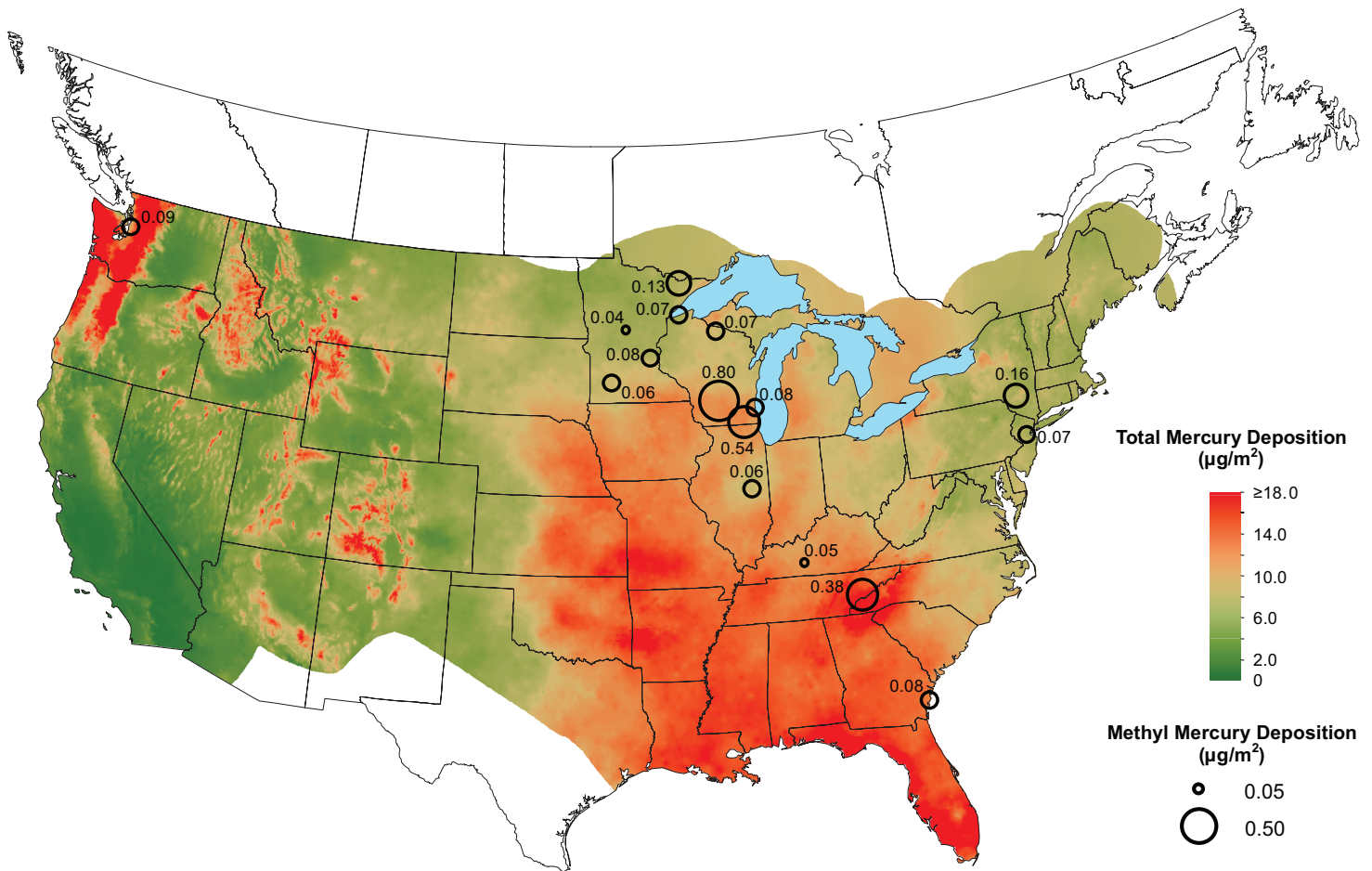
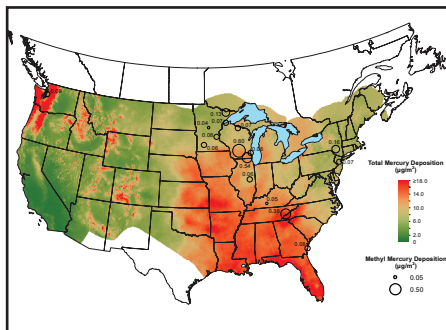




National Atmospheric Deposition Program

2013 Annual Summary





On the cover: The background gradient map represents the 2013 annual total mercury wet deposition flux (micrograms per square meter, $\mu\text{g}/\text{m}^2$) over the continental United States, as measured by the Mercury Deposition Network (MDN) and using the PRISM precipitation data. The circles represent the 2013 annual methyl mercury wet deposition flux ($\mu\text{g}/\text{m}^2$) as measured by the MDN.

When referencing maps or information in this report, please use the citation: National Atmospheric Deposition Program, 2014. National Atmospheric Deposition Program 2013 Annual Summary. NADP Data Report 2014-01. Illinois State Water Survey, University of Illinois at Urbana-Champaign, IL.

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2013 Highlights

The National Atmospheric Deposition Program (NADP) provides fundamental measurements that support informed decisions on environmental issues related to precipitation and atmospheric deposition chemistry, as well as atmospheric mercury and ammonia. NADP data are relevant to scientists, educators, policymakers, and the public. All data are available via the NADP website (<http://nadp.isws.illinois.edu>). Products available on this site include seasonal and annual averages, time series trend plots, and maps of concentration and deposition.

The NADP is composed of five networks, including the National Trends Network (NTN), the Atmospheric Integrated Research Monitoring Network (AIRMoN), the Mercury Deposition Network (MDN), the Atmospheric Mercury Network (AMNet), and the Ammonia Monitoring Network (AMoN). The table below summarizes the number of measurements made by each network in 2013.

