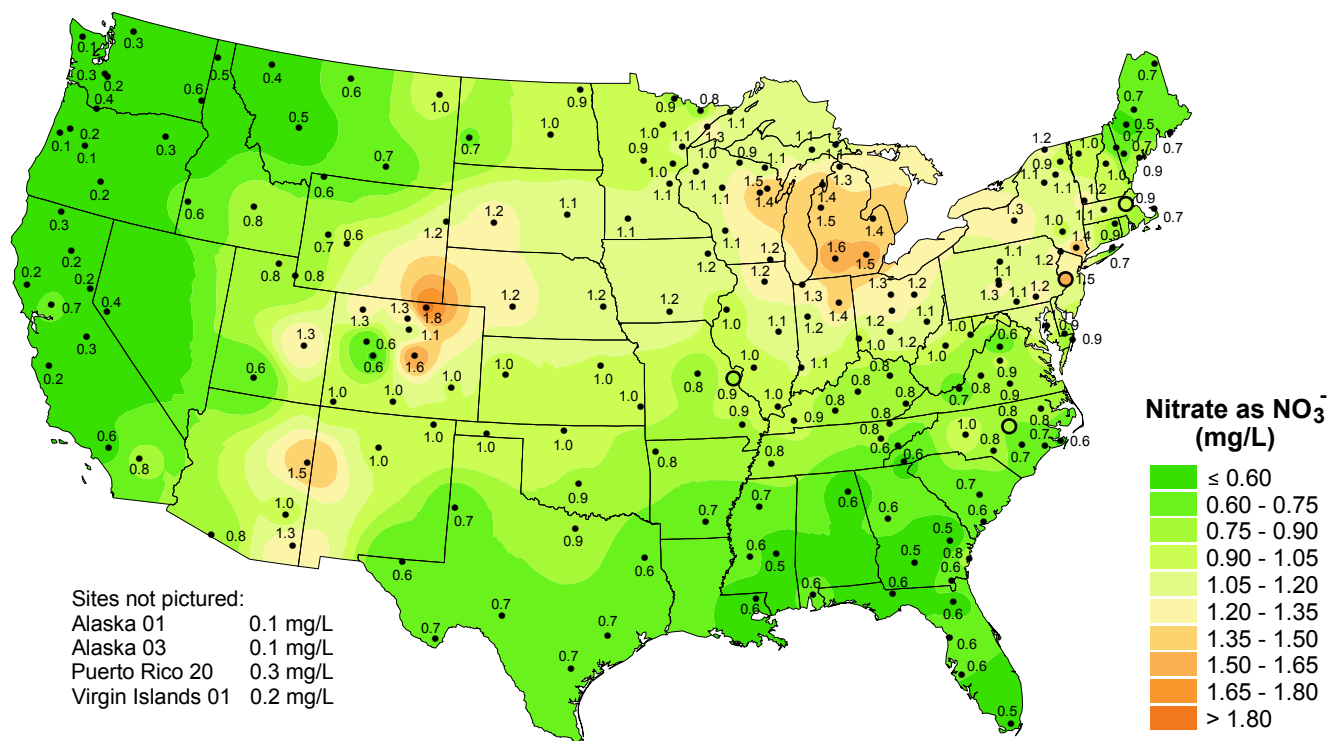
National Atmospheric Deposition Program/National Trends Network

Average annual hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory (top) and field laboratories (bottom), 2000-2004.



