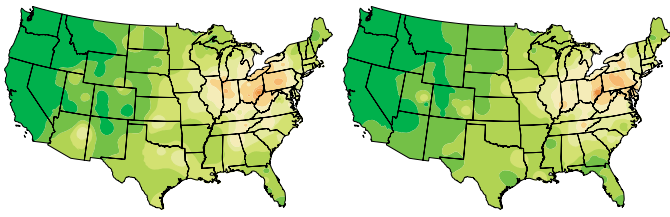
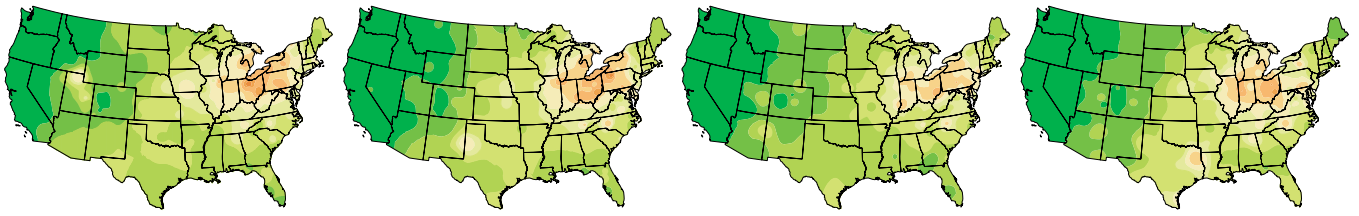
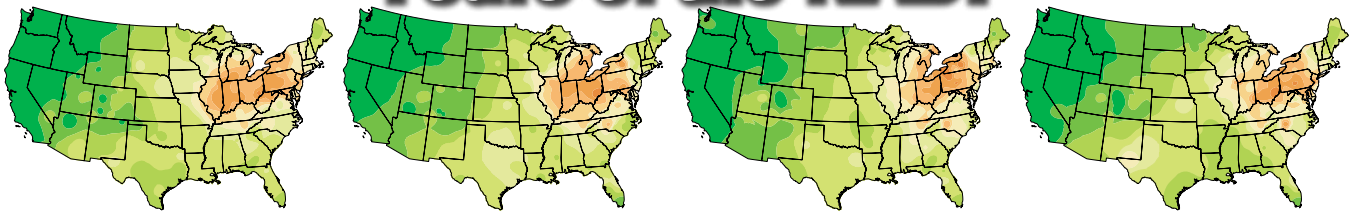


30

Years of the NADP



To the NADP Community

Over the past 30 years, the National Atmospheric Deposition Program has consistently monitored the nation's precipitation for different chemical constituents and their input to ecosystems around our continent. Our long-term mission is to provide quality-assured data and information in support of research on the exposure of managed and natural ecosystems and cultural resources to acidic compounds, nutrients, base cations, and mercury in precipitation. We strive to do this in an open and straightforward scientific manner, and to make these data readily available to all interested parties.

Since 1977, the NADP has measured approximately 400,000 samples, and has produced hundreds of maps to describe the spatial distribution of concentration and deposition of these chemical constituents. We have summarized our findings annually since 1981.

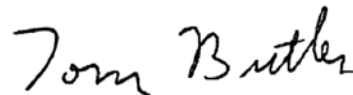
As the network grew, the maps have evolved from simple contour plots to full-color spatially interpreted maps. The underlying consistency of measurements and data quality assurance have made these critically important data available to foster science-based decision-making in many different areas of life, including research, education, agriculture, and policy analysis.

Given these measurements and the efforts of many, many people over the years, we have been able to clearly document how the chemical climate of North America is changing. As the maps on the next page show, the concentration of hydrogen ion (or acidity) has decreased markedly since the early 1980s. Concurrently, the deposition of sulfate ion has also decreased significantly, a finding that has been demonstrated over most of the nation, and has been consistent over the history of the network.

The NADP has also measured other constituents along with pH and sulfate. Even though increases

were not envisioned in network planning, monitoring of both nitrate and ammonia has shown a clear, dramatic increase in nitrogen deposition, largely from ammonia, to many ecosystems at the same time that acidity and sulfate were being reduced. The NADP has provided a valuable resource for scientists and others to use for many varied purposes, including the assessment of the impact of clean air legislation on precipitation chemistry.

Our 30 years of effort has been extremely worthwhile, based on our results, the demand for our data, and the abundant replication of our summary maps in articles, reports, and presentations. The continued use of our data over these many years is our best return; it is evidence that our data are a valuable and trusted national asset.