Summary of Network Measurements, 2013

Network	Measurements	Period	No. of sites
NTN	14,050	weekly	271
MDN	6,008	weekly	109
AIRMoN	977	daily	6
AMNet	46,520	hourly	18
AMoN	1,658	two week	64

The NADP website is the primary tool for disseminating data from the five NADP networks. In 2013, there were more than 26,000 registered users. Data were downloaded 27,800 times by agencies, universities, and K-12 schools, and our maps were downloaded more than 22,500 times.

Highlights:

- During 2013, 208 journal articles and reports were published using the NADP data.
- Two new text books used NADP information during 2013: (Millard's *Probability, Statistics and Information*, and Harris' *Exploring Chemical Analysis* [in Chinese]) as well as two dissertations and one thesis (Hale, Arizona State University; Fleming, Virginia Polytechnic Institute and State University; Jones, Virginia Polytechnic Institute and State University).
- Methyl mercury wet deposition data were first published in an NADP annual summary. See the cover and page 22 for more information.
- The NADP's Fall Meeting and Scientific Symposium was held in Park City, UT (Oct. 8-11, 2013) and focused on "Western U.S. Monitoring and Analysis: Progress and Current Issues". The meeting included 90 attendees (attendance was limited by the federal government shutdown), eight sessions, 44 oral presentations, and 37 posters. A webcast of the presentations was provided, an NADP first. On Friday, October 11, a special Nitrogen Flux Workshop was held. The workshop included discussions of U.S. nitrogen flux budgets, the increasing importance of ammonia, and the flux of organic nitrogen. See the NADP website for presentations (<http://nadp.isws.illinois.edu/conf/2013>).
- The 2014 Spring NADP Meeting was held in Ft. Lauderdale, FL on April 14-17, 2014.

- The upcoming 2014 Fall Meeting and Scientific Symposium will be held in Indianapolis, IN (Oct. 21-24, 2014).
- The NADP continued to convert its precipitation gages to an all-digital network, originating with a Technical Committee decision in 2006. As of October 2014, the wet deposition networks are now 90% digital, with 264 sites of 316 locations using a digital raingage.
- Preparation began for NTN sites at Florida Agricultural and Mechanical University (FAMU) and North Carolina Agricultural and Technical University (NCA&T), both of which are 1890 Land Grant Universities.
- The Mercury Litterfall Initiative continued operation in 2013 with 14 sites collecting litterfall (leaves, twigs, etc.) for measurement of mercury by the U.S. Geological Survey. See the map below for sites operating in 2013. More information is available at <http://nadp.isws.illinois.edu/newissues/litterfall>.
- NADP began assisting Asian scientists to develop the Asia Pacific Mercury Monitoring Network, a wet deposition observation network for mercury. Further support is provided through U.S. EPA and EPA-Taiwan.
- The Total Deposition Subcommittee (TDep) continued to develop a methodology to estimate total nitrogen and sulfur total deposition by integrating atmospheric measurements and modeled deposition velocity. Wet deposition observations from NADP, air concentrations from the Clean Air Status and Trends Network (CASTNET), the Ammonia Monitoring Network (AMoN), and the SouthEastern Aerosol Research and Characterization (SEARCH) network are combined with modeled deposition velocities using the Community Multiscale Air Quality (CMAQ) model. Results are described in Schwede and Lear, *Atmospheric Environment*, 2014 (92): 207-220.
- The NADP continued to scan historic field records as a long-term archive.



Sites monitoring mercury in leaf litterfall in 2013 as part of a special study initiative.

NADP Background

The NADP was established in 1977 under State Agricultural Experiment Station (SAES) leadership to address the problem of atmospheric deposition and its effects on agricultural crops, forests, rangelands, surface waters, and other natural and cultural resources. In 1978, sites in the NADP precipitation chemistry network first began collecting weekly, wet-only deposition samples. Chemical analysis was performed at the Illinois State Water Survey's Central Analytical Laboratory (CAL), located at the University of Illinois, Urbana-Champaign. The network was established to provide data on amounts, temporal trends, and geographic distributions of the atmospheric deposition of acids, nutrients, and base cations by precipitation.

Initially, the NADP was organized as SAES North Central Regional Project NC-141, which all four SAES regions further endorsed in 1982 as Interregional Project IR-7. A decade later, IR-7 was reclassified as National Research Support Project No. 3 (NRSP-3), which it remains. NRSP projects are multistate activities that support research on topics of concern to more than one state or region of the country. Multistate projects involve the SAES in partnership with the USDA National Institute of Food and Agriculture and other universities, institutions, and agencies. In October 1981, the federally supported National Acid Precipitation Assessment Program (NAPAP) was established to increase understanding of the causes and effects of acidic precipitation. This program sought to establish a long-term precipitation chemistry network of sampling sites away from point source influences. Due to its experience in organizing and operating a national-scale network, the NADP agreed to coordinate operation of NAPAP's National Trends Network (NTN). To benefit from identical siting criteria and operating procedures and a shared analytical laboratory, NADP and NTN merged with the designation NADP/NTN. This merger brought substantial new federal agency participation into the program. Many NADP/NTN sites were supported by the USGS, NAPAP's lead federal agency for deposition monitoring.

In October 1992, the AIRMoN was formed from the Multistate Atmospheric Power Production Pollution Study (MAP3S), which was operated by the Department of Energy and the National Oceanic and Atmospheric Administration (NOAA). MAP3S measured both wet deposition and estimated dry deposition (since discontinued) of the same NADP analytes. AIRMoN sites collect samples daily when precipitation occurs, and are analyzed for the same analytes as NTN samples.