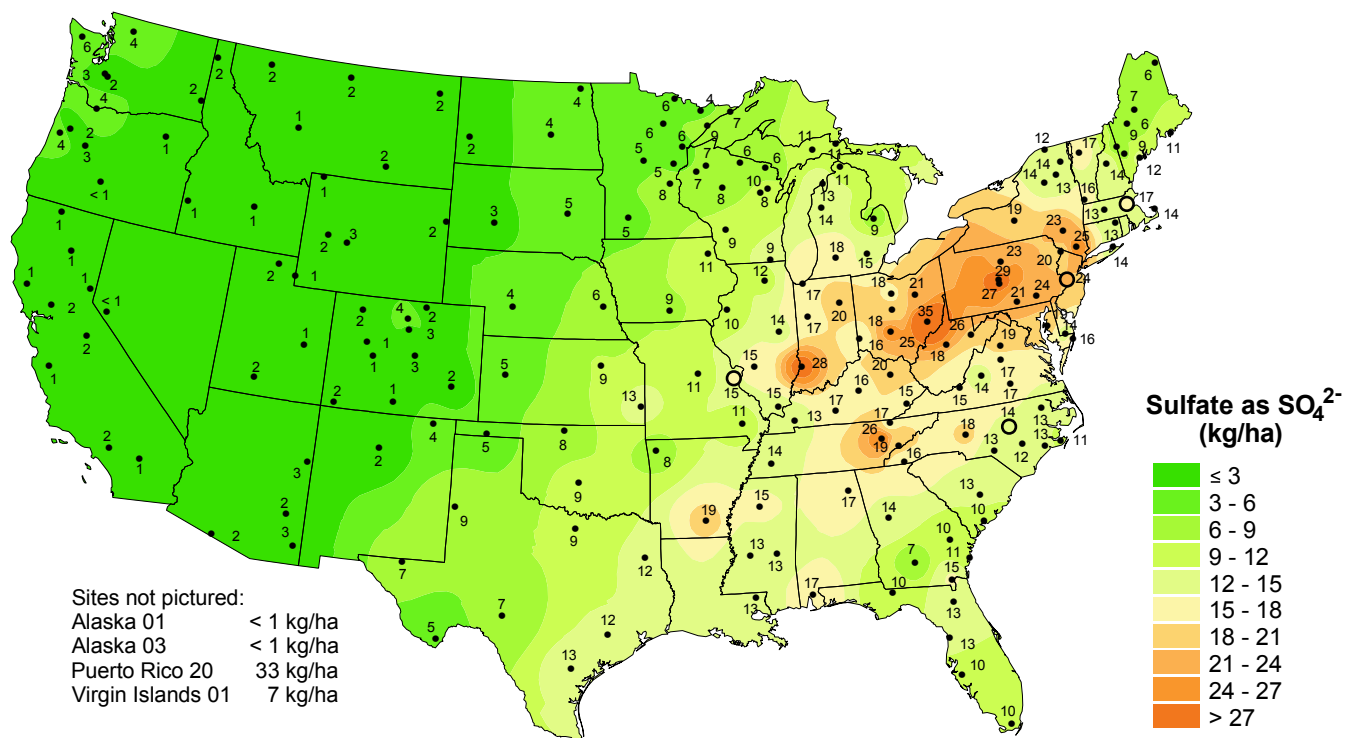
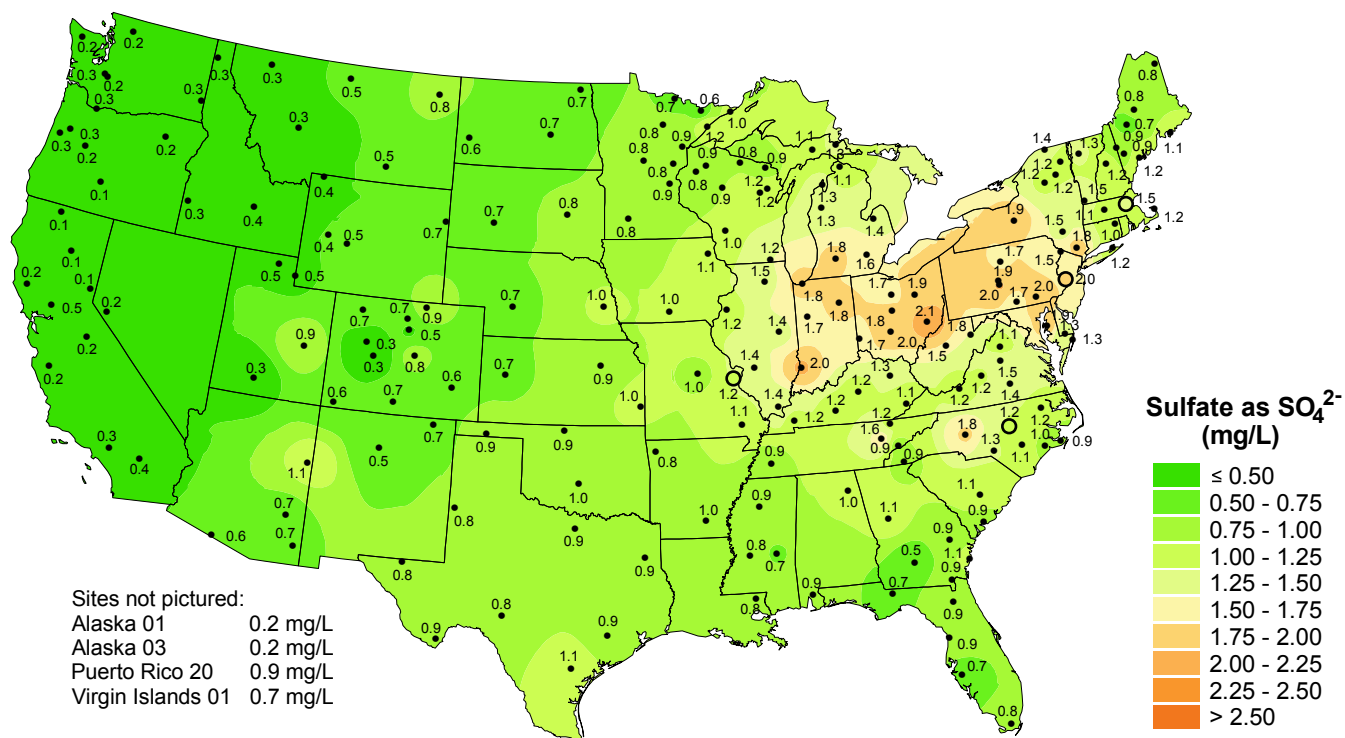
National Atmospheric Deposition Program/National Trends Network

Ammonium ion concentration (top) and wet deposition (bottom), 2004.



