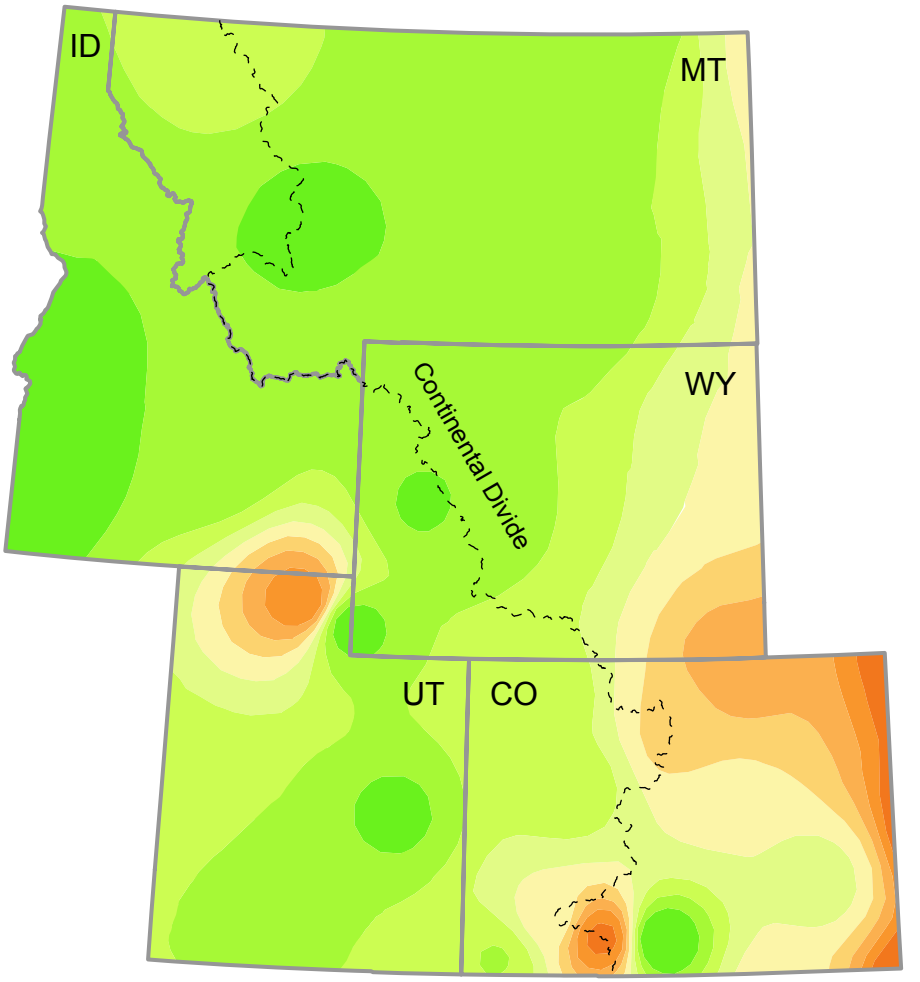
National Atmospheric Deposition Program
2006 Annual Summary



Average Annual Wet Deposition
of Inorganic Nitrogen (kg/ha), 2002-2006

1.0 1.3 1.6 1.9 2.2 2.5 2.8 3.1

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A Cooperative Research Support Program of the
State Agricultural Experiment Stations (NRSP-3)
Federal and State Agencies
and Private Research Organizations

2006 Highlights

The National Atmospheric Deposition Program (NADP) provides data that support informed decisions on air quality issues related to precipitation chemistry. Scientists, educators, policy-makers, and the public use NADP data via the NADP Web site (see back cover for address). This site enables on-line retrieval of individual data points, seasonal and annual averages, trend plots, concentration and deposition maps, reports, and other information. In 2006, the number of registered Web site users rose to nearly 33,000, representing 154 countries. Data downloads numbered 23,664, an increase of 27 percent from 2005. Users logged nearly 350,000 sessions, and the number of color concentration and deposition maps viewed in 2006 rose by nearly 30 percent, topping 121,000.

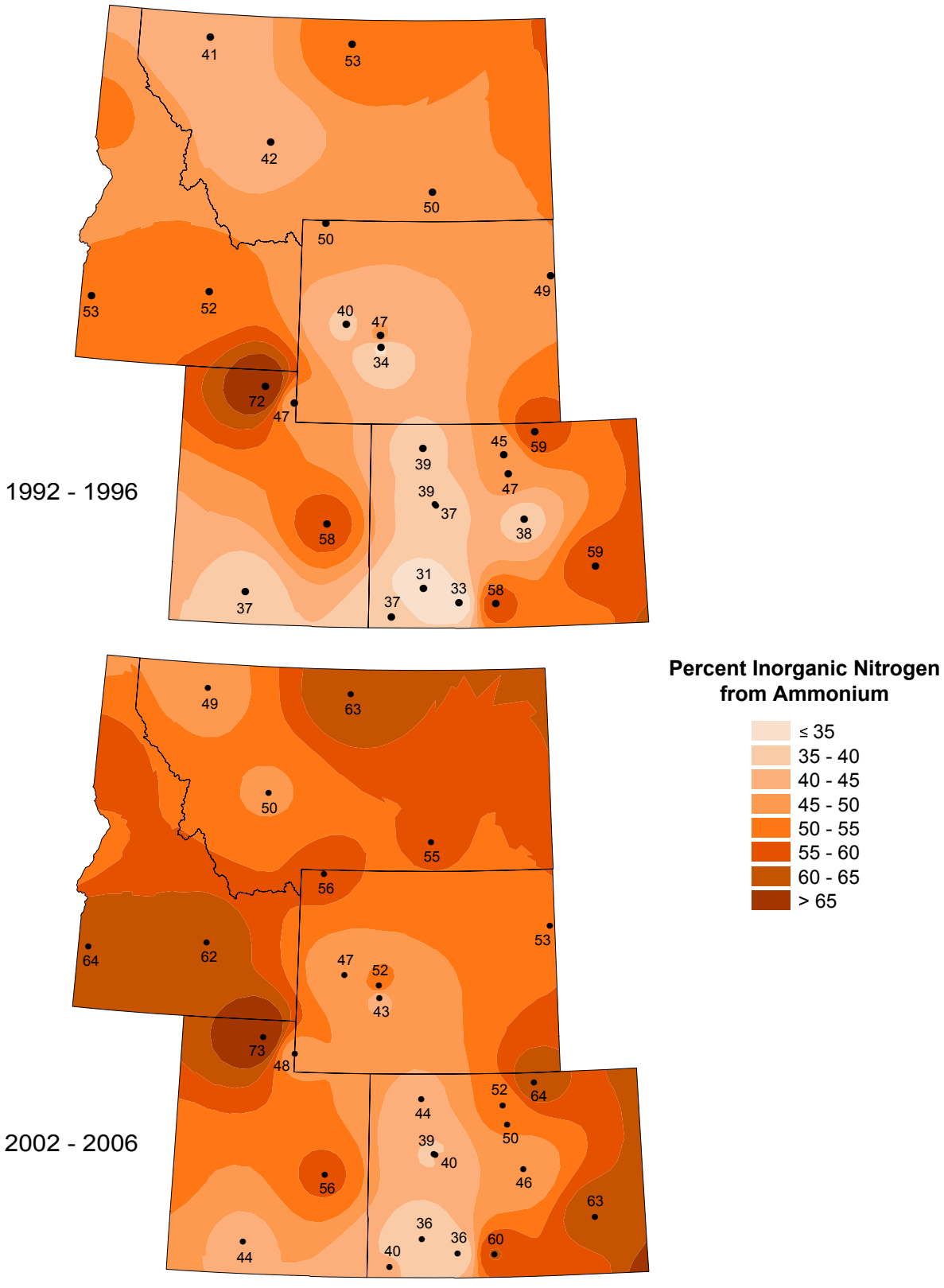
- The NADP partnered with the International Center for First-Year Undergraduate Chemistry Education (ICUC) to translate the NADP brochure, *Nitrogen in the Nation's Rain*, into Spanish (http://nadp.sws.uiuc.edu/lib/brochures/nbrochespanol.pdf).