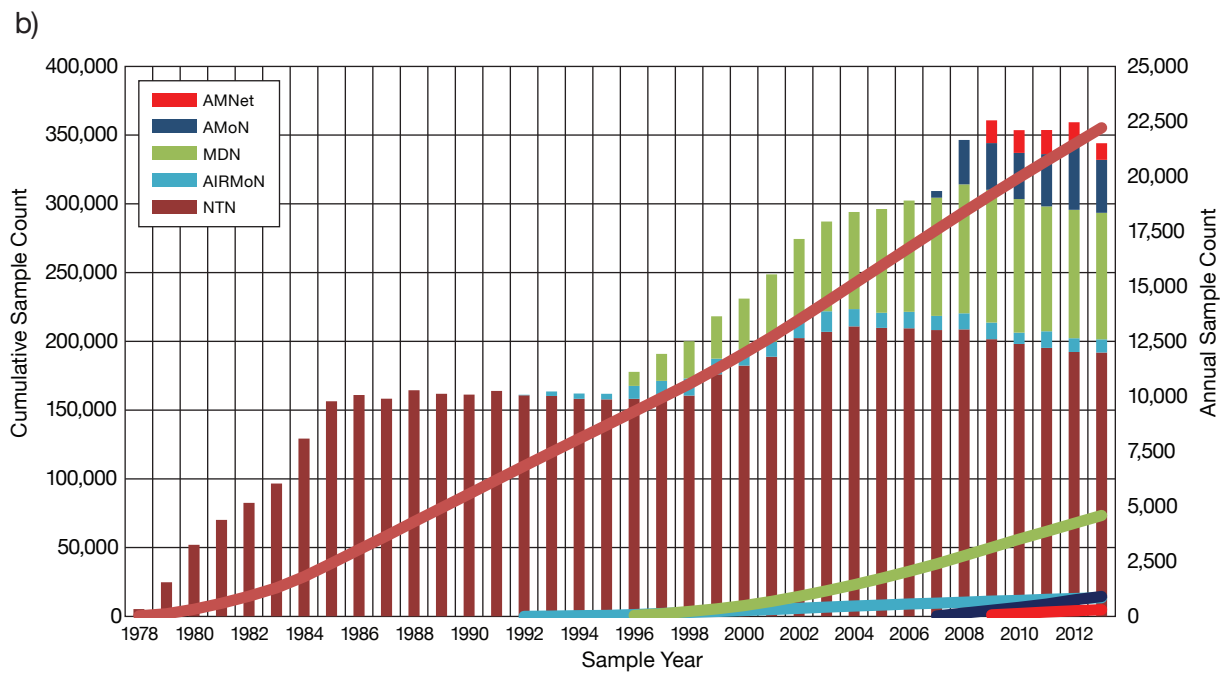
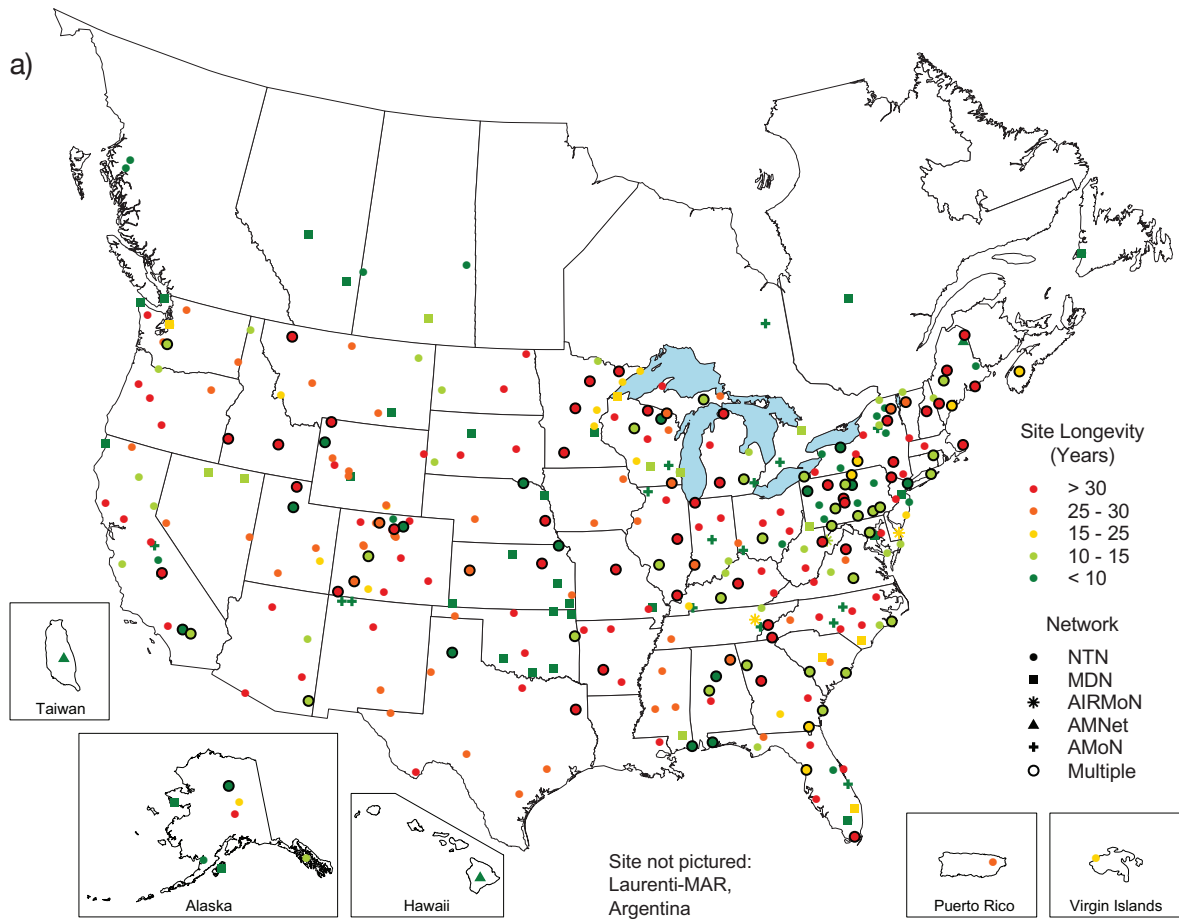
In January 1996, the NADP established the MDN, the third network in the organization. The MDN was formed to provide data on the wet deposition of mercury to surface waters, forested watersheds, and other receptors.