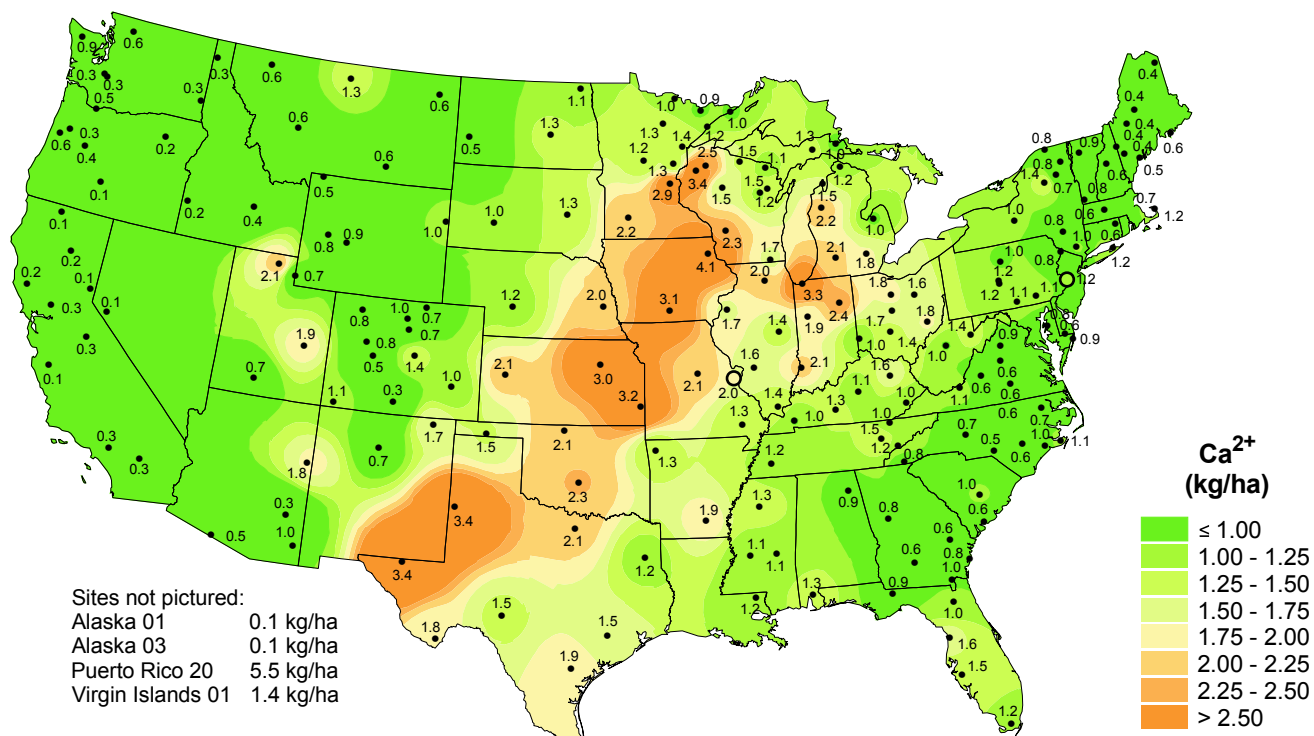
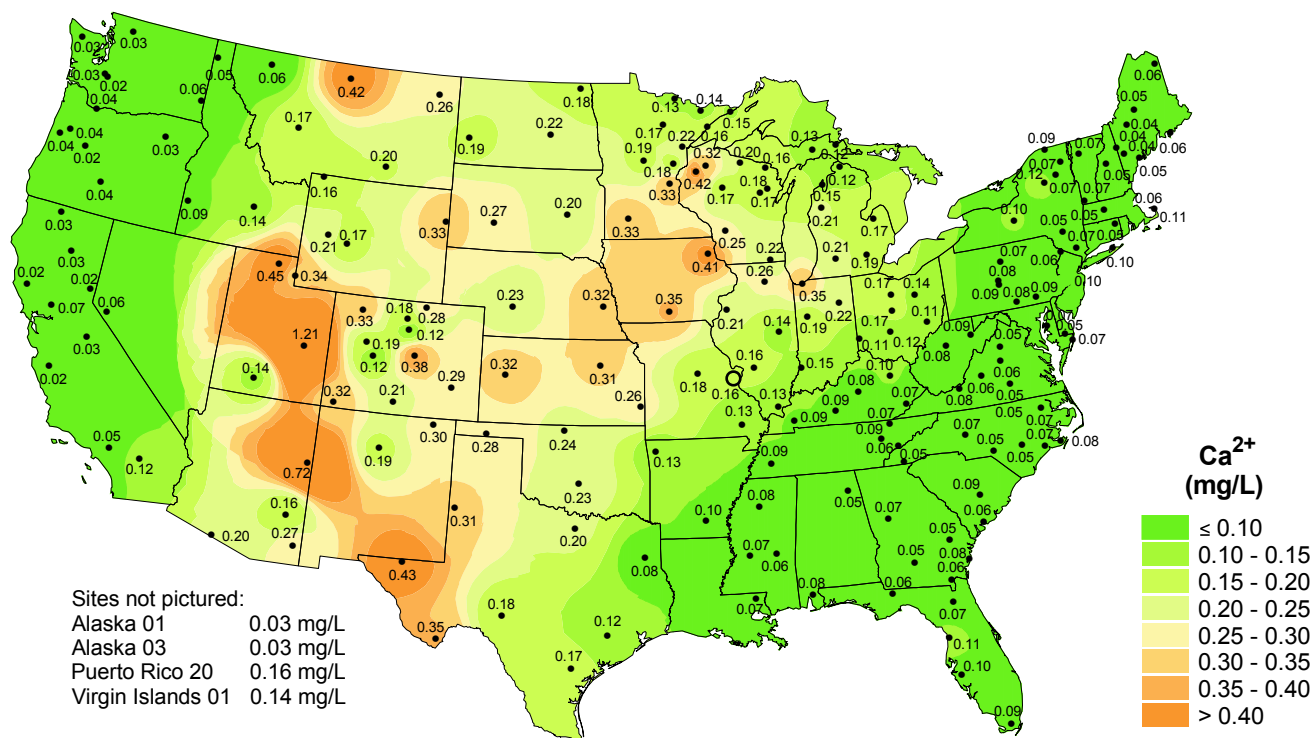
National Atmospheric Deposition Program/National Trends Network

Nitrate ion concentration (top) and wet deposition (bottom), 2004.