- The Upper Midwest Aerospace Consortium at the University of North Dakota produced an *Acid Rain* video that features NADP pH data. This video is an episode in the public TV series *Our Changing Planet*, designed to promote education and understanding of our planet.

- Authors of the *United States - Canada Air Quality Agreement, Progress Report 2006* used NADP data to evaluate progress under the agreement's Acid Rain Annex. Since signing the agreement in 1991, U.S. and Canadian sulfur dioxide emissions have decreased about 33 percent. Over this same period, NADP data showed similar reductions in U.S. sulfate deposition. The number of states receiving 20 kilograms per hectare per year (kg/ha/year) or more of sulfate deposition dropped from 12 states to one. A 20-percent reduction of U.S. nitrogen oxide emissions was accompanied by halving the area receiving nitrate deposition of 15-20 kg/ha/year. The report acknowledges that "without substantial atmospheric deposition monitoring networks, it would be impossible to accurately track and confirm that these air quality improvements are taking place."

- Scientists at NADP proposed an initiative to measure three airborne mercury fractions (gaseous elemental mercury, reactive gaseous mercury, and total particulate mercury) at monitoring stations following standard procedures. Data from this proposed new NADP network would be quality assured and accessible on the NADP Web site. See page 15 for a graph of air concentrations of mercury at a Beltsville, Maryland, site jointly supported by the U.S. Environmental Protection Agency - Office of Air and Radiation and National Oceanic & Atmospheric Administration - Air Resources Laboratory.

[**About the cover and figure on page 3:** The cover depicts 5-year (2002-2006) average annual wet deposition of dissolved inorganic nitrogen (DIN) from nitrate and ammonium at 27 National Trends Network (NTN) sites in five Rocky Mountain states. This map illustrates deposition fluxes based on measurements in a broader area. Compare this map and the one on page 5 for a national perspective. To include sites with high proportions of snow, NADP data completeness criteria (http://nadp.sws.uiuc.edu/documentation/completeness.asp) were relaxed from 75 percent to 60 percent, except for the criterion requiring precipitation depth measurements at least 90 percent of the time. The NADP collector has poor snow-capture efficiency; and 25 NTN sites in these states are at altitudes above 2000 meters and generally receive more than half their precipitation as snow. Maps on page 3 are based on the same sites as the cover and illustrate an increase in the fraction of DIN from ammonium. This increase occurred at all but two sites between the 1992-1996 and 2002-2006 periods and is now 50 percent or higher at more than half the sites.]



Percent of dissolved inorganic nitrogen from ammonium in wet deposition at NTN sites in five Rocky Mountain states shown on the cover.

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 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, the Atmospheric Integrated Research Monitoring Network (AIRMoN), joined the NADP in 1992, and had seven sites at the end of 2006. 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 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 98 sites at the end of 2006. All MDN samples are analyzed for total mercury, and some for the more toxic methyl mercury. Forty-eight states have advisories warning people to limit consumption of fish and wildlife from certain 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 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 from the collection bucket to a shipping bottle. All samples are sent to the CAL for analysis. The CAL also 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, which applies a final set of checks and resolves remaining discrepancies. The Program Office stores all NADP data and information in a database system that is accessible from the NADP Web site. Valid (i.e., unflagged) NTN data can be retrieved remotely through this on-line retrieval system. Flagged data are available by special request.

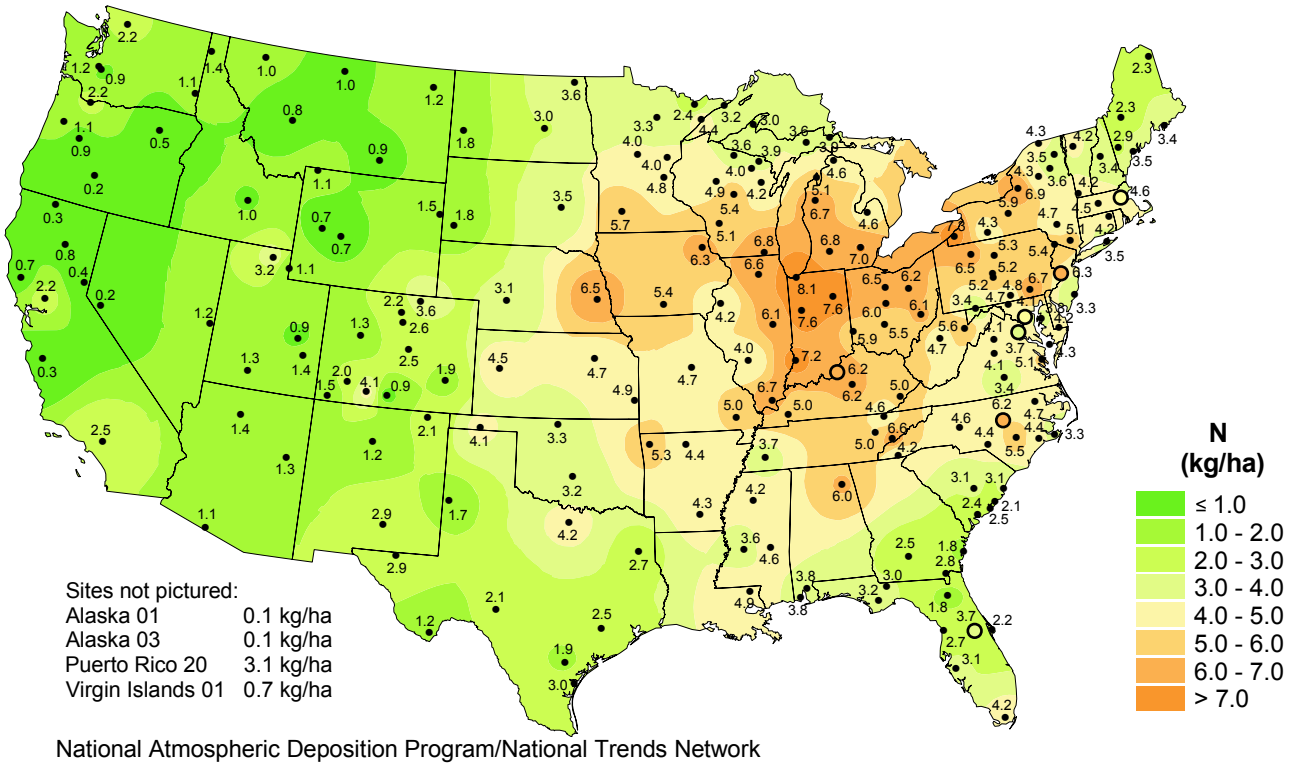
NTN Maps

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 2006, 207 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. Concentration or deposition values appear next to each site.