In October 2009, AMNet joined the NADP as its fourth network. AMNet measures the concentration of atmospheric mercury.

In October 2010, AMoN joined the NADP, measuring atmospheric ammonia concentrations using passive samplers on a two-week basis.

SAES project NRSP-3 was renewed in 2009. It offers a unique opportunity for cooperation among scientists from land-grant and other universities, government agencies, and non-governmental organizations. It provides a framework for leveraging the resources of more than 250 agencies to address contemporary and emerging issues of national importance.

Maps on the facing page show active sites in each of the five networks, and the length of time that each site has been operating. As of the end of 2013, there are 20 NTN sites that have been operating for each of NADP's 35 years of operation. The bar chart shows the number of annual samples collected by each network and year since 1978, along with the cumulative number of samples in each network.



a) Site longevity of active NADP sites in each network, and b) annual number of samples collected by each NADP network since 1978 (bar), including the cumulative number of samples (line). Counts for NTN, AIRMoN and MDN are weekly, AMoN are two week, and AMNet are site weeks sampled.

About the Maps

This map series is a principal product of the NADP. It summarizes the results of network operation for the most recent complete calendar year in map form. Additional maps and related geographic information are available on the NADP website. Black dots mark site locations that met NADP completeness criteria for 2013 (see the NADP website for details). Open circles designate urban sites, defined as having at least 400 people per square kilometer (km²) within a 15-km radius of the site. Other sites (e.g. Canadian sites) are too far removed from other observations to extend the contouring, and are represented as circles as well.

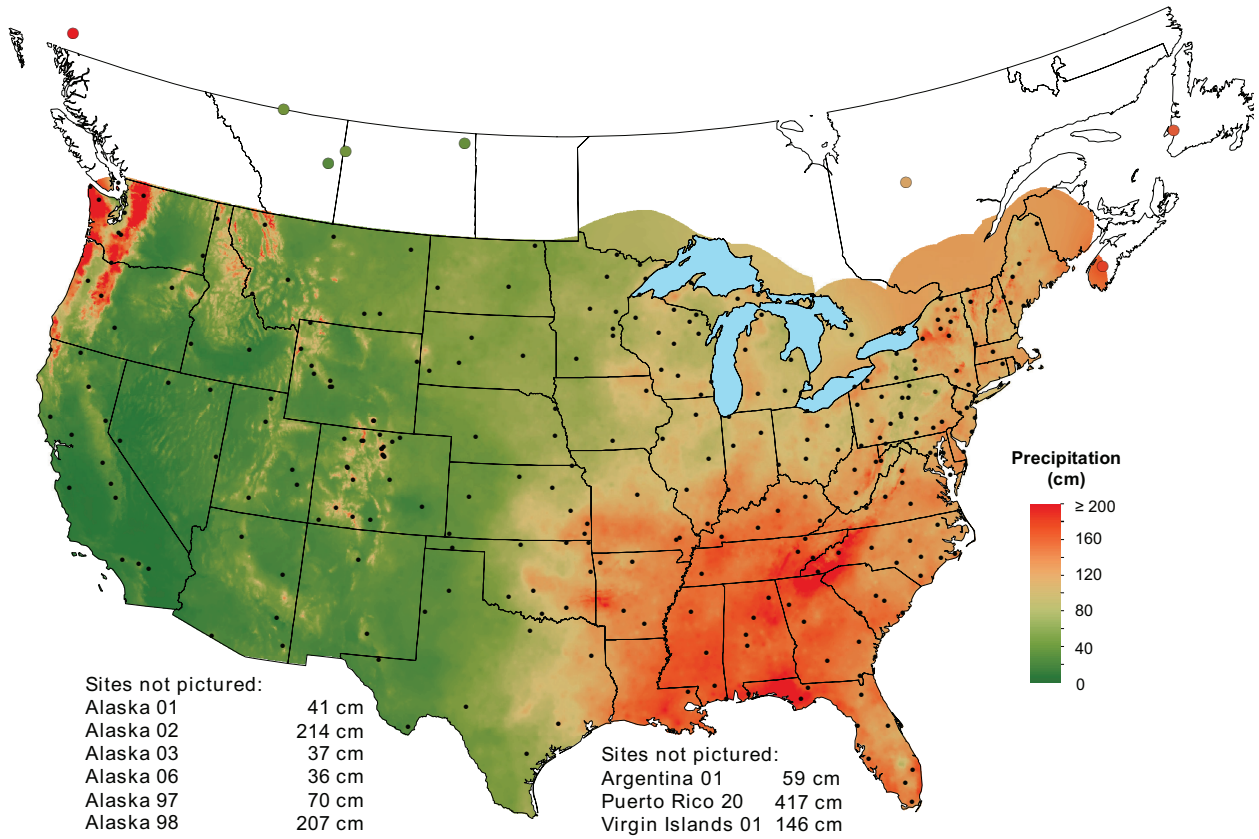
The map contour surface represents a gridded interpolation. Grid points within 500 km of each site are used in computations. Urban sites do not contribute to the contour surface. Colors represent interpolated values of concentration, deposition, or precipitation. Precipitation values are an adapted version of the U.S. precipitation grid developed by the PRISM Climate Group (“Parameter-elevation Regressions on Independent Slopes Model,” <http://prism.oregonstate.edu>, Sept. 2014). These annual precipitation estimates incorporate point data, a digital elevation model, and expert knowledge of complex climatic extremes to produce continuous grid estimates.