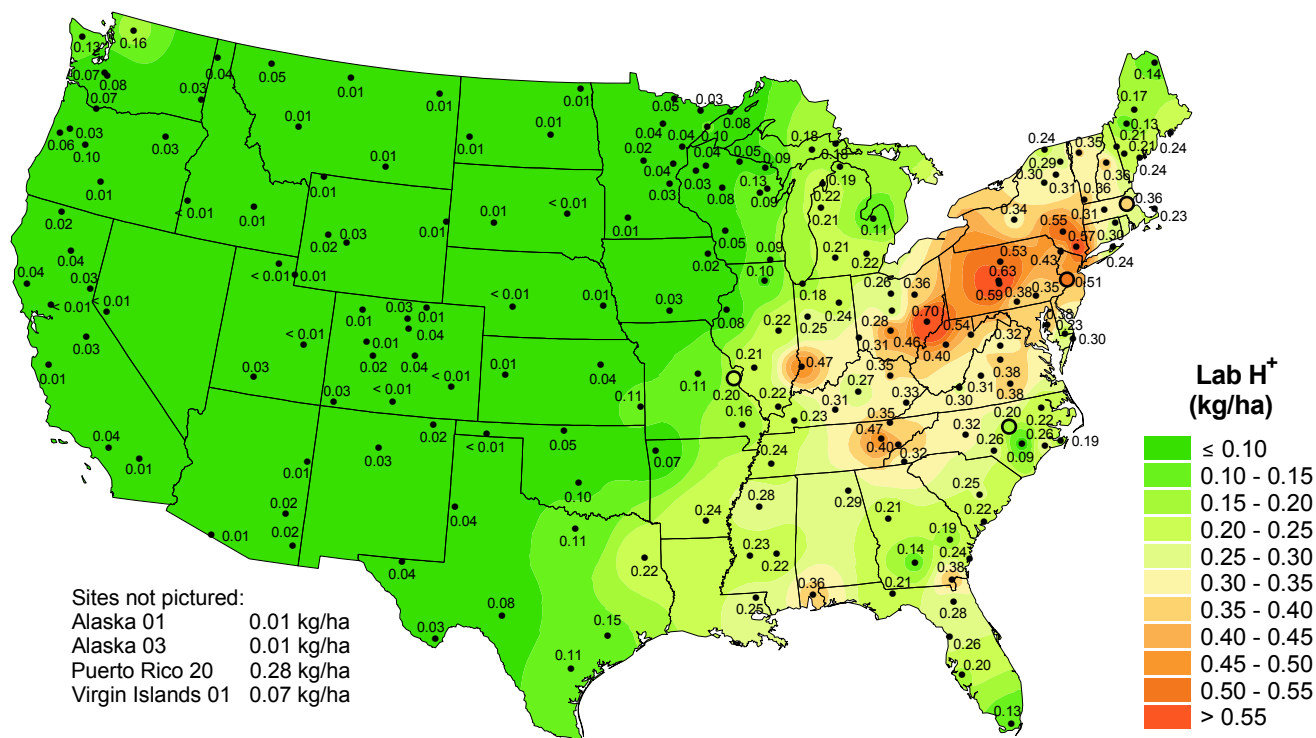
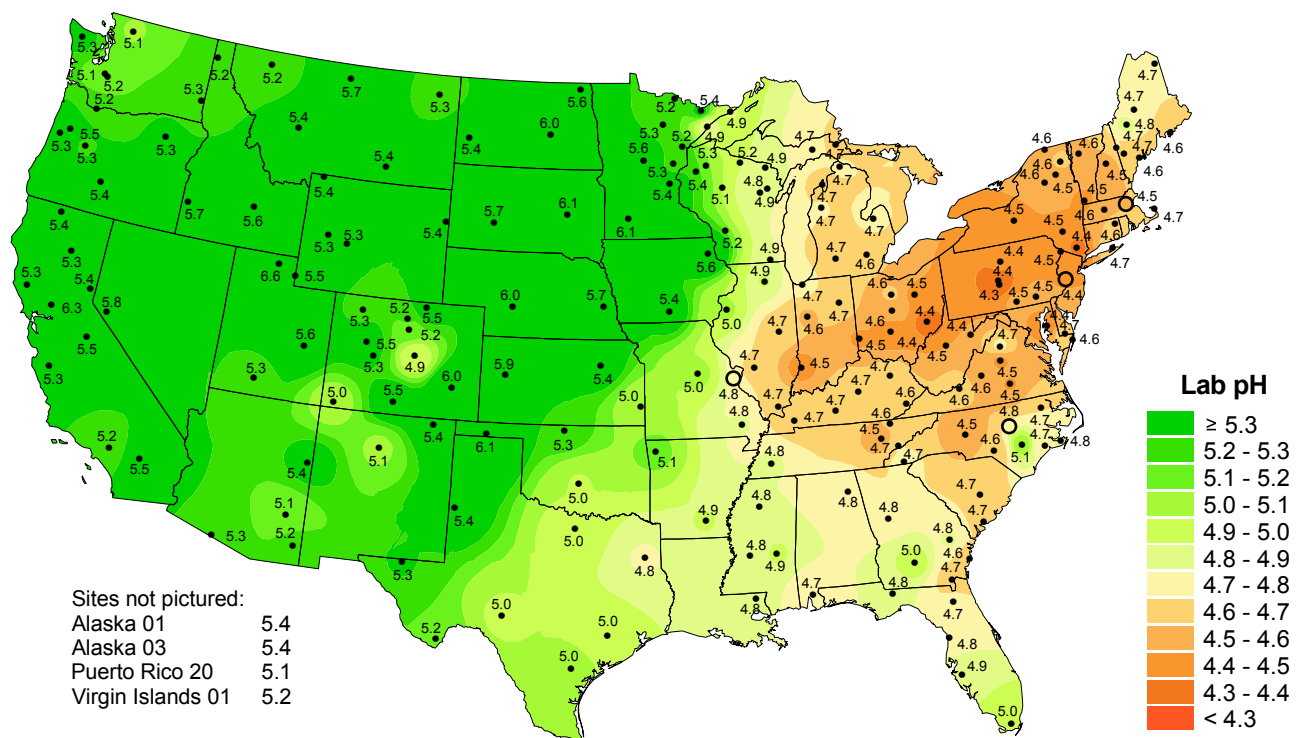
National Atmospheric Deposition Program/National Trends Network

Sulfate ion concentration (top) and wet deposition (bottom), 2004.