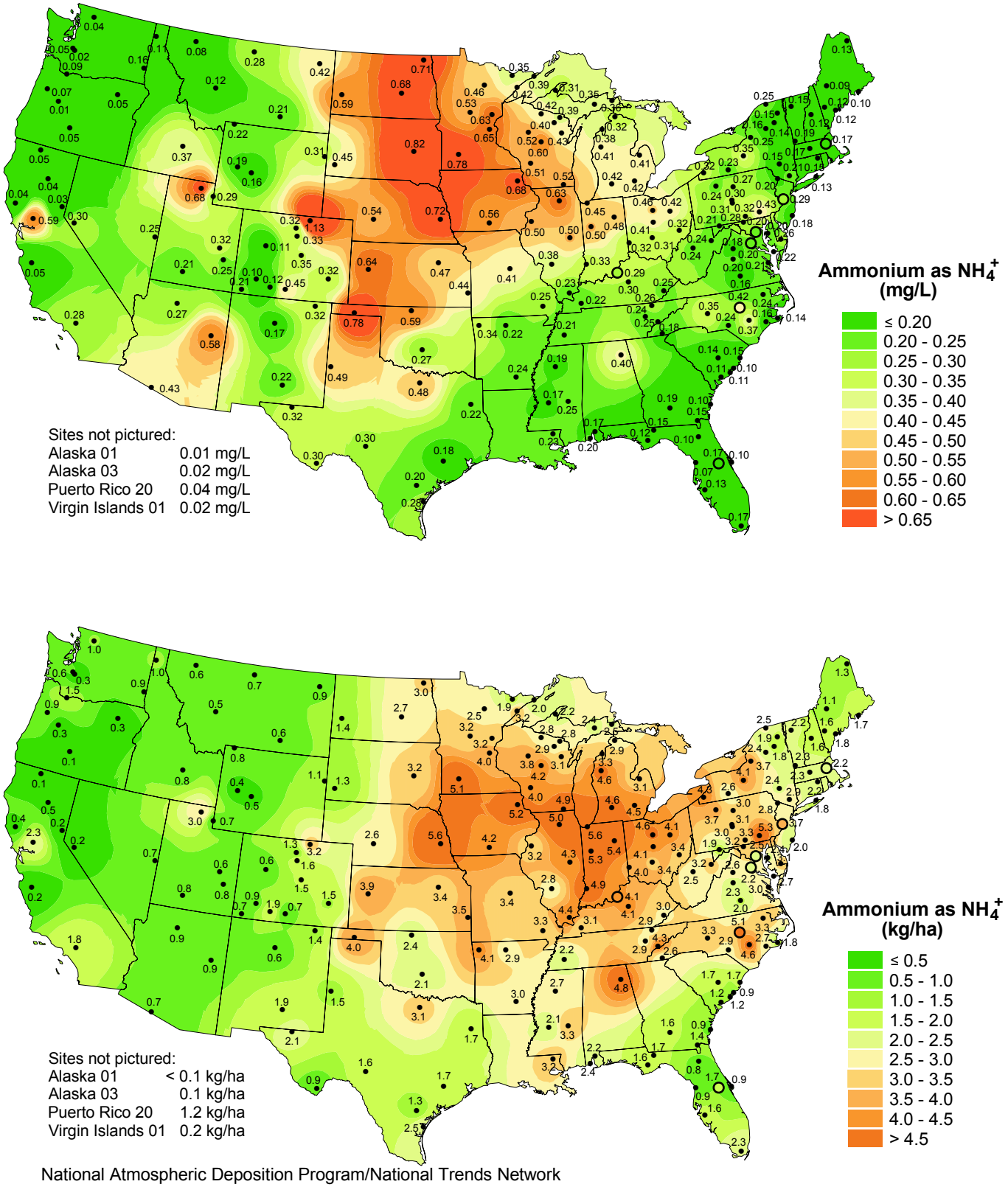
Color contours were created by using nonurban site values to compute an array of regularly spaced grid-point values across the nation. Sites within 500 km of each grid point were used in computations. Color contours and the color fill in the open circle of urban sites represent classes of concentrations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

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

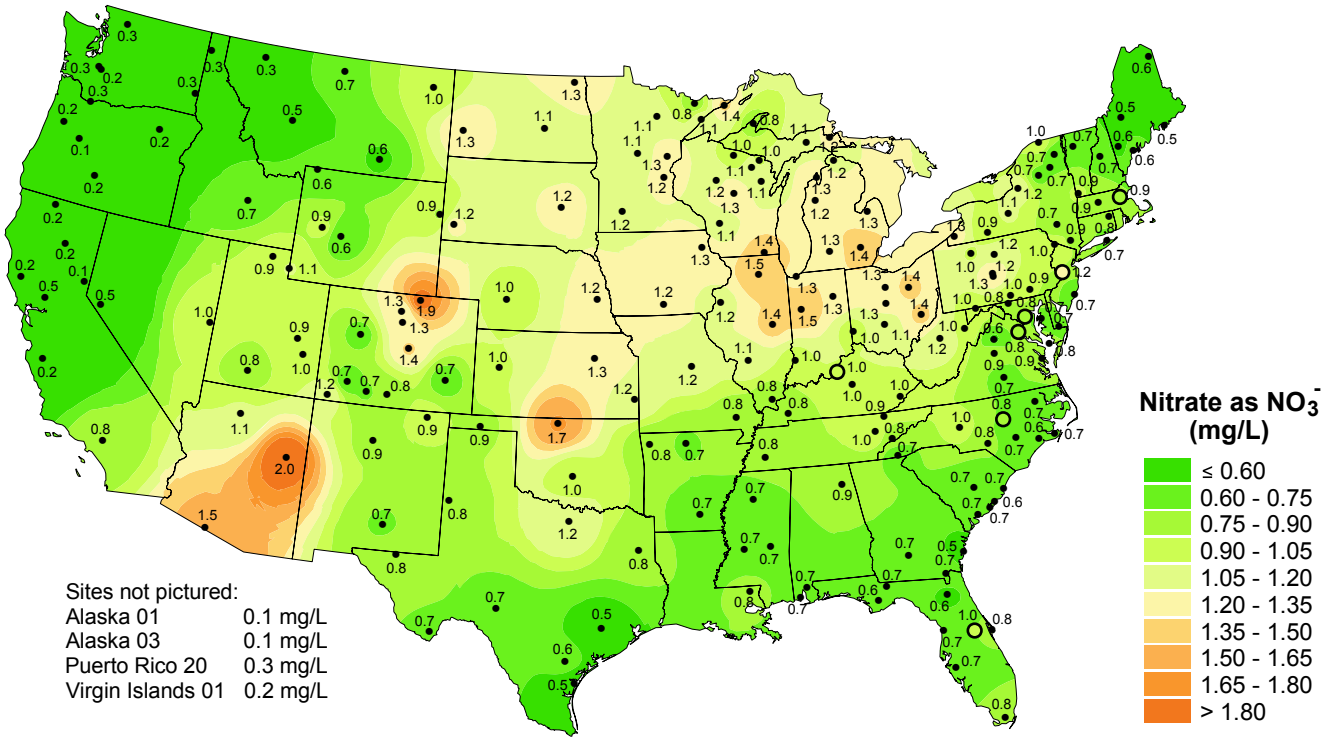
Explanation of Color Contours: Refer to the figure below, which has eight inorganic nitrogen deposition classes or contours. For example, the lightest green color in the legend represents 3.0 - 4.0 kilograms per hectare (kg/ha). Nitrogen deposition values in the area covered by this contour are greater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