Tom Butler, Chair

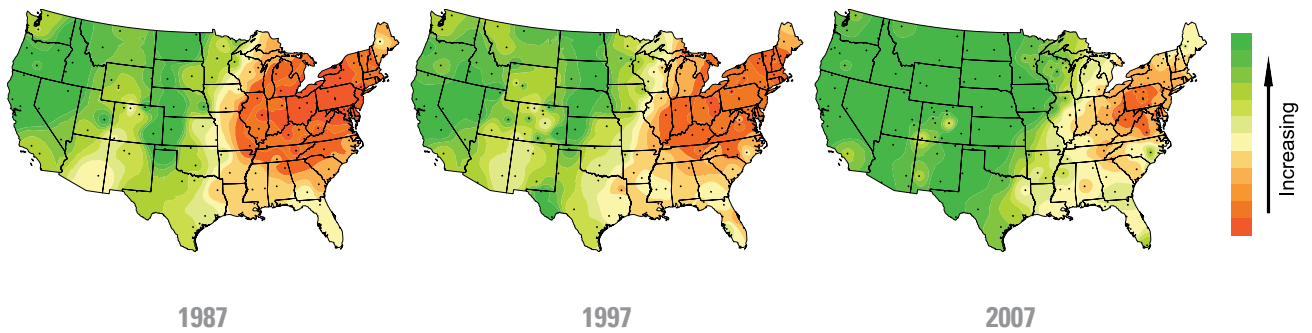


David A. Gay, Program Coordinator

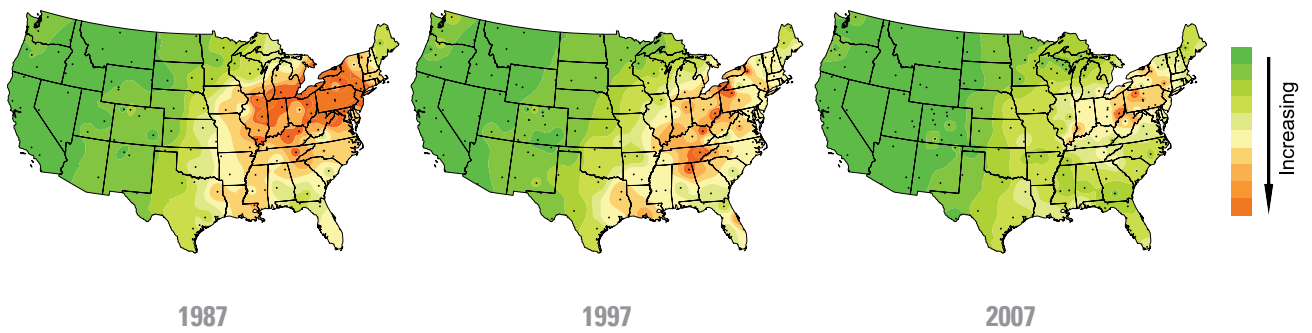


Van C. Bowersox, Past Program Coordinator

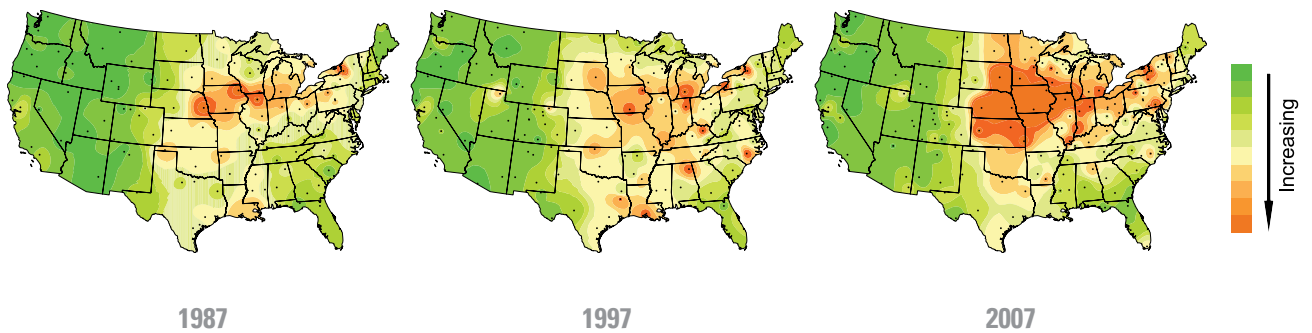
Lab pH



Sulfate Deposition



Ammonium Deposition



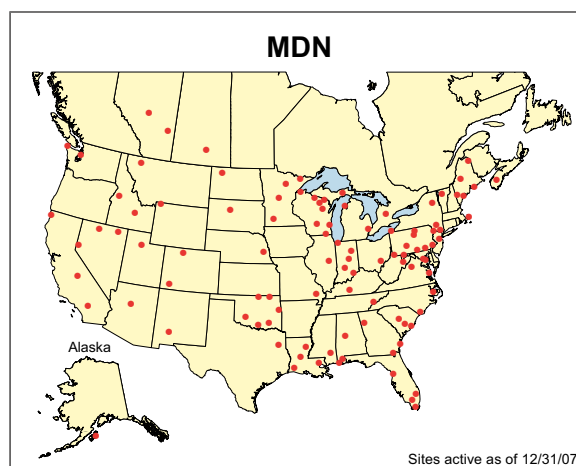
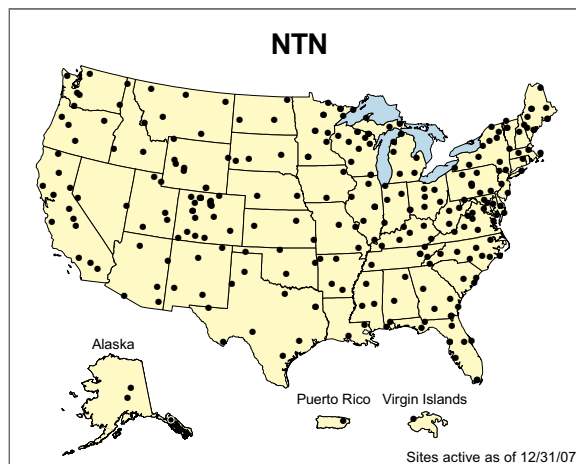
The annual spatial concentration of hydrogen ion (pH units) and the annual sulfate ion and ammonium ion deposition (kg/ha) for the three years (1987, 1997, and 2007), showing changes with time.

NADP Background

In 1977, 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 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 Precitation 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 as the National Trends Network (NTN).

A second network, the Atmospheric Integrated Research Monitoring Network (AIRMoN), joined the NADP in 1992, and had seven sites at the end of 2007. While measuring the same chemicals as NTN, AIRMoN sampling occurs daily rather than weekly. These higher resolution samples enhance researchers' ability to evaluate how emissions affect precipitation chemistry using computer models that simulate pollutant transport, chemical transformations, and deposition by precipitation. This network also evaluates alternative sample collection and preservation methods.

The Mercury Deposition Network (MDN) joined the NADP in 1996, and had 112 sites at the end of 2007. All MDN samples are analyzed for total mercury, and some for the more toxic methyl mercury. Researchers use MDN data to evaluate the role of precipitation as a source of mercury in these water bodies.



National Trends Network (NTN)

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

Site operators follow standard operational procedures to help ensure NTN data comparability and representativeness. They 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 to a shipping bottle. All samples are sent to the CAL for analysis. The CAL enters all field and laboratory data, and verifies and screens the data.

The CAL measures free acidity (H^+ as pH), conductance, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), and ammonium (NH_4^+). 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 for final checks and to resolve remaining discrepancies. The Program Office stores all NADP data and information in a database system accessible from the NADP Web site. Valid NTN data can be retrieved remotely through this online retrieval system.

NTN MAPS

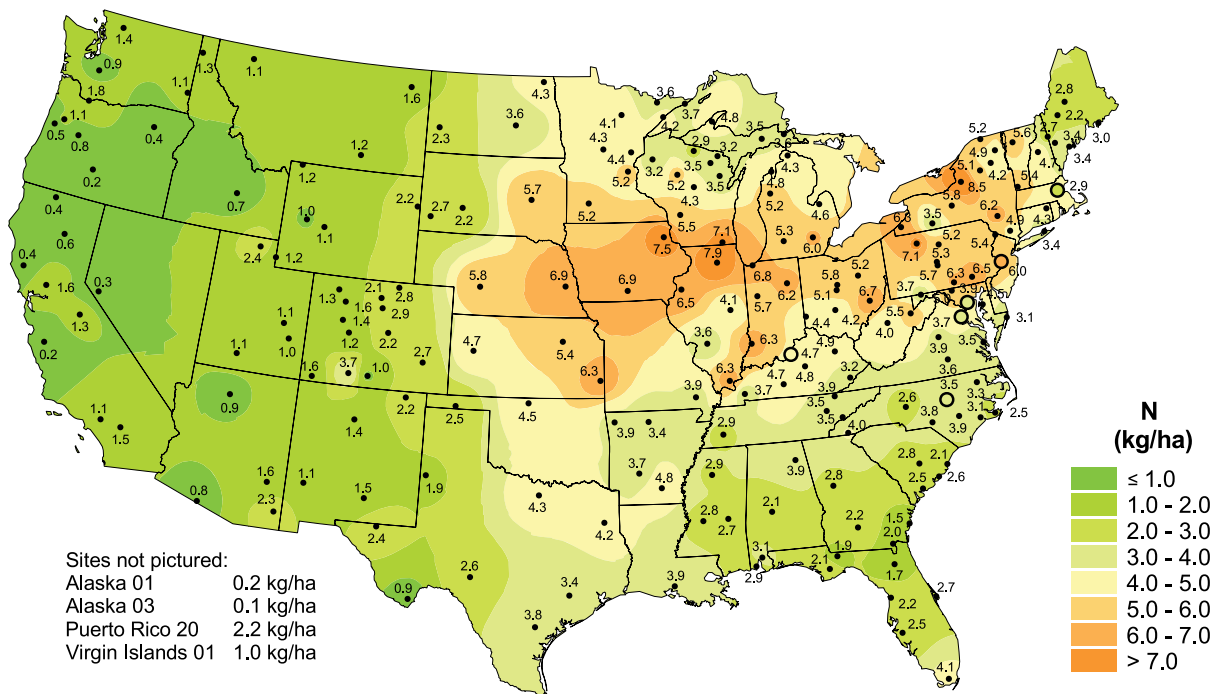
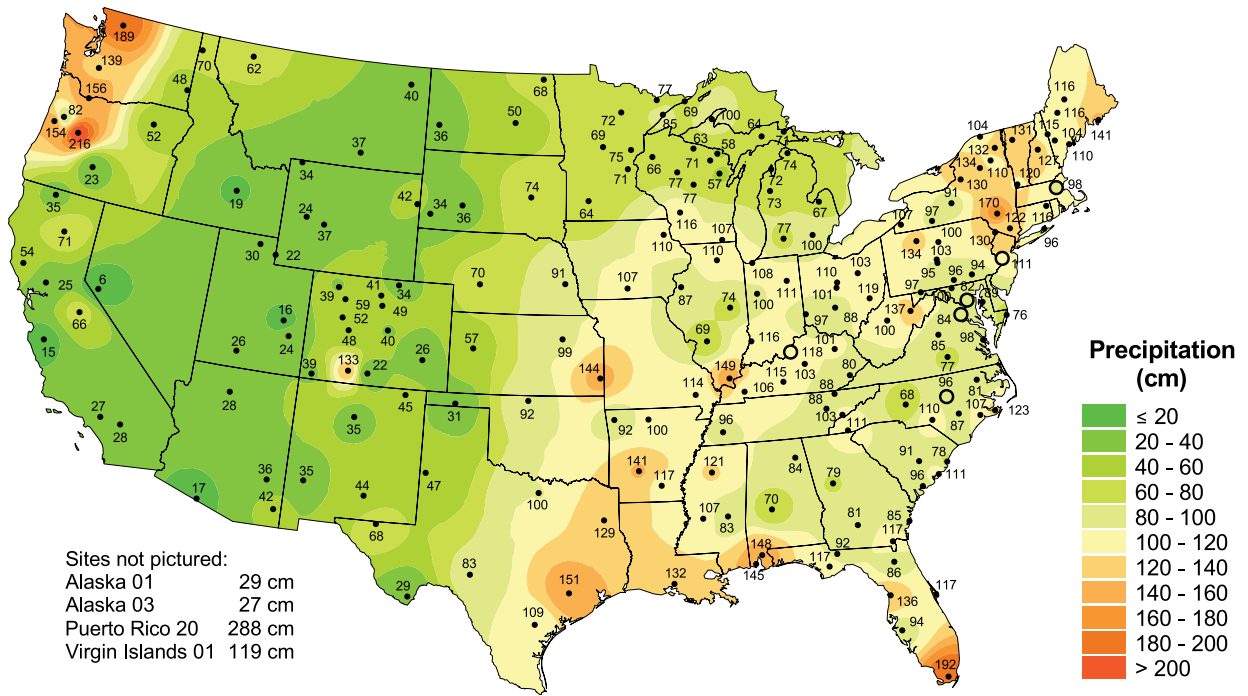
The NTN maps show spatial variability in the precipitation-weighted average concentration and