NADP precipitation observations are used to supplement the PRISM precipitation grids through an

inverse distance weighting over 20 km around all NADP network sites (see the NADP website for specific information). PRISM precipitation data are strictly for the continental U.S., so the precipitation gradient north of the U.S./Canadian border is based solely on NADP precipitation data. The resulting precipitation map is used to generate the deposition maps.

The precipitation figure on the facing page has a continuous gradient of color from dark green (low values) to yellow (middle values) to dark red (high values). The dark green region begins at 0 centimeters (cm) ranging to over 200 cm (dark red). The concentration and deposition maps follow this same format, with specified units on each map. All maps back to 1994 are available in this format from the NADP website.

Notes for 2013 maps: 1) the ongoing drought along the West Coast is very evident, particularly along the Sierra Mountain Range. The lower precipitation is evident throughout the deposition maps, 2) due to the 2013 federal government shutdown, it is estimated that twelve sites were unable to meet completeness criteria required for an annual aggregation. These sites would have been included in this summary if samples were collected during the shutdown period.



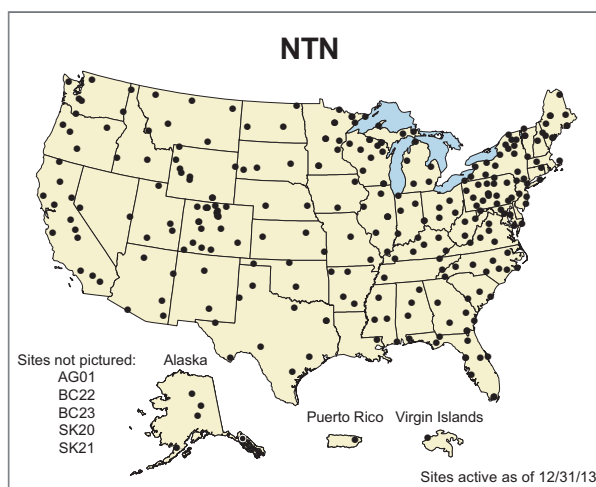
Total annual precipitation for 2013, using precipitation measurements from the NADP and PRISM (in cm).

National Trends Network (NTN)

The NTN is the largest North American network that provides a long-term record of precipitation chemistry. Sites are mostly located away from urban areas and point sources of pollution, although a few urban sites are present. Each site has a precipitation collector and raingage. The automated collector ensures sampling only during precipitation (wet-only sampling). Site operators follow standard operating procedures to help ensure NTN data comparability and representativeness across the network. Weekly samples are collected each Tuesday morning, using containers provided by the CAL. All samples are sent to the CAL for analysis of free acidity (H^+ as pH), specific conductance, and calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), bromide (Br^-), and ammonium (NH_4^+) ions. The CAL also measures orthophosphate ions (PO_4^{3-} , the inorganic form), but only for quality assurance as an indicator of sample contamination. The CAL reviews field and laboratory data for accuracy and completeness, and flags samples that were mishandled, compromised by equipment failure, or grossly contaminated. Data from the NTN are available on the NADP website (<http://nadp.isws.illinois.edu/ntn/>).