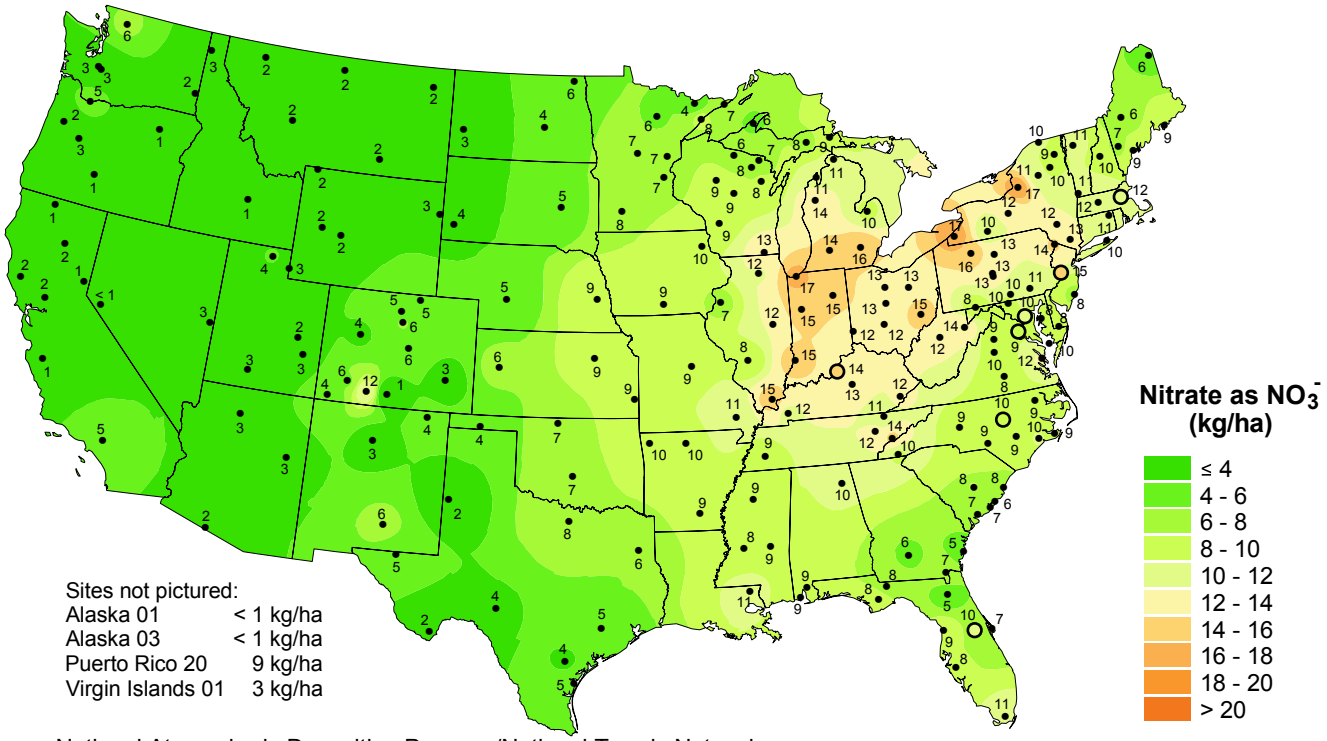


Inorganic nitrogen wet deposition from nitrate and ammonium, 2006.



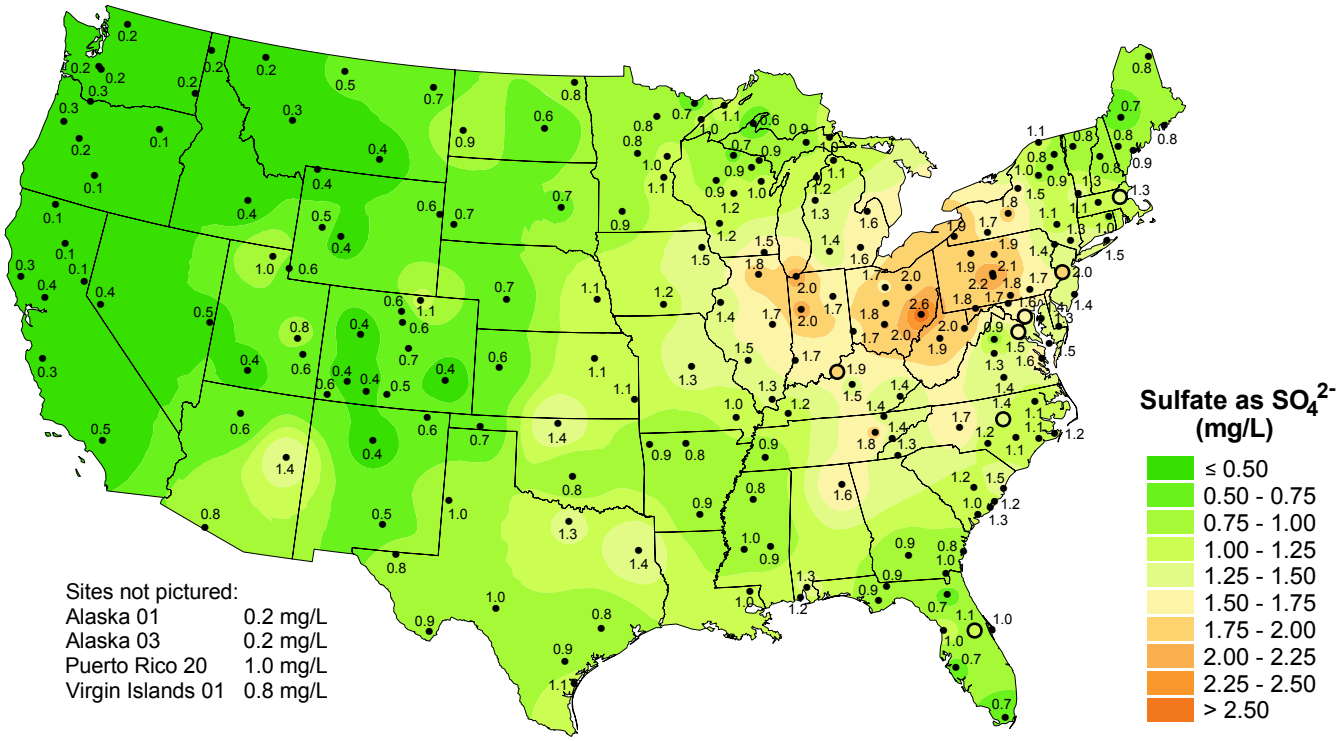
Ammonium ion concentration (top) and wet deposition (bottom), 2006.