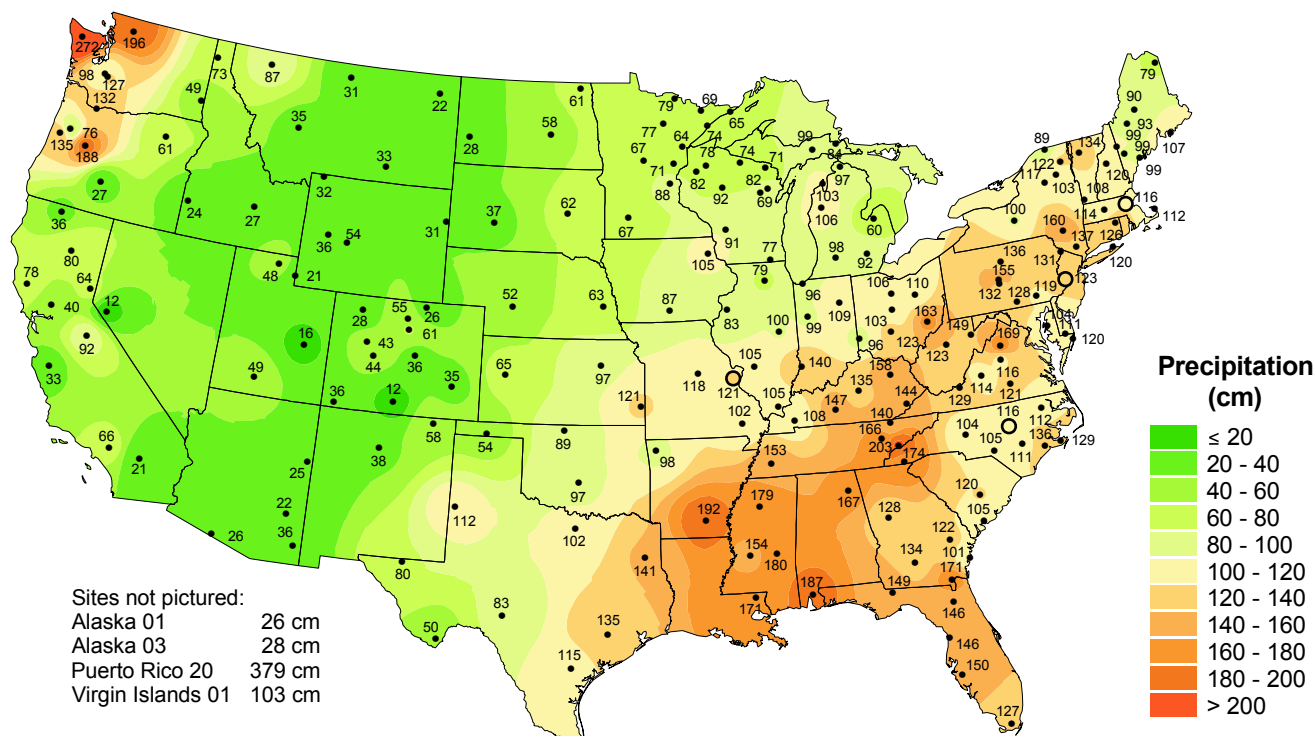
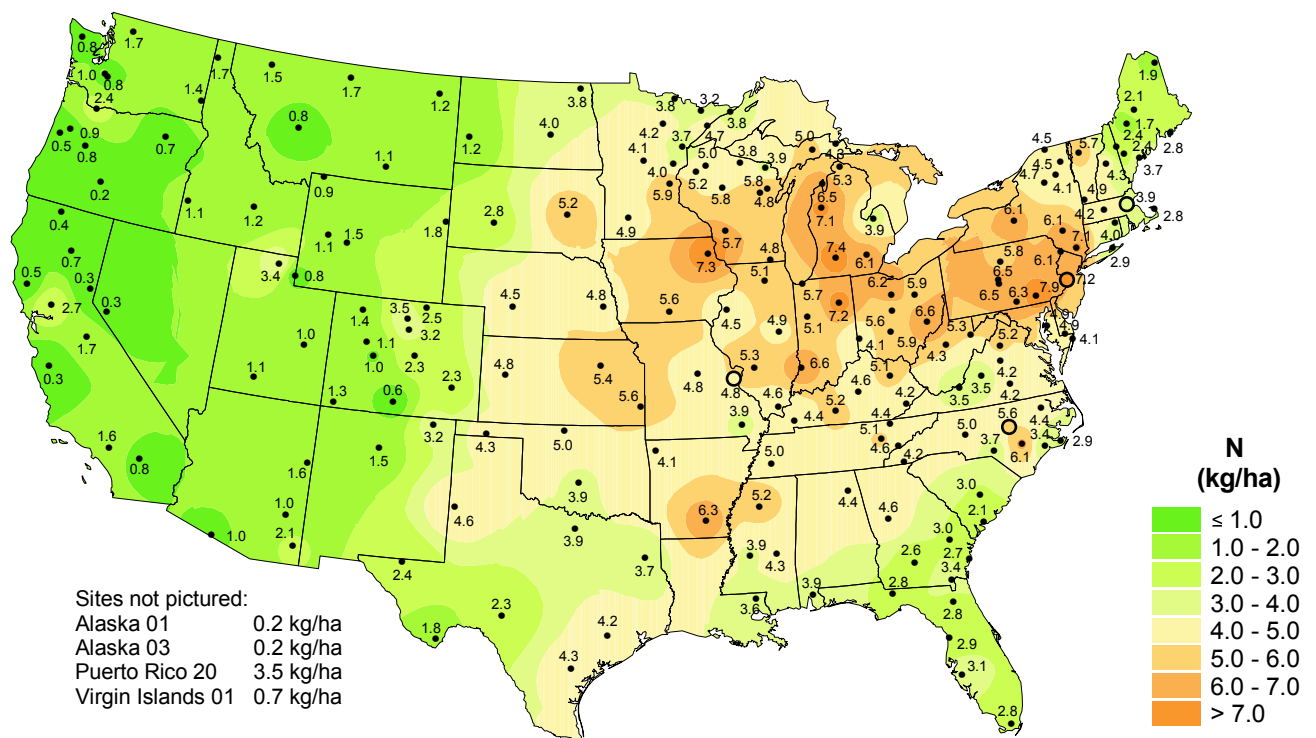
National Atmospheric Deposition Program/National Trends Network

Calcium ion concentration (top) and wet deposition (bottom), 2004.



National Atmospheric Deposition Program/National Trends Network

Hydrogen ion concentration as pH (top) and wet deposition (bottom) from pH measurements made at the Central Analytical Laboratory, 2004.



National Atmospheric Deposition Program/National Trends Network

Inorganic nitrogen wet deposition from nitrate and ammonium (top)
and total precipitation (bottom), 2004.

Mercury Deposition Network

The MDN is the only network providing a long-term record of mercury (Hg) in precipitation in the United States (80 sites), Canada (7 sites), and Mexico (2 sites). All MDN sites follow standard procedures and have uniform precipitation chemistry collectors and gages. The automated collector has the same basic design as the NTN collector but is modified to preserve mercury. Modifications include a glass funnel, connecting tube, bottle for collecting samples, and an insulated enclosure to house this sampling train. The funnel and connecting tube reduce sample exposure to the open atmosphere and limit loss of dissolved mercury. As an additional sample preservation measure, the collection bottle is charged with 20 mL of a one percent hydrochloric acid solution.

Site operators collect samples Tuesday morning or daily within 24 hours of the start of precipitation. In 2004, only the Devil's Lake site in south-central Wisconsin opted to collect samples daily. With each MDN sample, the entire sampling train is replaced with one that is cleaned by the Mercury Analytical Laboratory (HAL) at Frontier Geosciences, Inc., Seattle, Washington. Rigorous cleaning procedures ensure that each sampling train component is essentially mercury-free. The HAL supplies the collection bottles already charged with the hydrochloric-acid preservative. By following those procedures and stringent sampling protocols, the MDN is able to report mercury concentrations below 1 part per trillion (<1 nanogram/liter).

All MDN samples are sent to the HAL, which analyzes all forms of mercury in a single measurement and reports this as total mercury concentration. At the end of 2004, 17 MDN sites also opted for methyl mercury analysis. The HAL reviews field and laboratory data for completeness and accuracy, and flags samples that were mishandled, compromised by precipitation collector failures, or grossly contaminated. The

HAL delivers all data and information to the NADP Program Office for final checks and resolution of remaining discrepancies. Data then are made available on the NADP Web site.