wet deposition of selected acidic ions, nutrients, and base cations on regional and national scales. Only sites meeting NADP data completeness criteria are included. In 2007, 208 sites met these criteria. Black dots mark site locations. 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. Urban sites do not contribute to the contours. Concentration or deposition values appear next to each site.

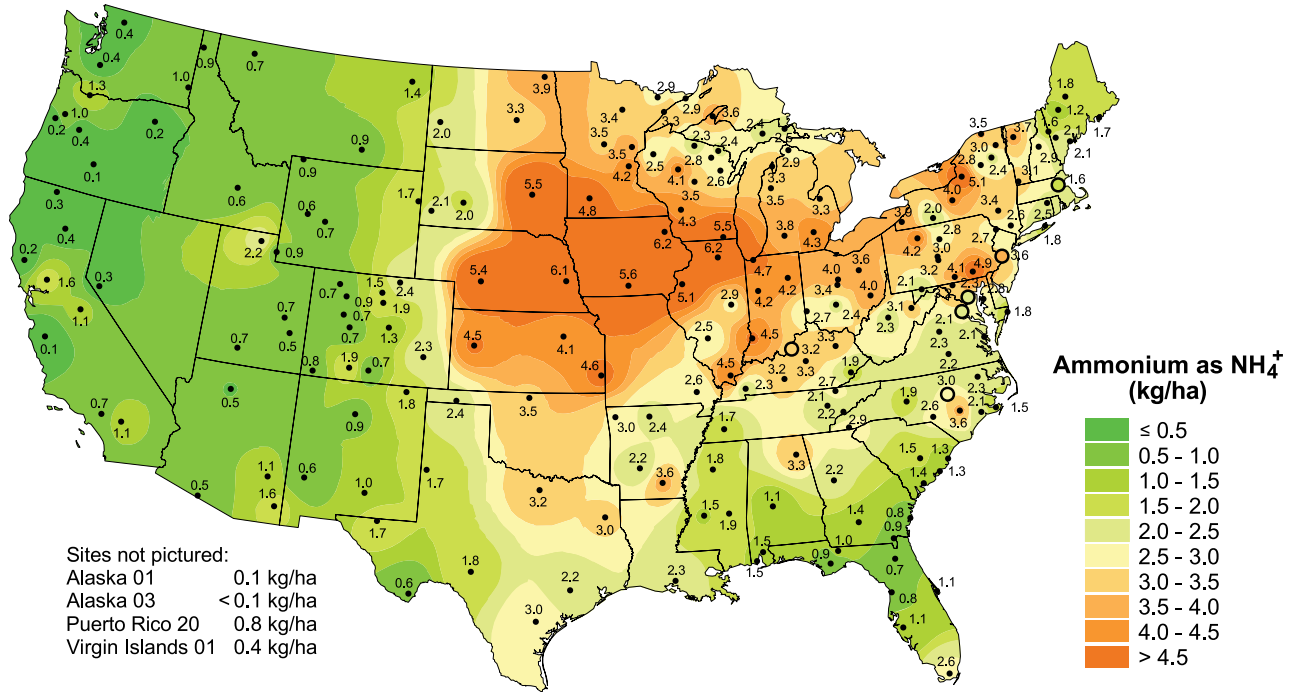
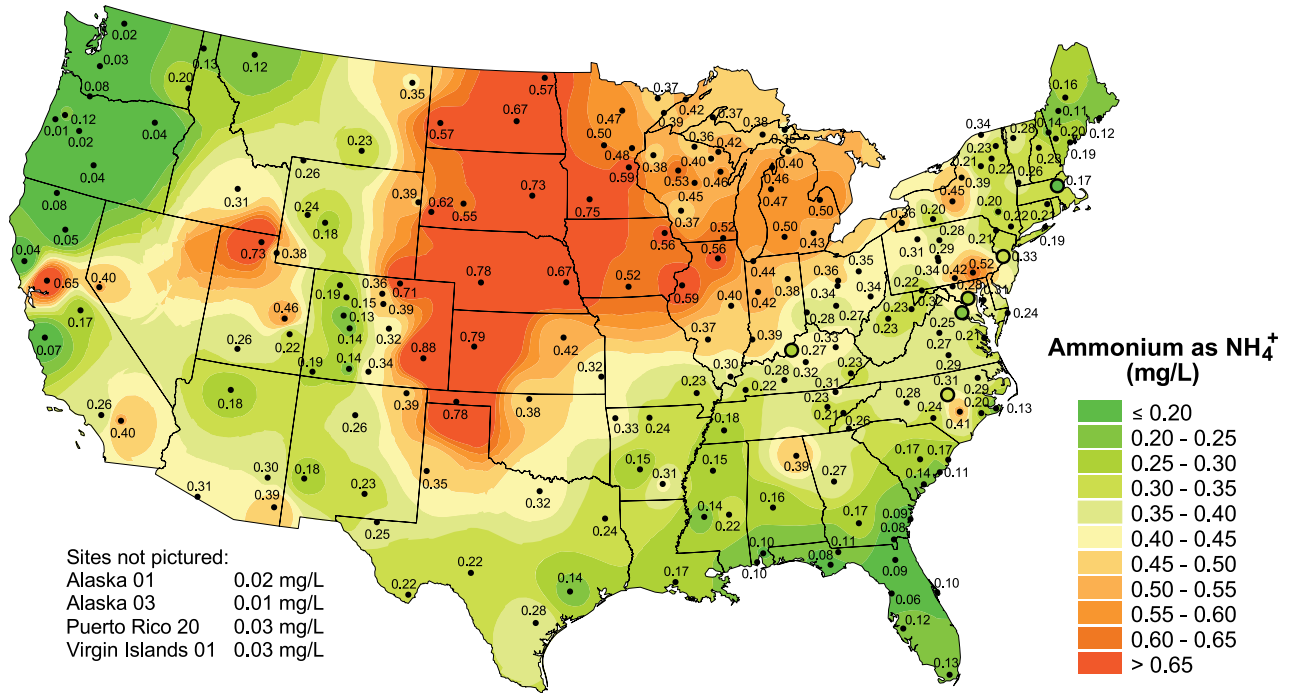
Color contours were created by using nonurban site values to compute an array of regularly spaced grid-point values across the nation. Sites within 500 km of each grid point were used in computations. Color contours and the color-fill in the open circle of urban sites represent classes of concentrations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

In addition to the maps of total precipitation and inorganic nitrogen ("N", i.e., $NH_4^+ + NO_3^-$) wet deposition, concentration and deposition maps are included for NH_4^+ , NO_3^- , SO_4^{2-} , Ca^{2+} , and laboratory-measured pH. Maps of Mg^{2+} , Na^+ , K^+ , and Cl^- are not included but are available from the NADP Web site.