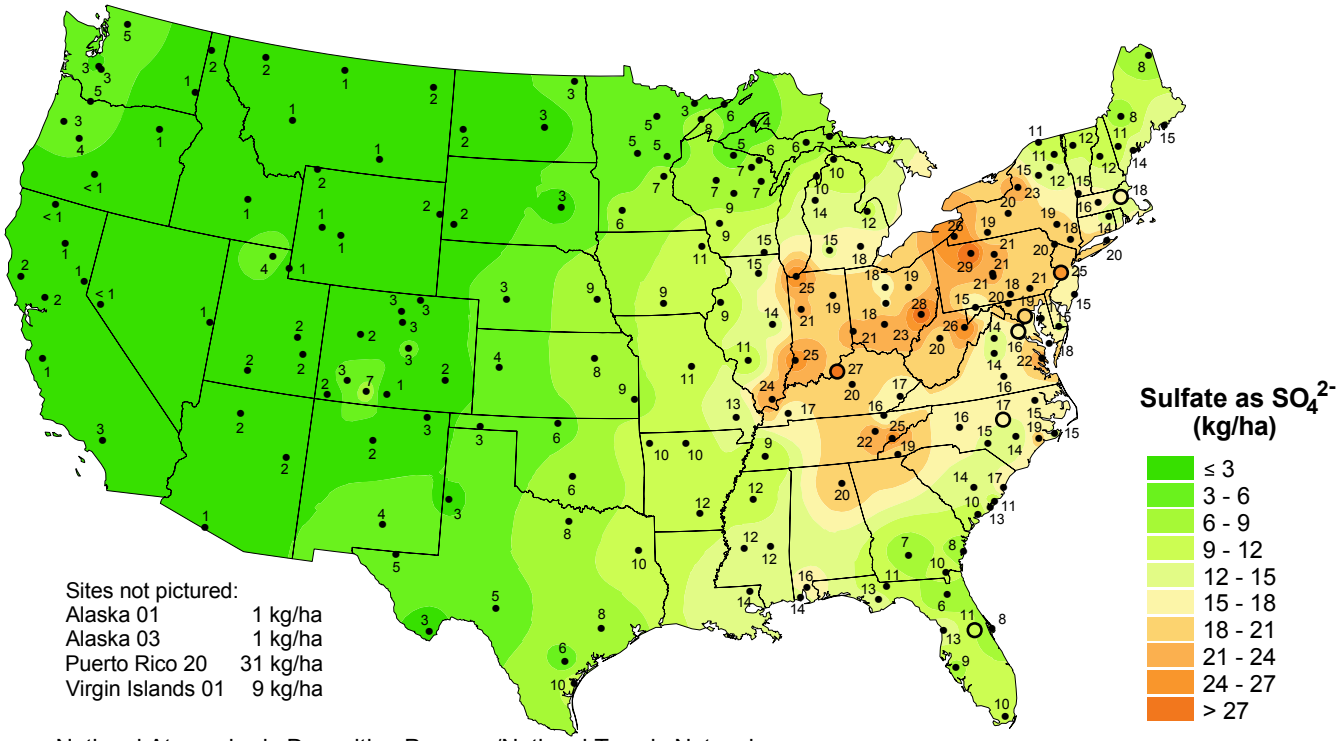




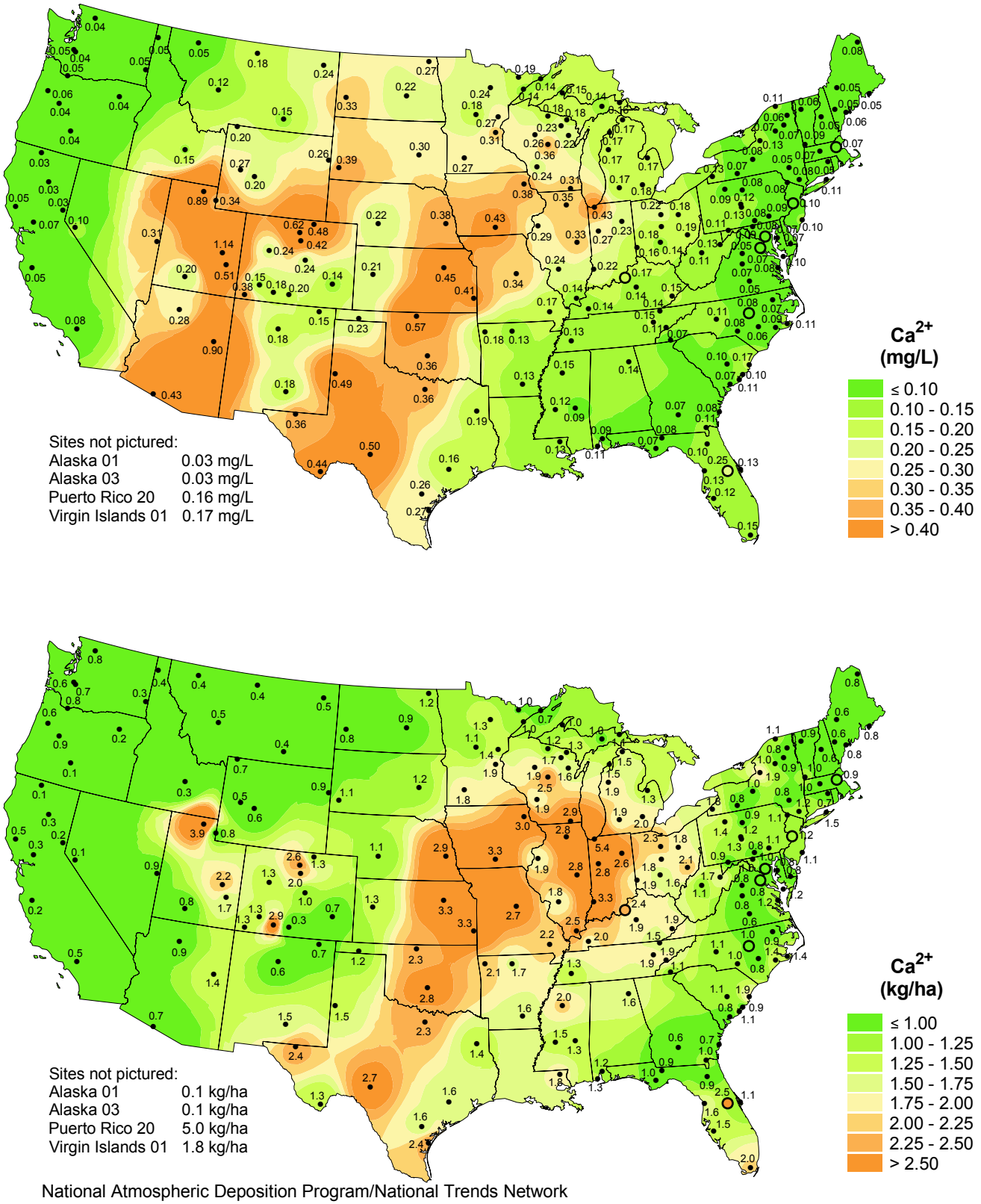
National Atmospheric Deposition Program/National Trends Network

Nitrate ion concentration (top) and wet deposition (bottom), 2006.