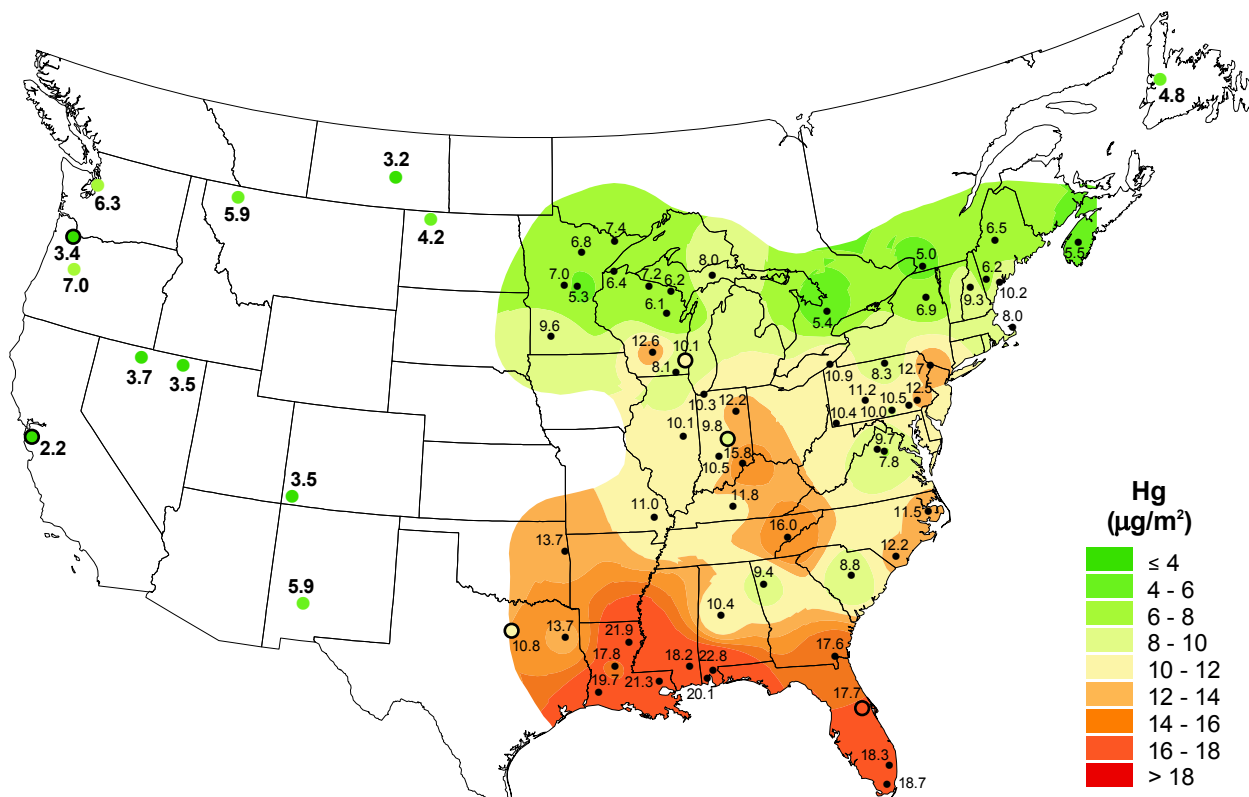
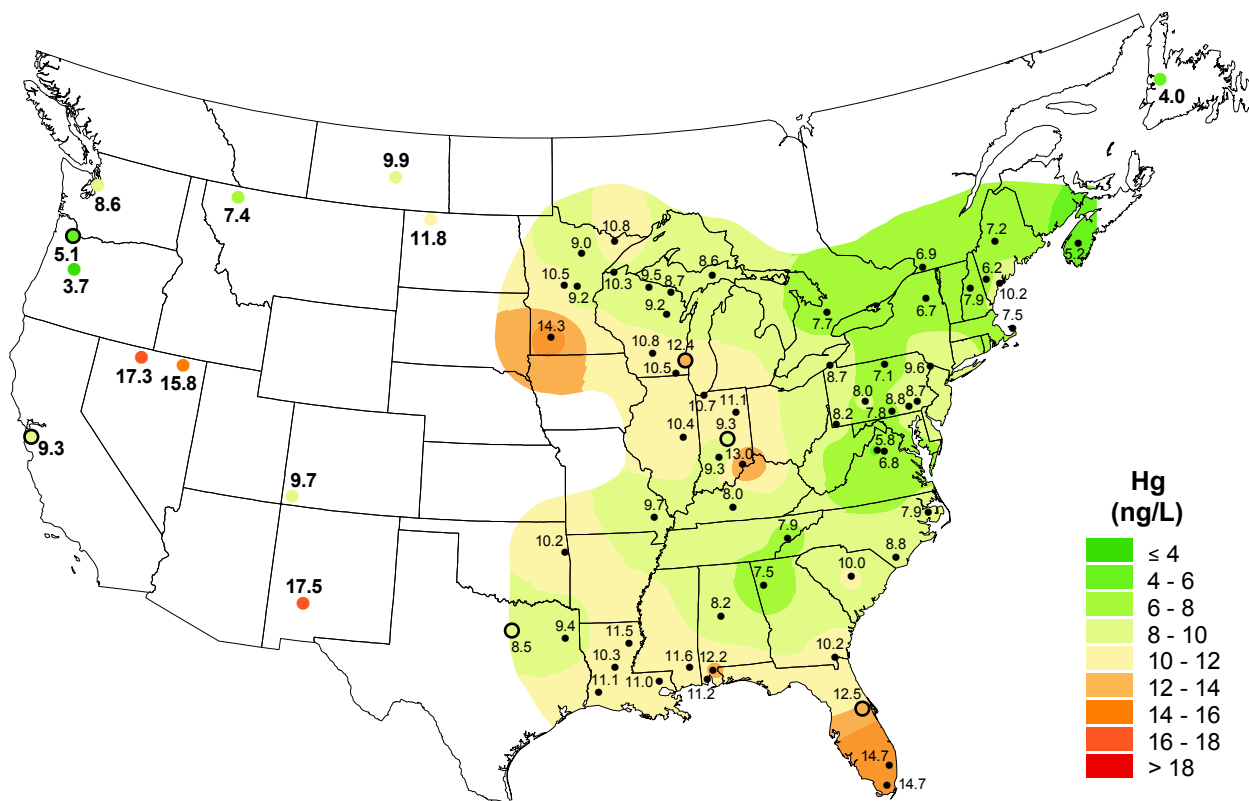
MDN Maps

The MDN maps on page 13 show spatial variability in the precipitation-weighted average concentration and wet deposition of total mercury. Only sites meeting NADP data completeness criteria are included. In 2004, 73 sites met these criteria.