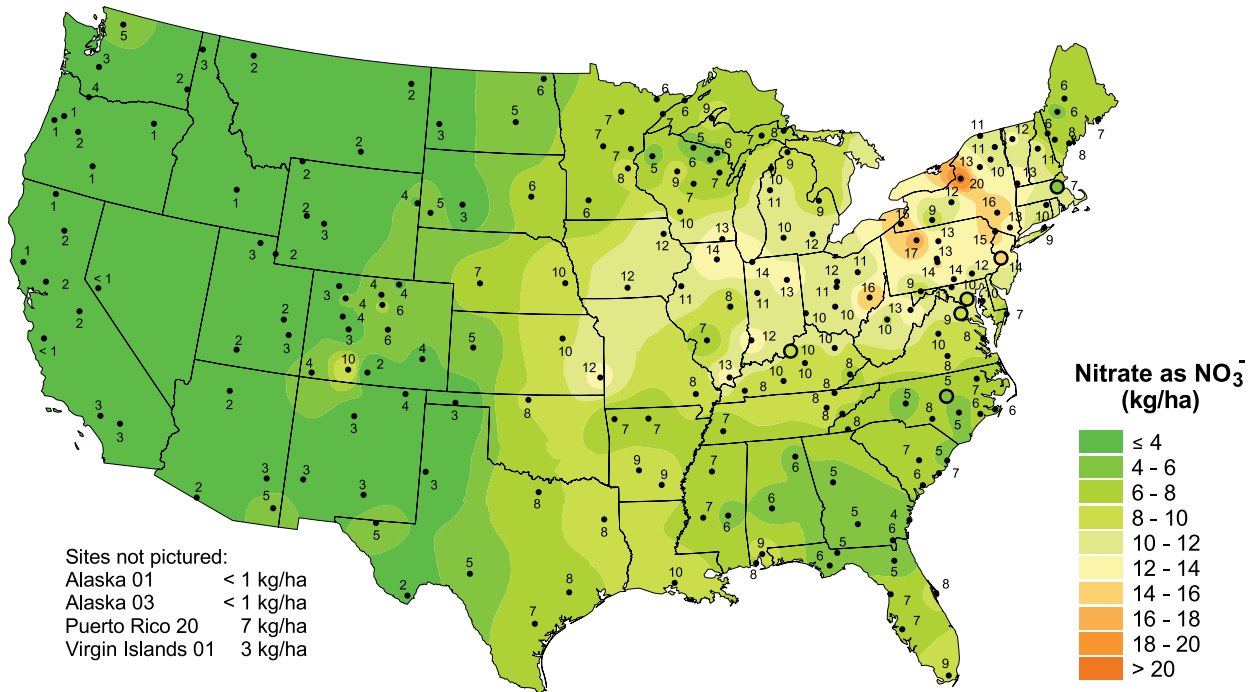
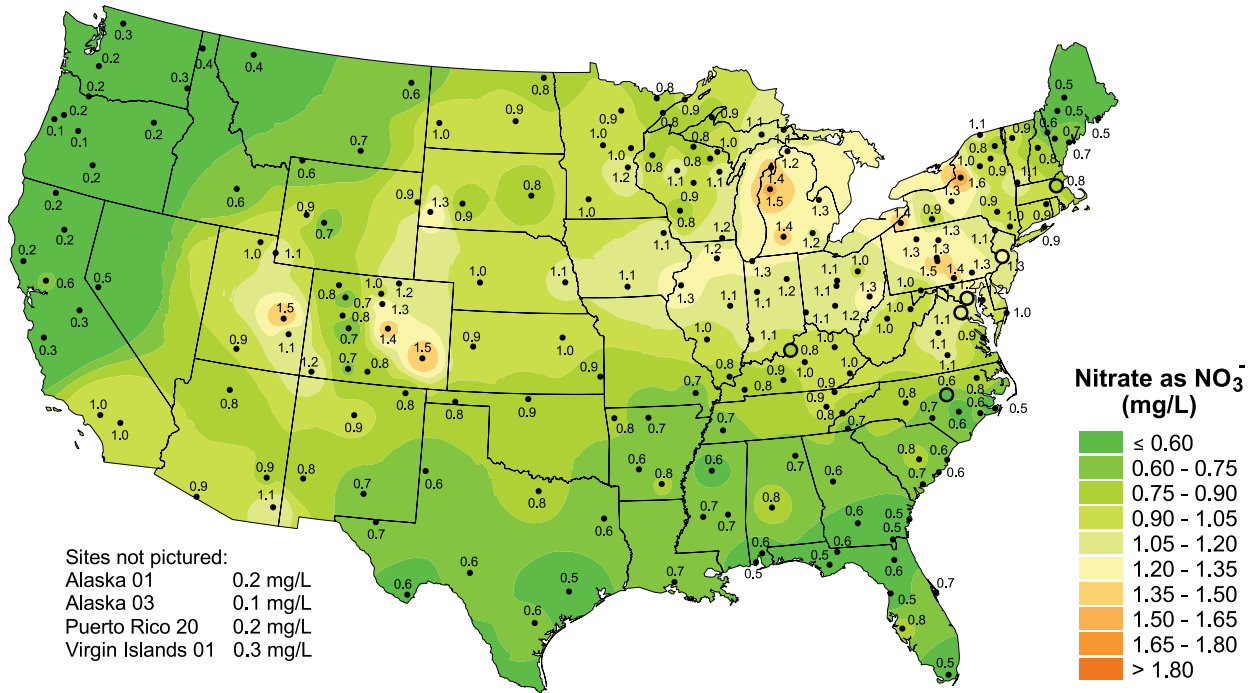
Explanation of Color Contours: Refer to the bottom figure on the next page, which has eight inorganic nitrogen deposition classes or contours. For example, the lightest green color in the legend represents 3.0–4.0 kilograms per hectare (kg/ha). Nitrogen deposition values in the area covered by this contour are greater than 3.0 kg/ha and less than or equal to 4.0 kg/ha.