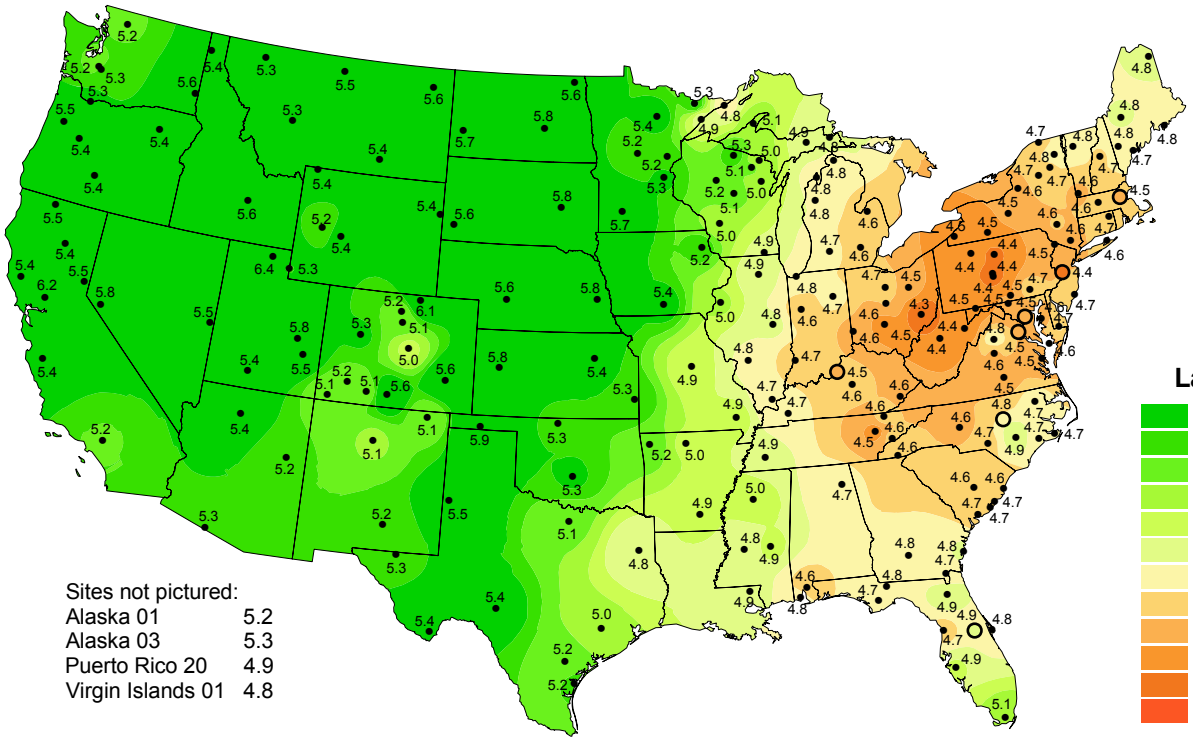


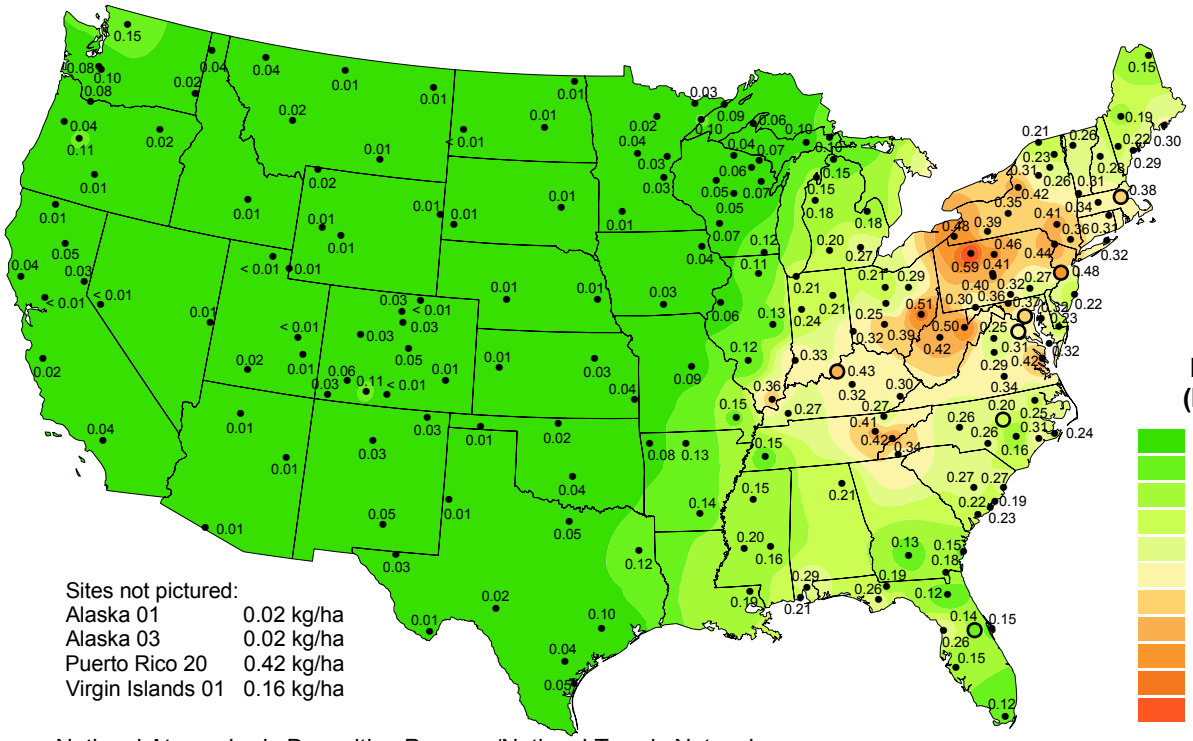


Sulfate ion concentration (top) and wet deposition (bottom), 2006.



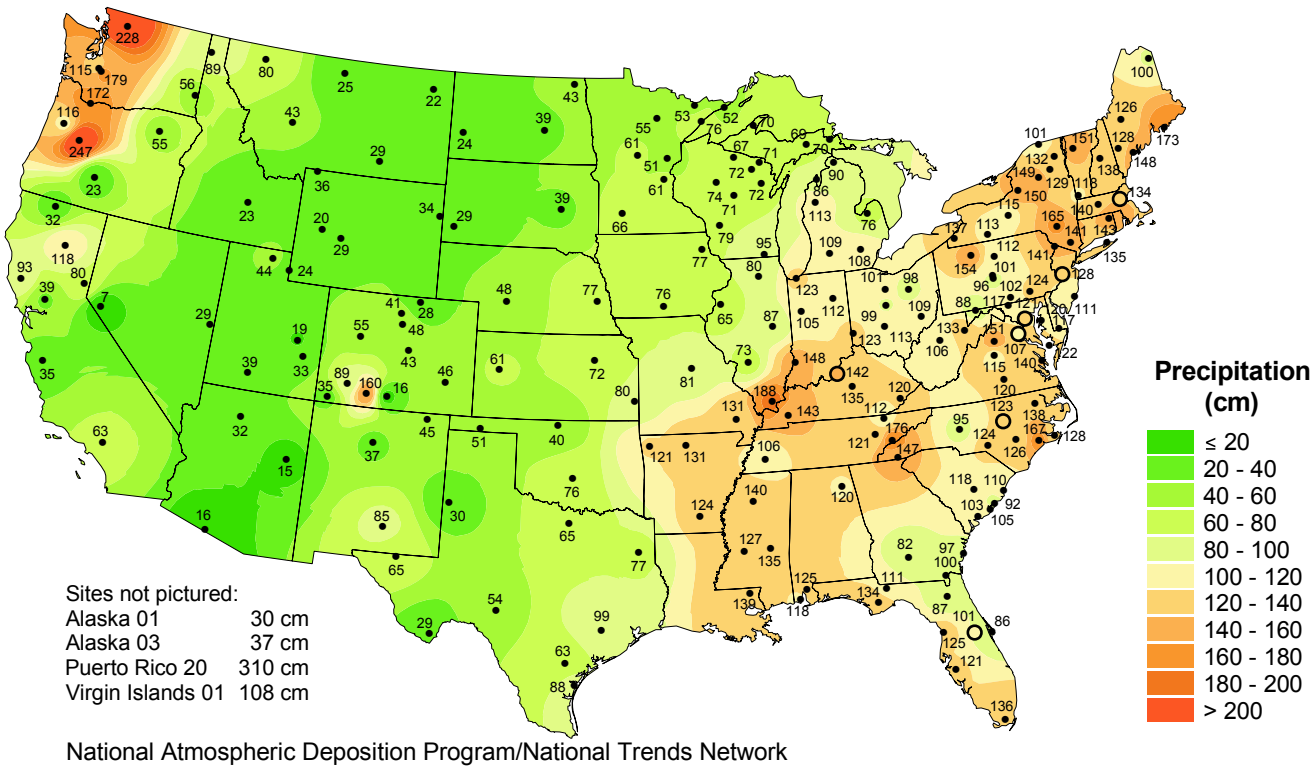
Calcium ion concentration (top) and wet deposition (bottom), 2006.





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, 2006.



Total precipitation, 2006.

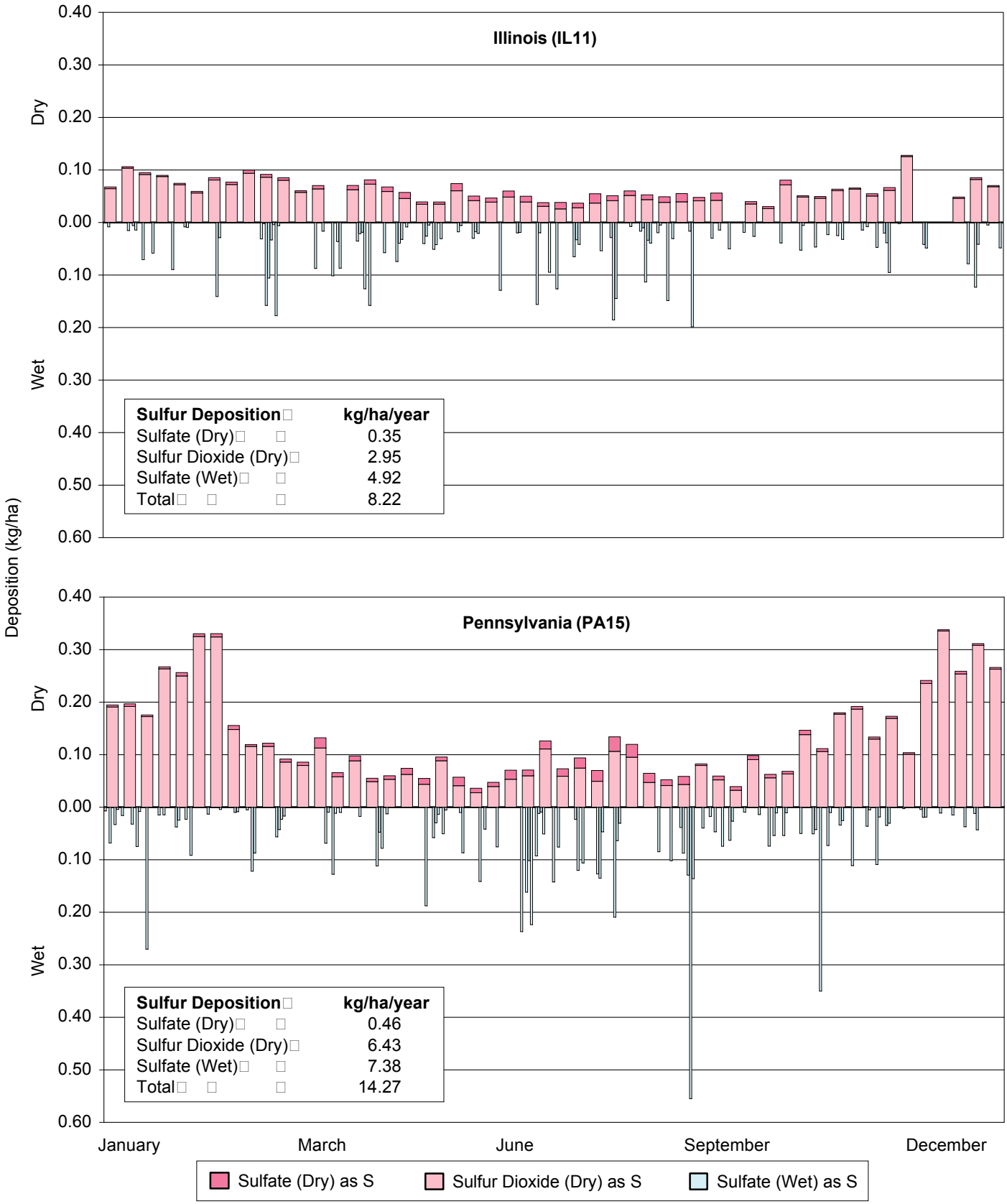
Atmospheric Integrated Research Monitoring Network