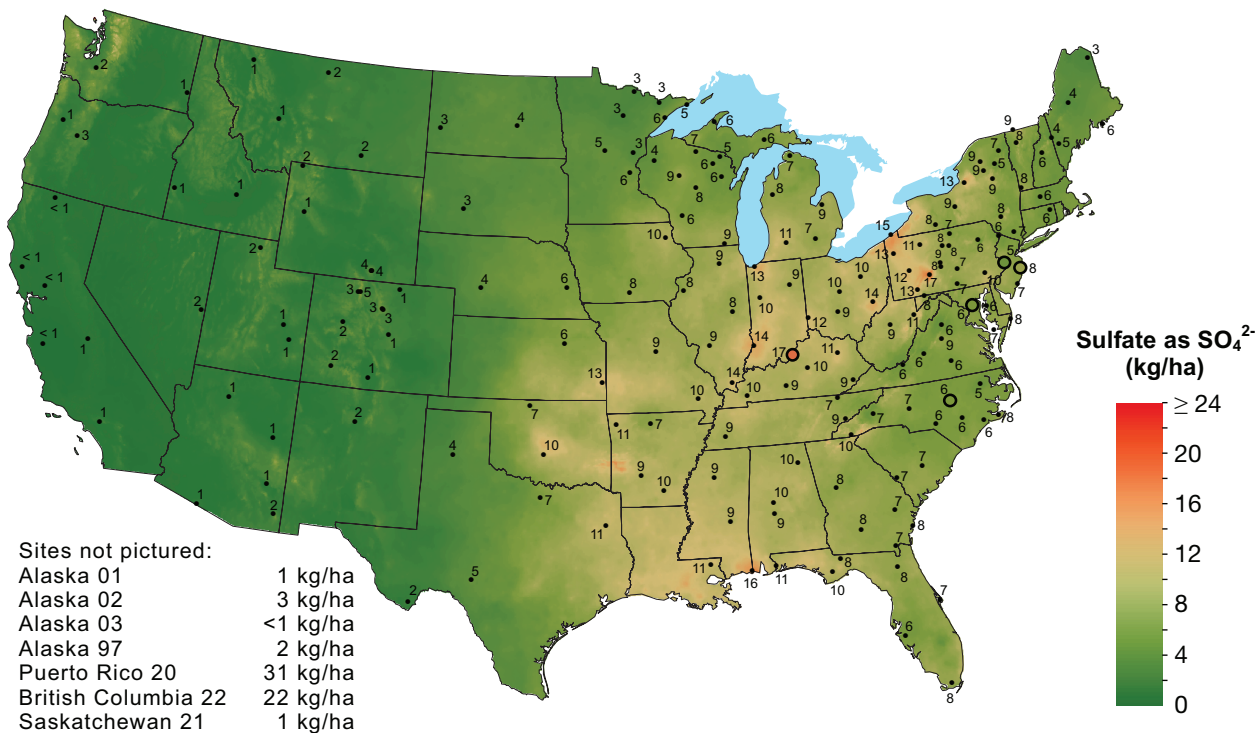
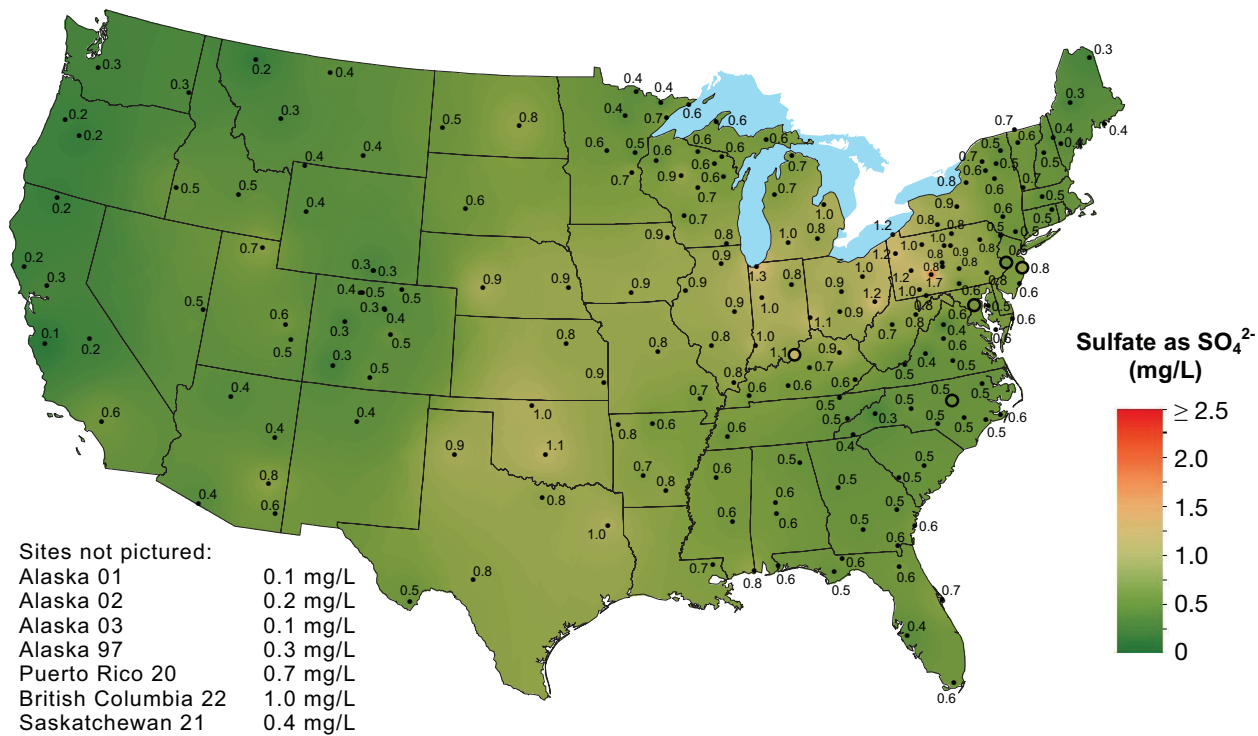
NTN Maps

The maps on pages 11 through 19 show precipitation-weighted mean concentration and annual wet deposition for select acidic ions, nutrients, and base