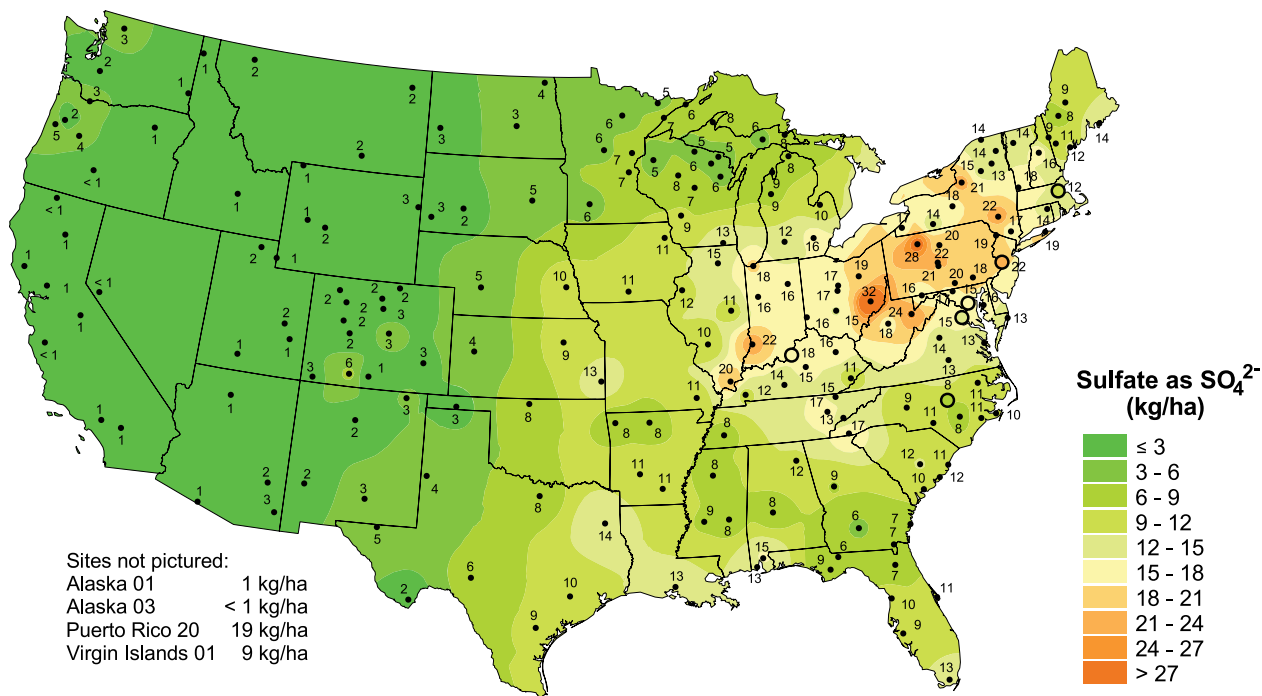
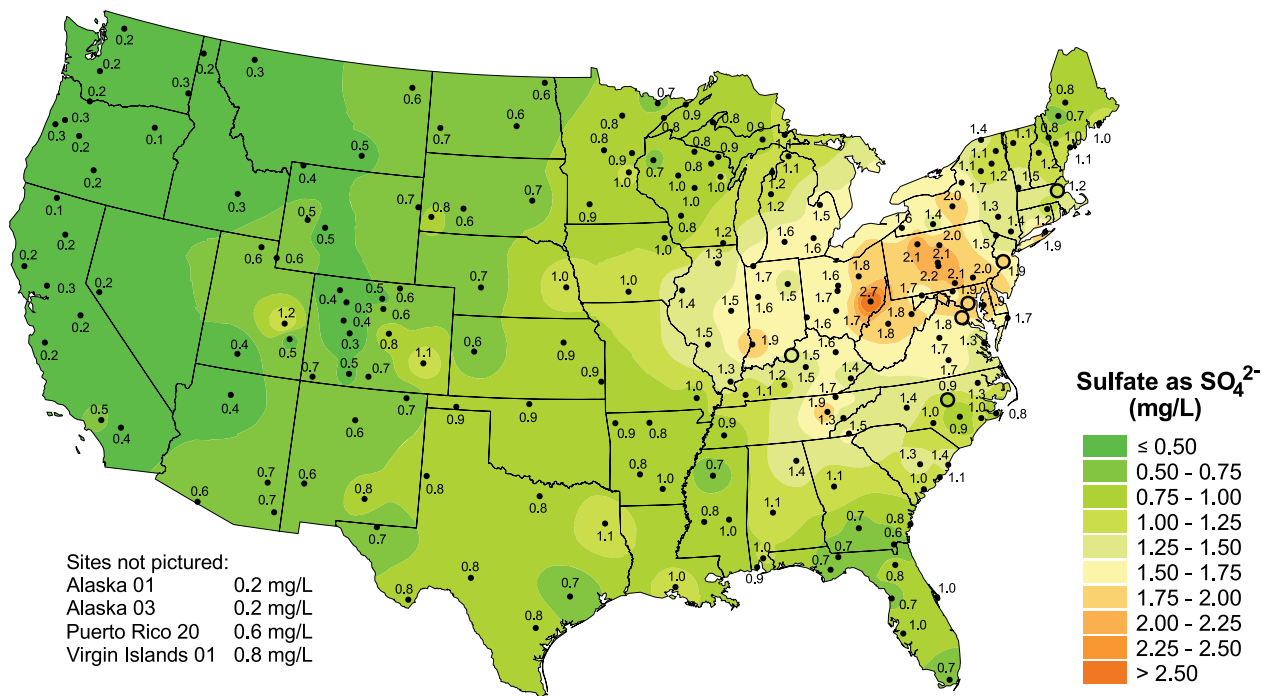
Total precipitation (top) and inorganic nitrogen wet deposition from nitrate and ammonium (bottom), 2007.



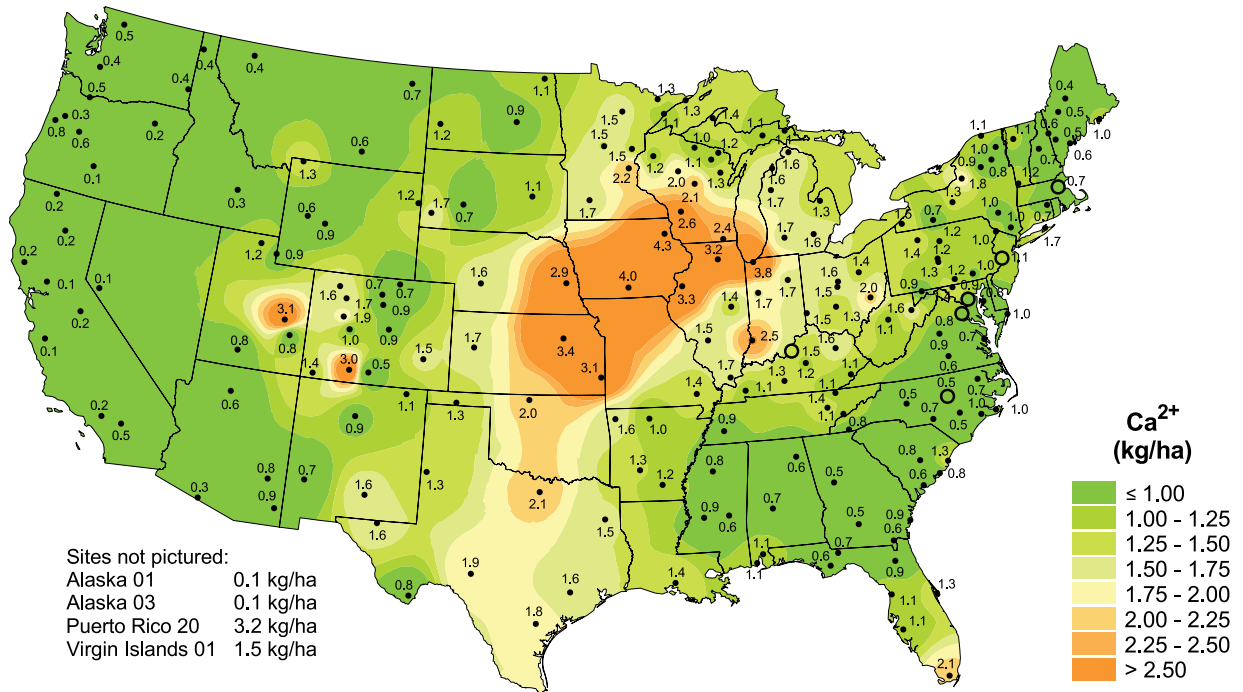
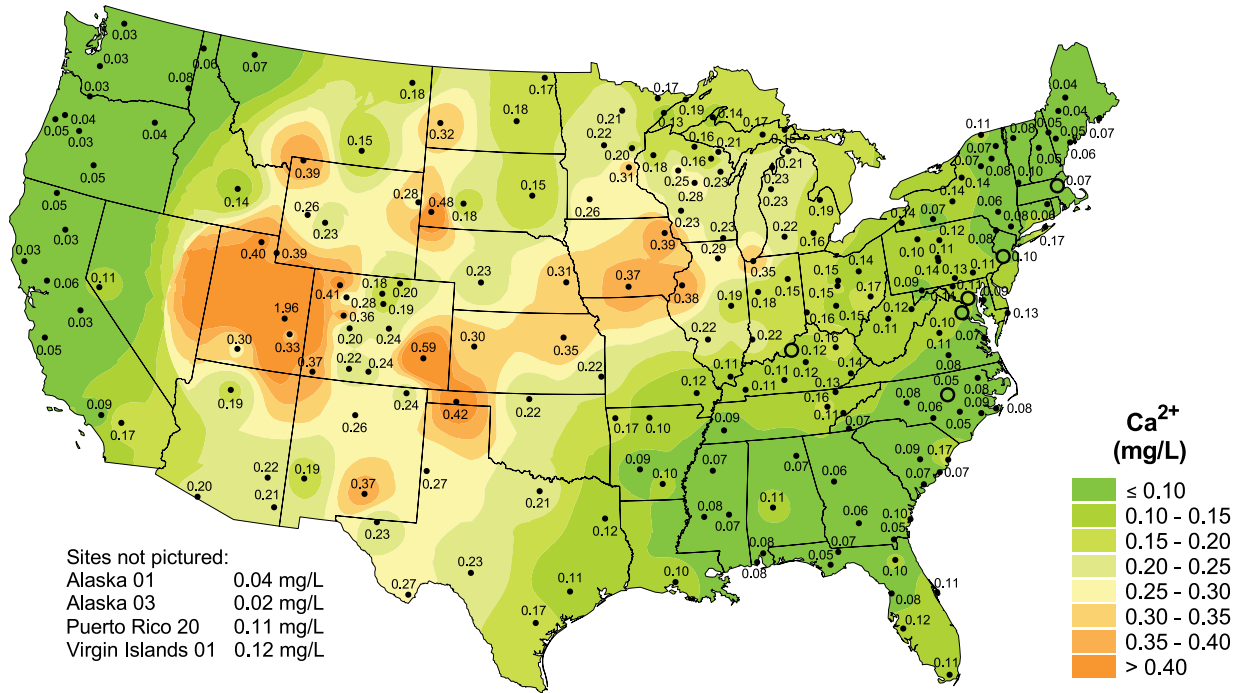
Ammonium ion concentration (top) and wet deposition (bottom), 2007.