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 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, although low-volume AIRMoN samples are not diluted to accommodate a complete analysis, as is standard NTN procedure. Another difference is that during data review, the CAL assigns a quality rating code before sending AIRMoN data to the NADP Program Office for final checks and posting on the Web site.

AIRMoN Data

Bar charts on page 12 show the 2006 wet and dry sulfur deposition at sites in Illinois and Pennsylvania with co-located AIRMoN and Clean Air Status and Trends Network (CASTNet) sites (http://www.gov/castnet/). Wet deposition data (blue) are from daily AIRMoN sulfate measurements. Dry deposition data (red) are from CASTNet gaseous sulfur dioxide and particulate sulfate measurements. Dry deposition was calculated from the product of weekly-average atmospheric concentration measurements and modeled dry deposition velocities, which were based on meteorological data, and information on land cover, vegetation, and surface conditions. Gaps in the dry deposition results occur where measurements did not meet completeness criteria.



AIRMoN daily wet deposition of sulfur from sulfate in precipitation and CASTNet weekly dry deposition of sulfur from gaseous sulfur dioxide and particulate sulfate.

Mercury Deposition Network

The MDN is the only network providing a long-term record of mercury (Hg) concentrations in precipitation in the United States (90 sites) and Canada (8 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 2006, 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 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 ensures 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 concentrations. At the end of 2006, 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.

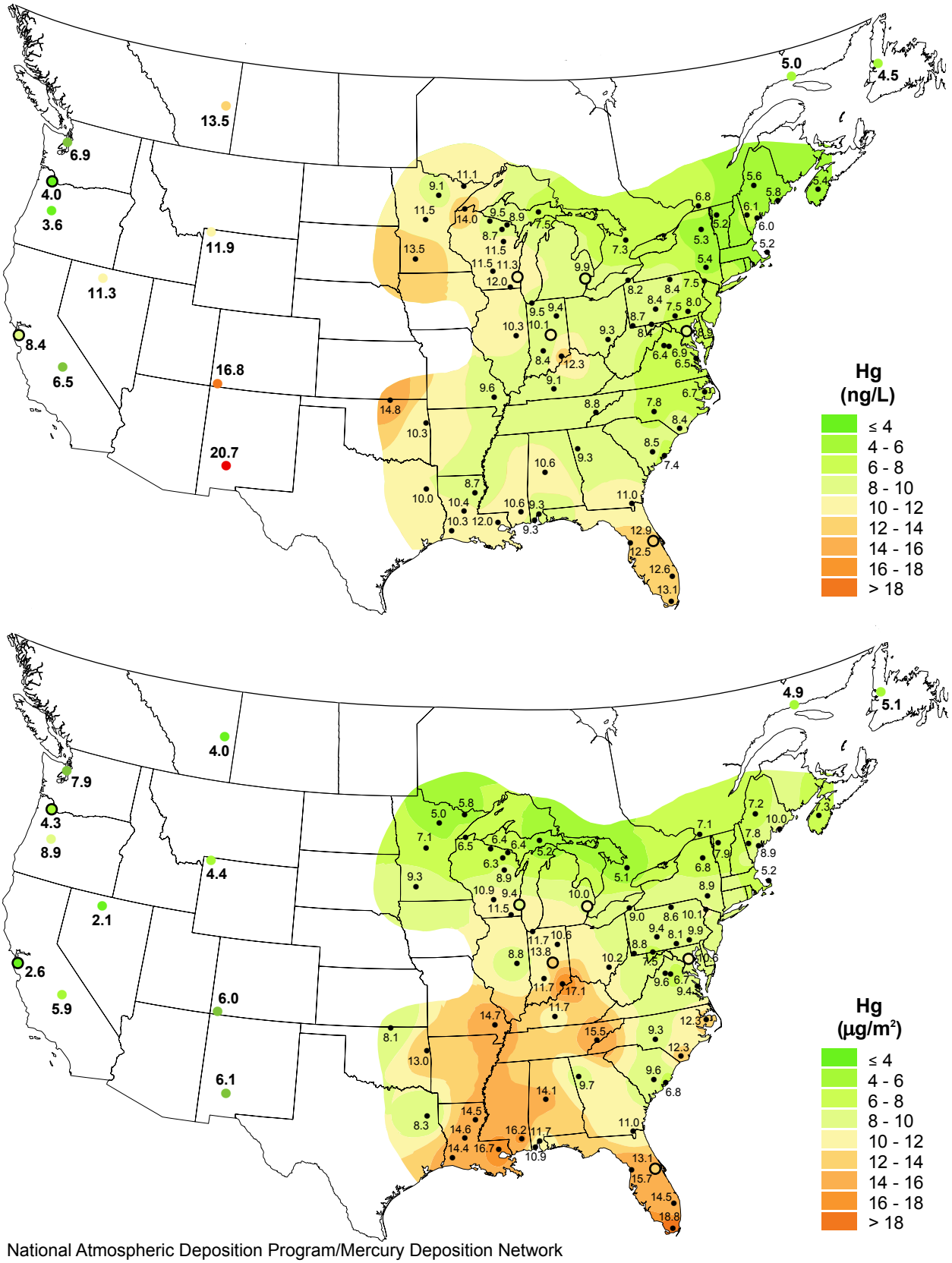
MDN Maps

The MDN maps on page 14 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 2006, 81 sites met these criteria.