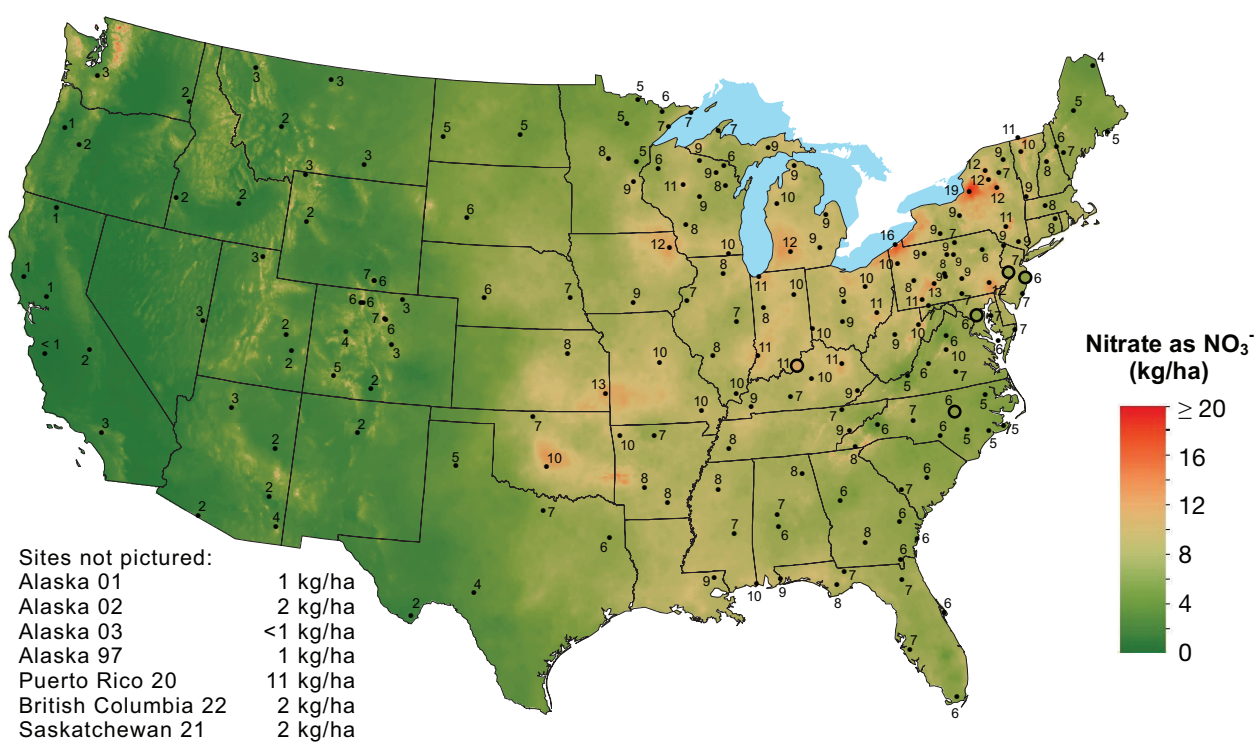
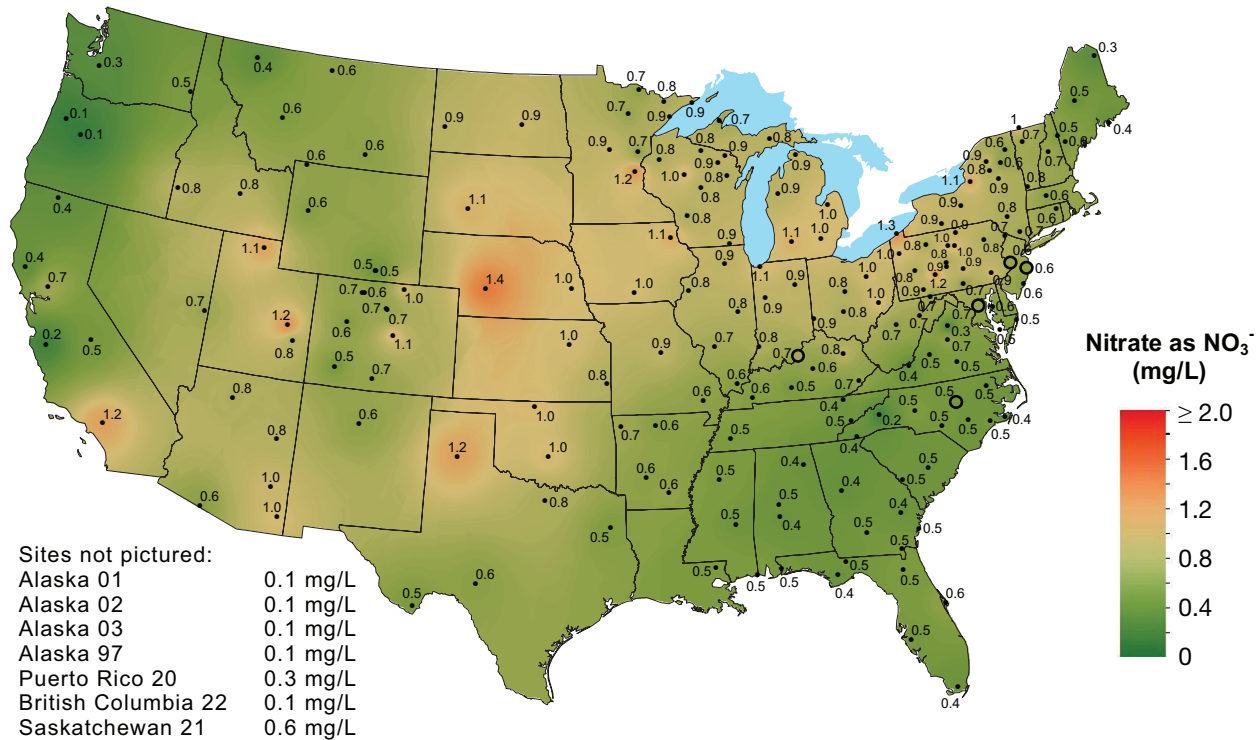


cations. Spatial variability in these species can be seen both on a regional and a national scale. In 2013, 197 of the 266 active sites met NADP completeness criteria. Concentration and deposition maps are included for SO_4^{2-} , NO_3^- , NH_4^+ , pH, Ca^{2+} , Mg^{2+} , Cl^- , and Na^+ . Maps of Br^- and K^+ are not included in this report, but are available from the NADP website.