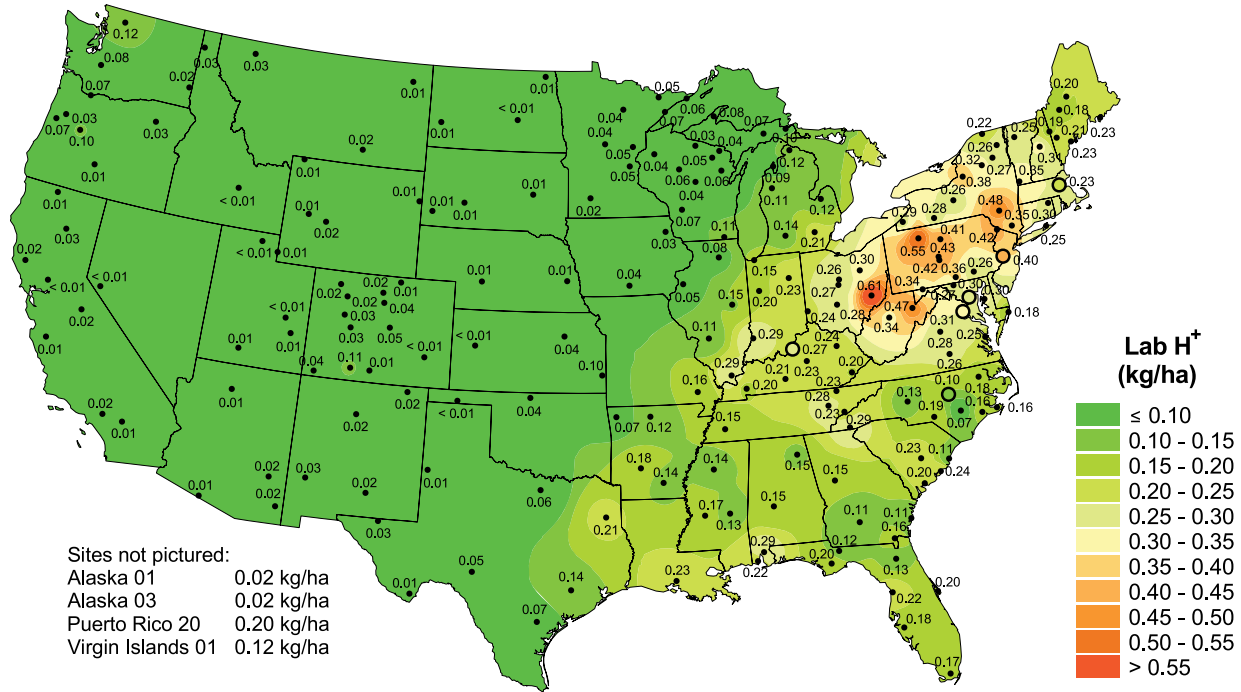
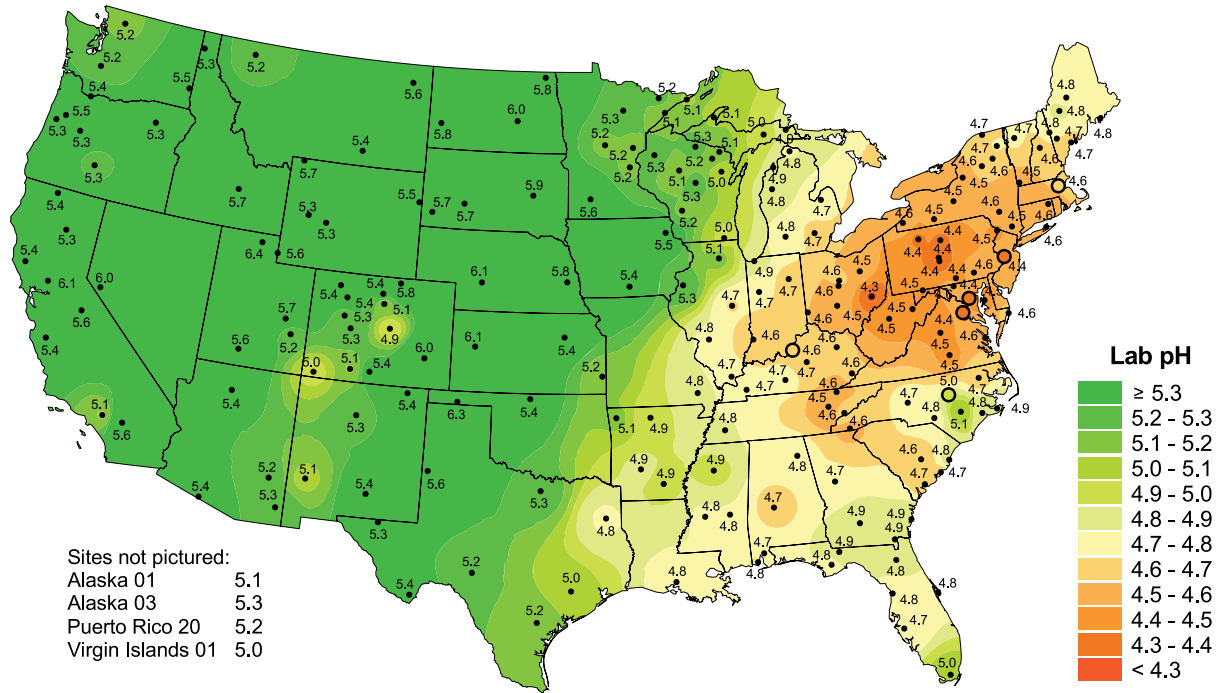
Nitrate ion concentration (top) and wet deposition (bottom), 2007.