In the eastern United States and southern Canada, color contours display the concentration and deposition distributions. Black dots mark nonurban sites. Open circles designate urban sites. Concentration or deposition values appear next to each site.

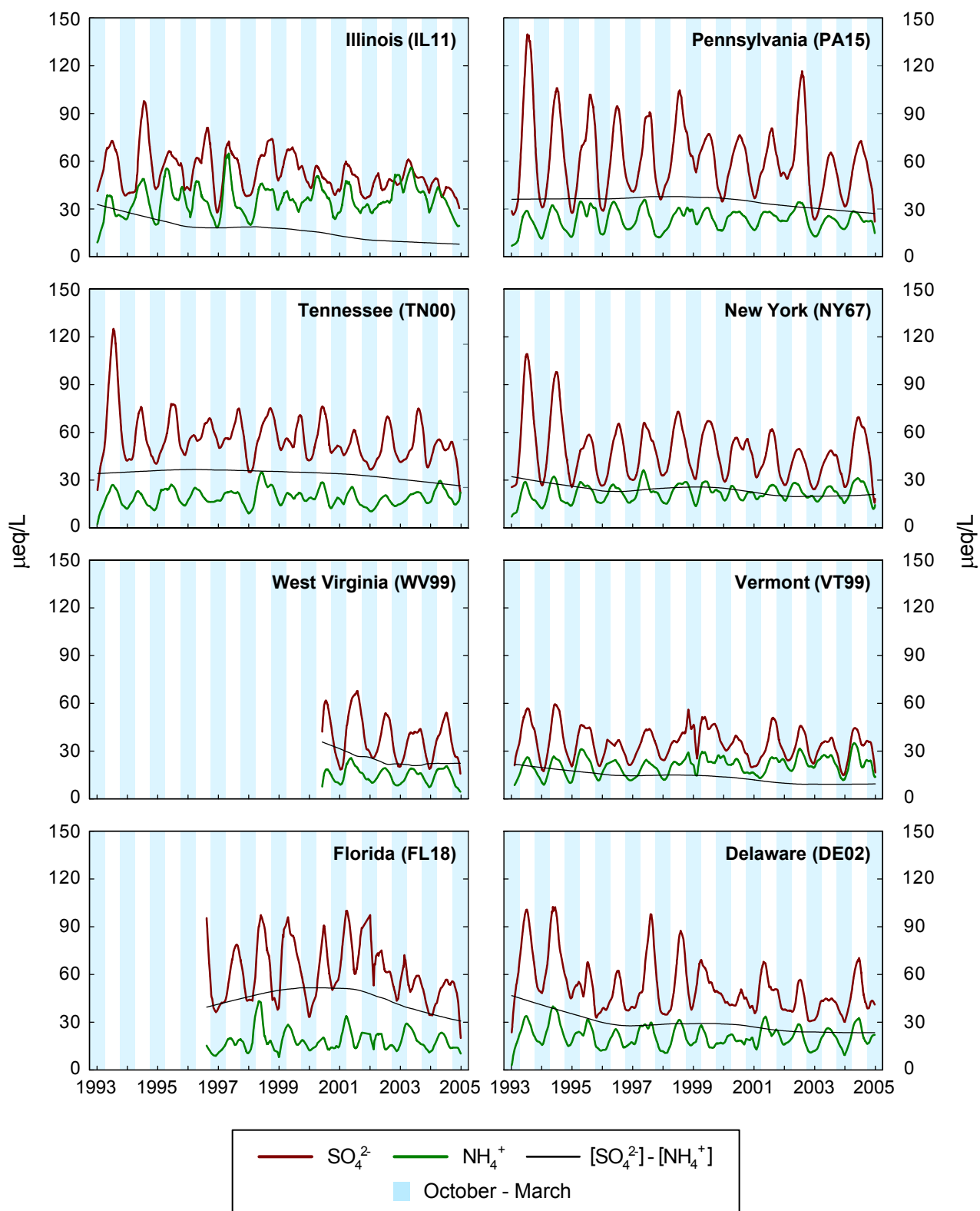
Color contours were created by using nonurban site values to compute an array of regularly spaced grid-point values. Sites within 500 km of each grid point were used in computations. In the area covered by color contours, it was necessary to have two or more data points occurring within 500 km of each grid point. The boundary of the color-contoured area was trimmed at the coastline and over land 250 km from outermost data points. The landward boundary was smoothed. Color contours and the color fill in the open circle of urban sites represent classes of concentrations or depositions in the legend. Outside of the color-contoured area where data are too sparse to draw contours, colored dots mark site locations. Dot colors represent concentration or deposition classes in the legend.

Methyl Mercury. Methyl mercury is highly toxic and builds up in fish tissue, resulting in advisories warning people to limit fish consumption. All states except Alaska, Iowa, Kansas, Utah, and Wyoming have some form of advisory (see <http://www.epa.gov/ost/fish>).



National Atmospheric Deposition Program/Mercury Deposition Network

Total mercury concentration (top) and wet deposition (bottom), 2004.



Smoothed plots of sulfate (SO_4^{2-}) and ammonium (NH_4^+) concentrations and concentration differences ($\text{SO}_4^{2-} - \text{NH}_4^+$) at AIRMoN sites active at the end of 2004. (See text for a description of the smoothing technique.)

Atmospheric Integrated Research Monitoring Network

At AIRMoN sites, samples are collected daily within 24 hours of the start of precipitation, often providing data for all or part of a single storm. Single-storm data facilitate studies of atmospheric processes and the development and testing of computer simulations of these processes. Making data available for these studies is a principal AIRMoN goal.

The AIRMoN sites are equipped with the same automated wet-only deposition collector and precipitation gage used at NTN sites. Each site also has a National Weather Service standard gage for reporting storm total precipitation. Site operators weigh the collection bucket to determine sample volume and then transfer the sample to a shipping bottle. Only CAL-cleaned containers are used. For volumes less than 50 milliliters (mL), operators send the samples to the CAL for analysis. For samples of 50 mL or more, they first measure pH and conductance on a 16 mL aliquot before sending the remainder to the CAL.