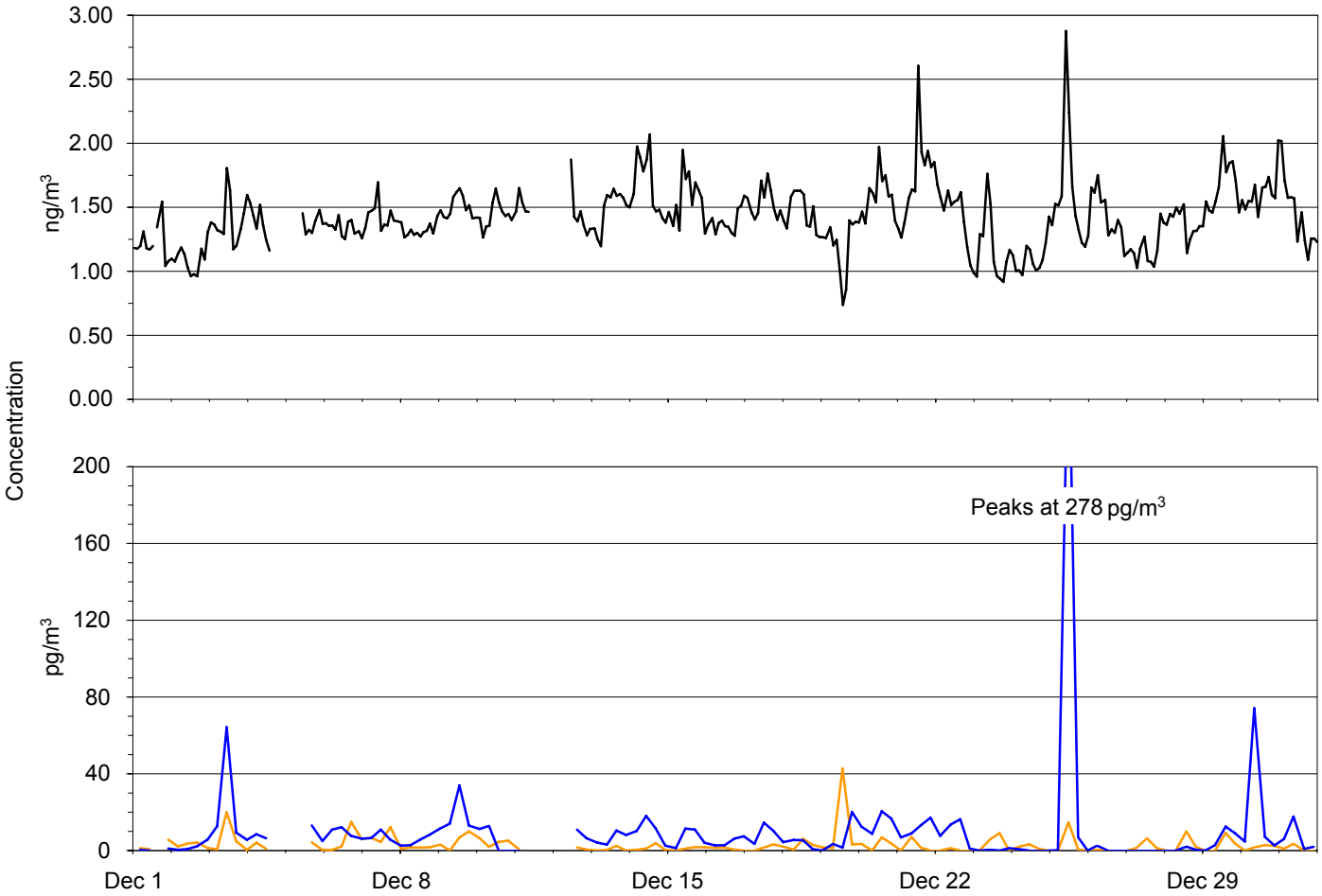
In the eastern United States and southern Canada, color contours display the concentration and deposition distributions. Black dots mark site locations, and open circles designate urban sites. Concentration or deposition values appear next to each site.

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 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/ost/fish).



Total mercury concentration (top) and wet deposition (bottom), 2006.



Preliminary one-hour average GEM (black) and six-hour average RGM (orange) and TPM (blue) concentrations at Beltsville, Maryland, December 2006.

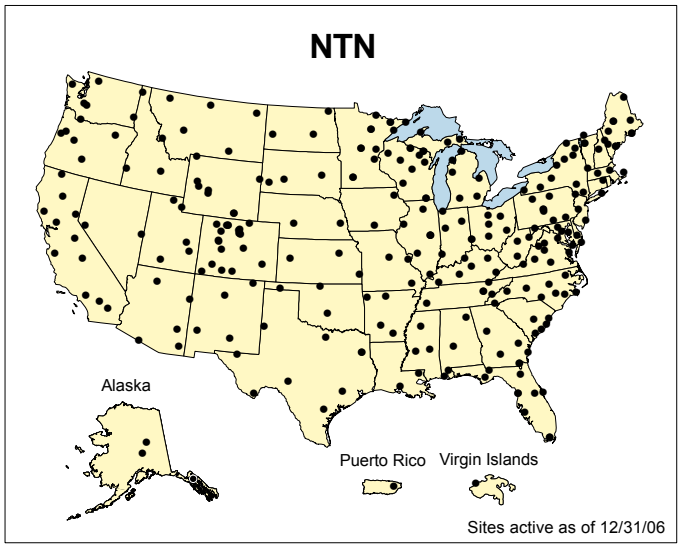
Atmospheric Mercury Initiative

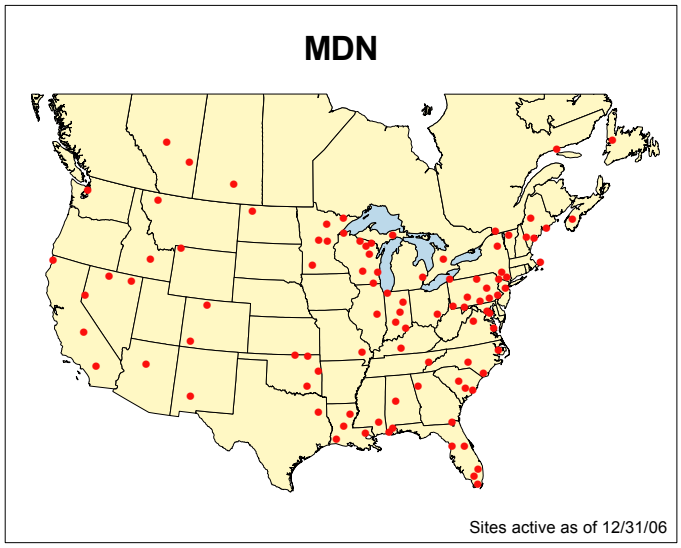
The atmospheric mercury initiative (http://nadp.sws.uiuc.edu/mtn/) seeks to measure air concentrations of gaseous and particulate mercury at a network of monitoring stations representing a broad range of environments (rural, suburban, urban, near source, and sensitive ecosystem). Stations would follow standard procedures, based on methods developed by U.S. EPA scientists and other researchers. Data would be quality assured and accessible online from the NADP Web site.

Goals of the initiative include:

- Quantifying the spatial distributions and temporal trends of airborne mercury,
- Providing data for evaluating predictive and diagnostic models and for assessing source-receptor relationships, and
- Facilitating dry deposition estimates and, combined with wet deposition measurements, total mercury deposition estimates.

The graphs above display concentrations of three airborne mercury fractions: (1) gaseous elemental mercury (GEM), (2) reactive gaseous mercury (RGM), and (3) total particulate mercury (TPM). Measurements are from a one-hour sampling period followed by a one-hour analysis period during which sampling is suspended. During the sampling period, GEM is reported every five minutes. Values in the graph are one-hour averages of the five-minute measurements. During the sampling period, RGM is captured on a potassium chloride coated quartz annular denuder, and then a quartz filter collects TPM. During analysis, RGM and TPM are thermally desorbed, converted to GEM, and measured. The RGM and TPM values in the graph are six-hour average concentrations.





Note:

When referencing maps or information in this report, please use the citation: National Atmospheric Deposition Program. 2007. *National Atmospheric Deposition Program 2006 Annual Summary*. NADP Data Report 2007-01. 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. 2007-39138-18202). Any findings or conclusions in this publication do not necessarily reflect the views of the U.S. Department of Agriculture, other sponsors, or the Illinois State Water Survey.

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. Telephone: (217) 333-7871 Fax: (217) 333-0249 e-mail: nadp@sws.uiuc.edu