Sulfate ion concentration (top) and wet deposition (bottom), 2007.



Calcium ion concentration (top) and wet deposition (bottom), 2007.



Hydrogen ion concentration as pH (top) and wet deposition (bottom) from pH measurements made at the Central Analytical Laboratory, 2007.

Atmospheric Integrated Research Monitoring Network (AIRMoN)

At AIRMoN sites, samples are collected daily within 24 hours of the start of precipitation, often providing data for individual storm events. 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.

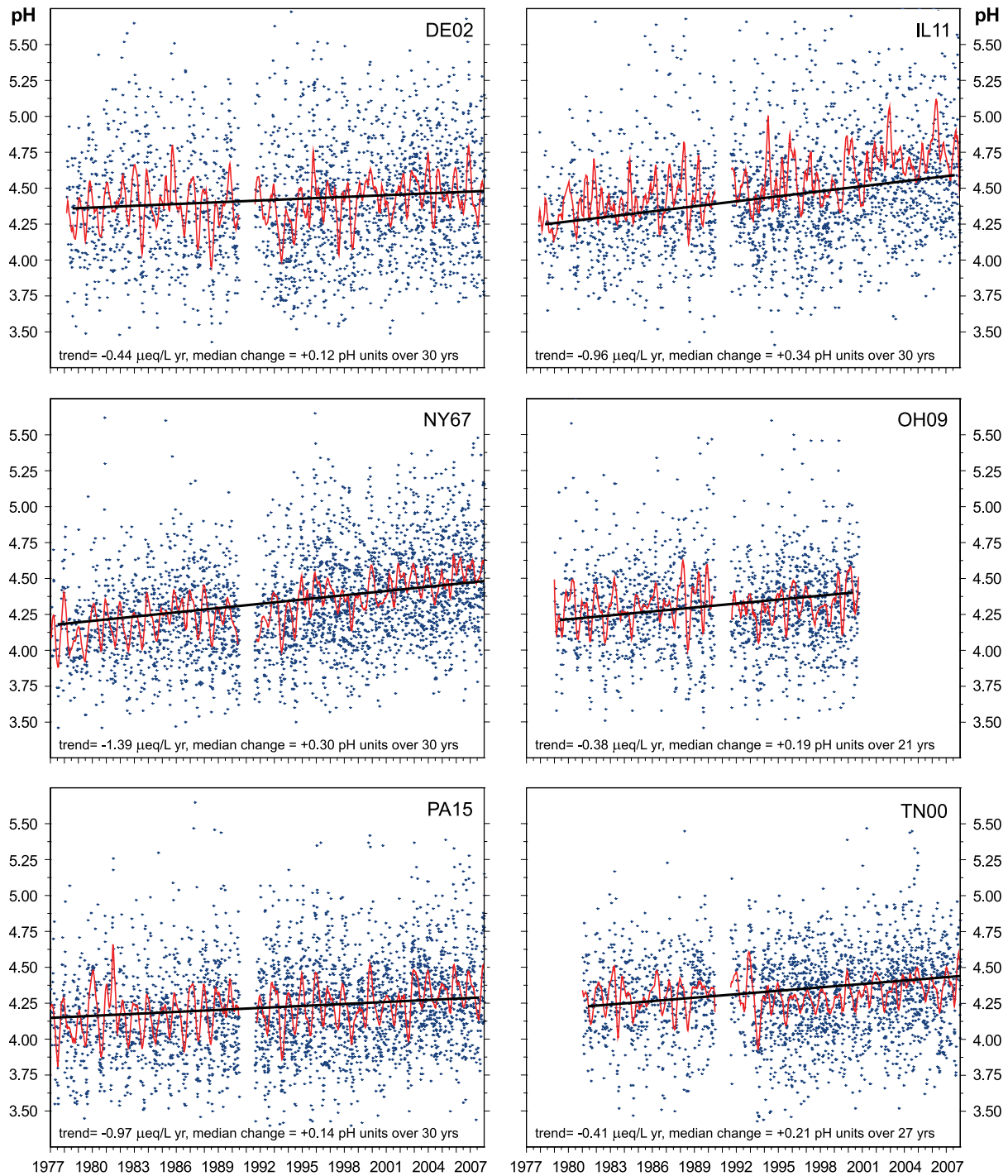
The AIRMoN sites are equipped with the same wet-only deposition collector and precipitation gage used at NTN sites. Each site also has a National Weather Service standard gage for reporting storm total precipitation. Samples are refrigerated after collection and are sent in chilled, insulated shipping containers to the CAL, where they are kept refrigerated until analysis. Refrigeration retards chemical changes. Chemical analyses and data screening procedures for AIRMoN and NTN are similar.

AIRMoN DATA

The timelines on page 13 show combined AIRMoN observations and earlier measurements from the Department of Energy's Multistate Atmospheric Power Production Pollution Study (MAP3S) with analyses made at both Battelle Northwest Laboratory and a short-term continuation at the Institute for Ecosystem Studies (IES), Cornell University. The project was transferred to the National Oceanic and

Atmospheric Administration and continued formally as the NADP's AIRMoN program, with analysis by the Central Analytical Laboratory, University of Illinois. Many MAP3S sites became NADP sites during this transition. Together, these data constitute the longest U.S. network record of precipitation chemistry.

Hydrogen ion concentration trends for these combined site measurements were investigated using the non-parametric Seasonal Kendall trend test over the 30-year records for most stations (21 years for OH09, 27 years for TN00). Graphs on the facing page show the valid pH measurements as blue dots, with a locally-weighted least squares smoothing (LOWESS) function fit to the data shown as a red line. The median pH change between the first and last full year of observations is shown as a black line. The Seasonal Kendall trend/Sen's slope estimator, or the median H⁺ concentration change, is noted in each graph. Each trend was significant at the 90 percent confidence level. Current AIRMoN site VT99 had no MAP3S predecessor, but shows an equivalent H⁺ trend of -1.05 µeq/L - yr, or an increase of +0.23 pH units over 15 years (1993 through 2007). Data gaps are present at project interruptions, and high pH outlier values were left off scale.



The pH measurements and hydrogen ion trends for six combined AIRMoN and MAP3S sites, including valid pH measurements (blue dot), a LOWESS plot (red line), median change (black line and text), and the Seasonal Kendall trends (text). All significant at $\alpha=0.10$. IES data are also included.

Mercury Deposition Network (MDN)

The MDN is the only network providing a long-term record of mercury (Hg) concentrations in precipitation in the United States (106 sites) and Canada (6 sites). All MDN sites follow standard procedures and have uniform precipitation 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 1 percent hydrochloric acid solution.

Site operators collect samples every Tuesday morning or daily within 24 hours of the start of precipitation. In 2007, the Devil's Lake site in south-central Wisconsin, the Underhill site in northern Vermont, and the Yorkville site in northwestern Georgia opted to collect daily samples. 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 ensures that each sampling train component is 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 concentrations. At the end of 2007, 22 MDN sites also opted for methyl mercury concentration measurements. 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.