Samples are refrigerated after collection and are sent to the CAL in chilled insulated shipping containers. They are kept refrigerated until analysis at the CAL. Refrigeration retards chemical changes. Chemical analyses and data screening procedures for AIRMoN and NTN are similar, although low-volume AIRMoN samples are not diluted to accommodate a complete analysis, as is standard NTN procedure. During the AIRMoN data review, the CAL also assigns an overall quality rating code before sending data to the NADP Program Office for final checks and posting on the NADP Web site.

AIRMoN Data

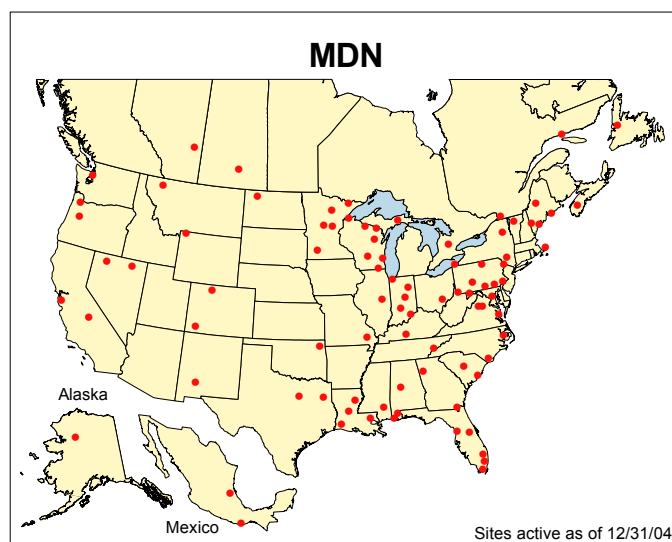
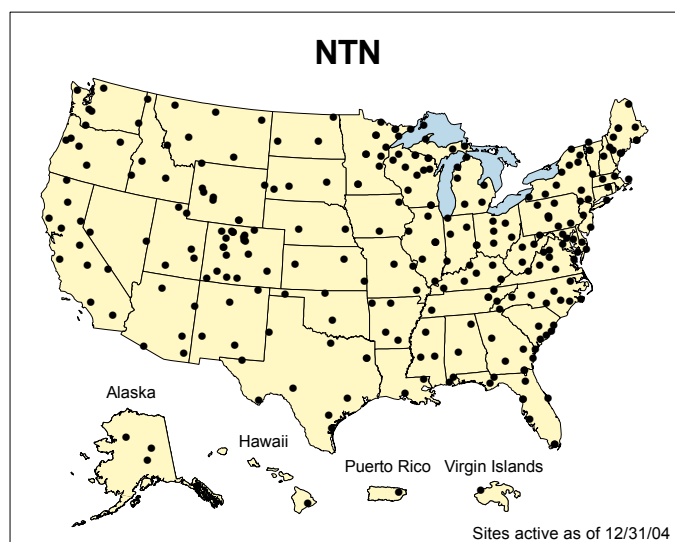
Line graphs on page 14 show sulfate and ammonium concentrations and sulfate-minus-ammonium-concentration differences for the eight AIRMoN sites active at the end of 2004. A locally weighted least squares smoothing (LOWESS)

function was applied to individual data points. The LOWESS method is especially suited for smoothing unequally spaced highly scattered data, such as AIRMoN measurements.

For the sulfate and ammonium graphs, the LOWESS smoothing window was set for 180 days. This filtered out short-duration variations and accentuated seasonal cycles. For the concentration difference line, the smoothing window was widened to filter out all but long-term changes. Sulfate and ammonium concentrations exhibit seasonal cycles that vary by site and over time. Except for the Illinois site, the sulfate line is always above the ammonium line. Sulfate-minus-ammonium differences tend to decrease over time at many sites, suggesting long-term trends in concentrations of sulfate, ammonium, or both.

Urban Sites. Most NADP sites were installed predominantly away from urban areas, but some are in an urban area, either due to original site placement or to land-use changes since site installation. In recognition of the potential influence of urban sources on precipitation chemistry and deposition, the NADP decided that urban sites would be shown but no longer included in the graphical interpolation used to create color isopleth maps. Urban sites were defined as having 400 or more people per square km within a 15-km radius of the site. Below is a list of urban NADP sites and their network affiliations:

CA72 - San Jose (MDN)
FL32 - Orlando (MDN)
IL19 - Argonne (NTN)
IN26 - Fort Harrison State Park (MDN)
MA13 - East (NTN)
MO43 - Tyson Research Center (NTN)
NC41 - Finley Farm (NTN)
NJ00 - Washington Crossing (NTN)
OR01 - Beaverton (MDN)
TX50 - Fort Worth (MDN)
WI22 - Milwaukee (MDN)



Note:

When referencing maps or information in this report, please use the citation: National Atmospheric Deposition Program. 2005. *National Atmospheric Deposition Program 2004 Annual Summary*. NADP Data Report 2005-01. Illinois State Water Survey, Champaign, IL.



The NADP is National Research Support Project - 3: A Long-Term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition. More than 250 sponsors support the NADP, including private companies and other nongovernmental organizations, universities, local and state government agencies, State Agricultural Experiment Stations, national laboratories, Native American organizations, Canadian government agencies, the National Oceanic and Atmospheric Administration, the Environmental Protection Agency, the Tennessee Valley Authority, the U.S. Geological Survey, the National Park Service, the U.S. Fish & Wildlife Service, the Bureau of Land Management, the U.S. Department of Agriculture - Forest Service, and the U.S. Department of Agriculture - Cooperative State Research, Education, and Extension Service (under agreement no. 2002-39138-11964). Any findings or conclusions in this publication do not necessarily reflect the views of the U.S. Department of Agriculture or other sponsors.

The NADP Program Office is located at the Illinois State Water Survey, an affiliated agency of the University of Illinois and a Division of the Illinois Department of Natural Resources. All NADP data and information, including color contour maps in this publication, are available from the NADP Web site:

<http://nadp.sws.uiuc.edu>

*For further information, special data requests, or to obtain copies of this publication, contact the NADP Program Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820.
e-mail: nadp@sws.uiuc.edu*