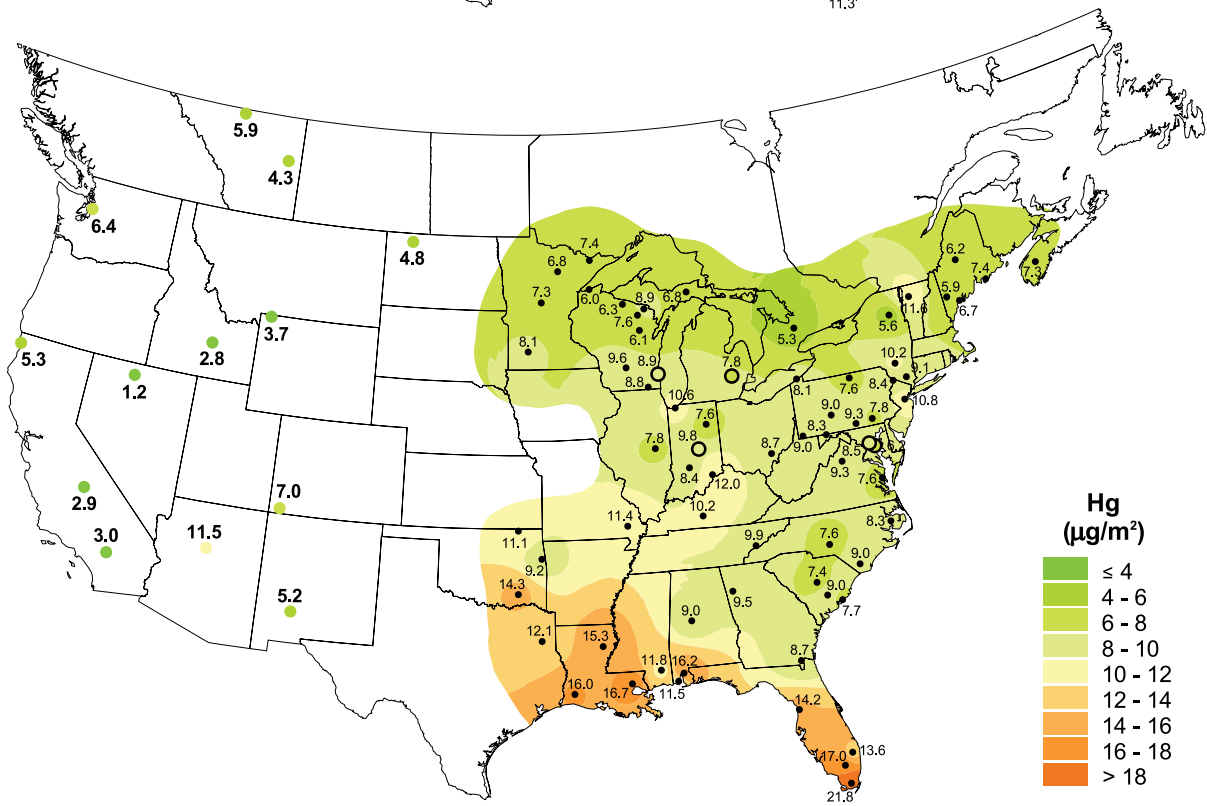
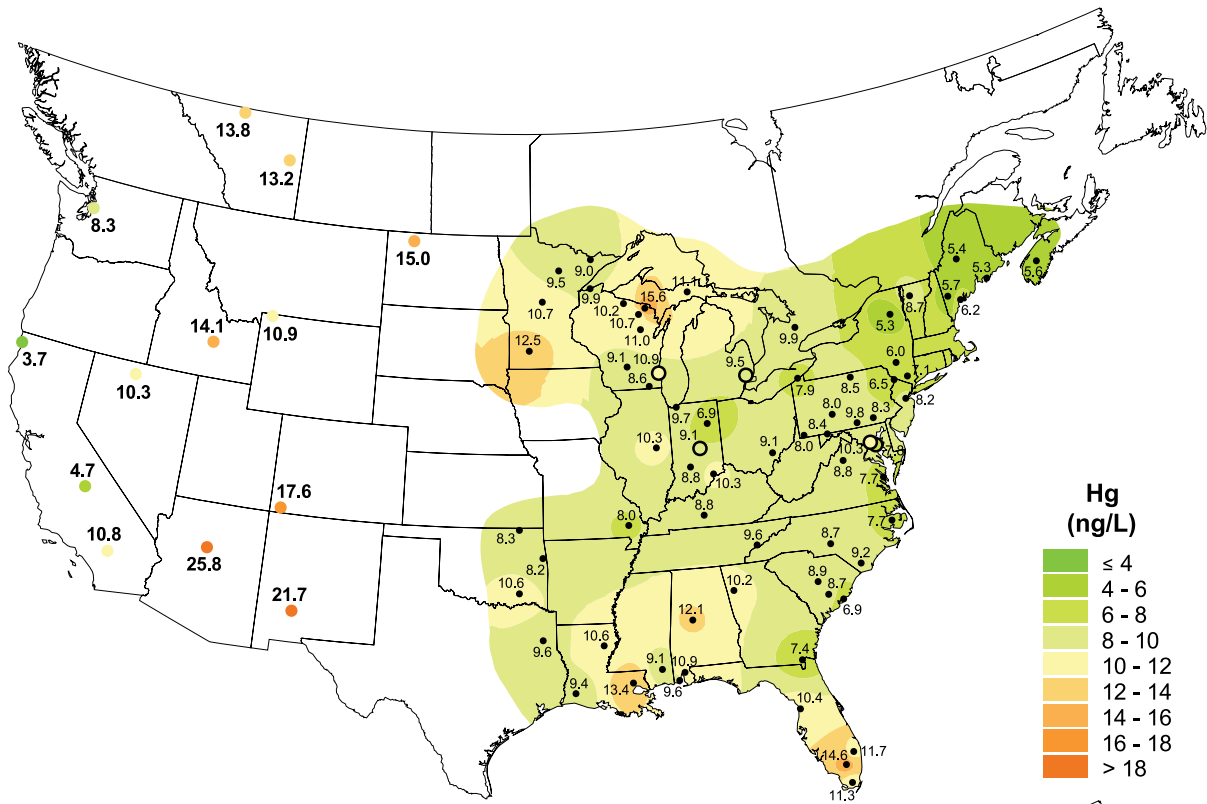
MDN MAPS

The MDN maps on the facing page show spatial variability in the precipitation-weighted annual average concentration and wet deposition of total mercury. Only sites meeting NADP data completeness criteria are included. In 2007, 83 sites met these criteria.

In the eastern United States and southern Canada, color contours display the concentration and deposition distributions. Black dots mark site locations, and 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 color-fill in the open circle of urban sites represent classes of concentrations or depositions in the legend. Outside the color-contoured area where data are too sparse to draw contours, colored dots mark site locations. Dot colors represent concentration or deposition classes as indicated 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 and Wyoming have some form of advisory (see <http://www.epa.gov/waterscience/fish>).



Total mercury concentration (top) and wet deposition (bottom), 2007.

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. 2007-39138-18202). Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the sponsors, the Illinois State Water Survey, or the University of Illinois.

On the cover: The cover shows the entire collection of precipitation sulfate concentration maps (1982-2007) as reported by the National Atmospheric Deposition Program. The precipitation-weighted annual average sulfate concentration in precipitation is depicted across the North American network. Mapping processes have changed over the years, and three types of maps are shown in their original format.

These maps show the dramatic reduction in sulfate concentrations over the years, indicating a significant change in the nation's chemical climate. This same chemical change is shown in three summary panels on page 3.

Champaign, IL

September 2008

ISWS Data/Case Study 2008-03 and NADP Data Report 2008-01

The NADP Program Office is located at the Illinois State Water Survey at the University of Illinois.

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, data requests, or to obtain copies of this publication, contact: NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820, Tel: (217) 333-7871, Fax: (217) 333-0249, E-mail: nadp@sws.uiuc.edu.

Note: When referencing maps or information in this report, please use the citation: National Atmospheric Deposition Program. 2008. *National Atmospheric Deposition Program 2007 Annual Summary*. NADP Data Report 2008-01. Illinois State Water Survey, University of Illinois at Urbana-Champaign, Champaign, IL.