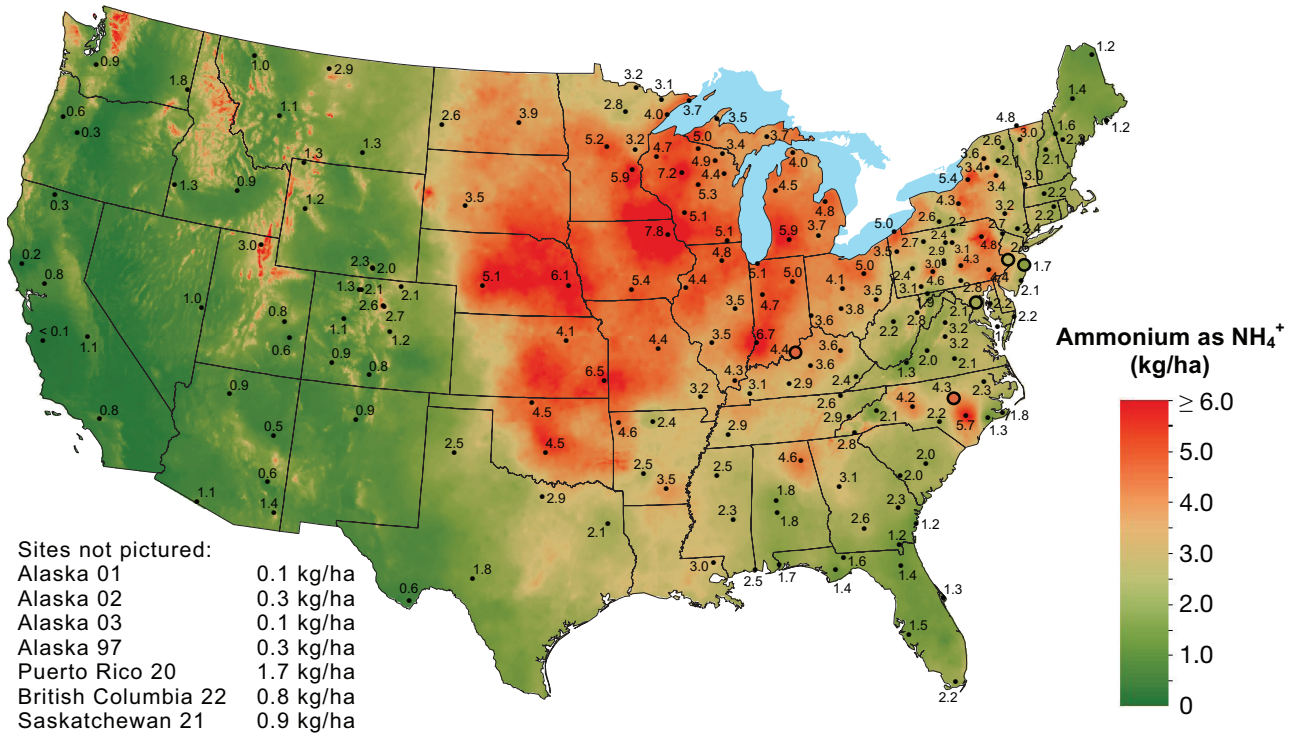
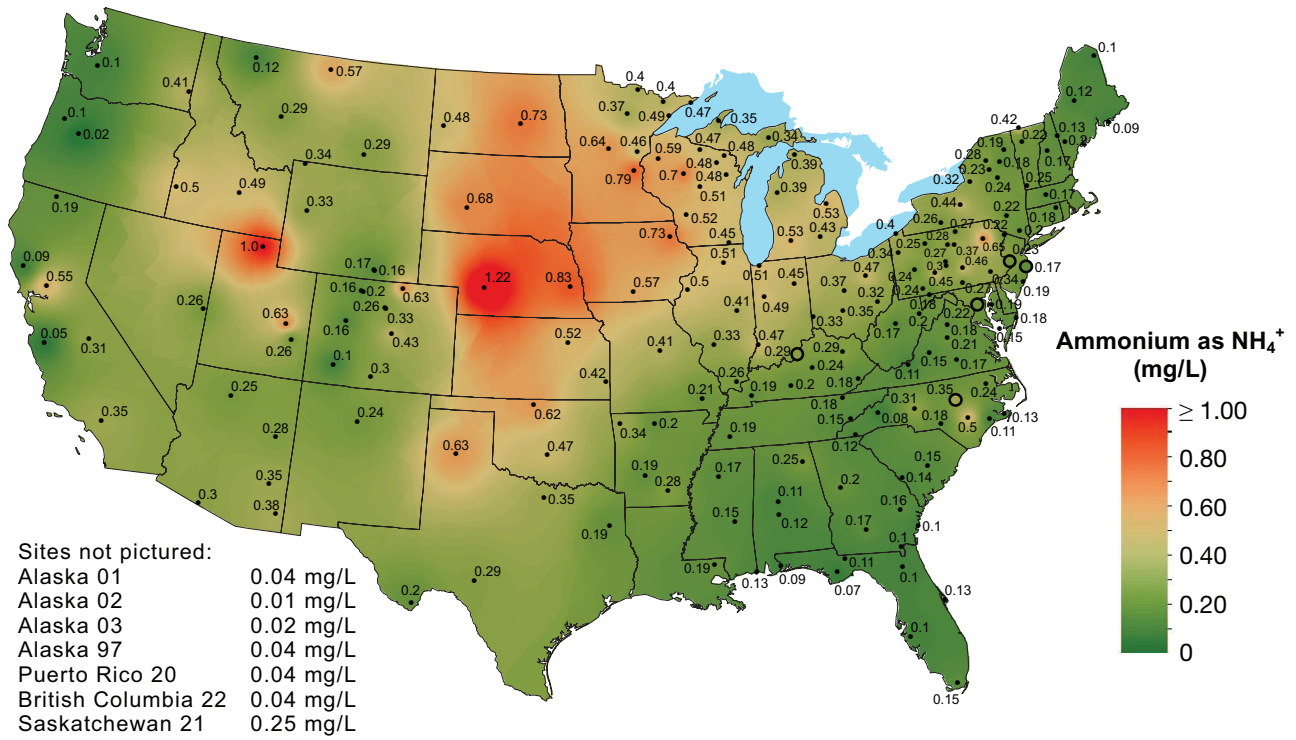
Maps for wet deposition of inorganic nitrogen ("N", i.e., $NO_3^- + NH_4^+$) and nitrogen + sulfur ("N + S") are also included. N + S (i.e., $NO_3^- + NH_4^+ + SO_4^{2-}$) is mapped as hydrogen ion equivalents per hectare for the year (eq/ha).



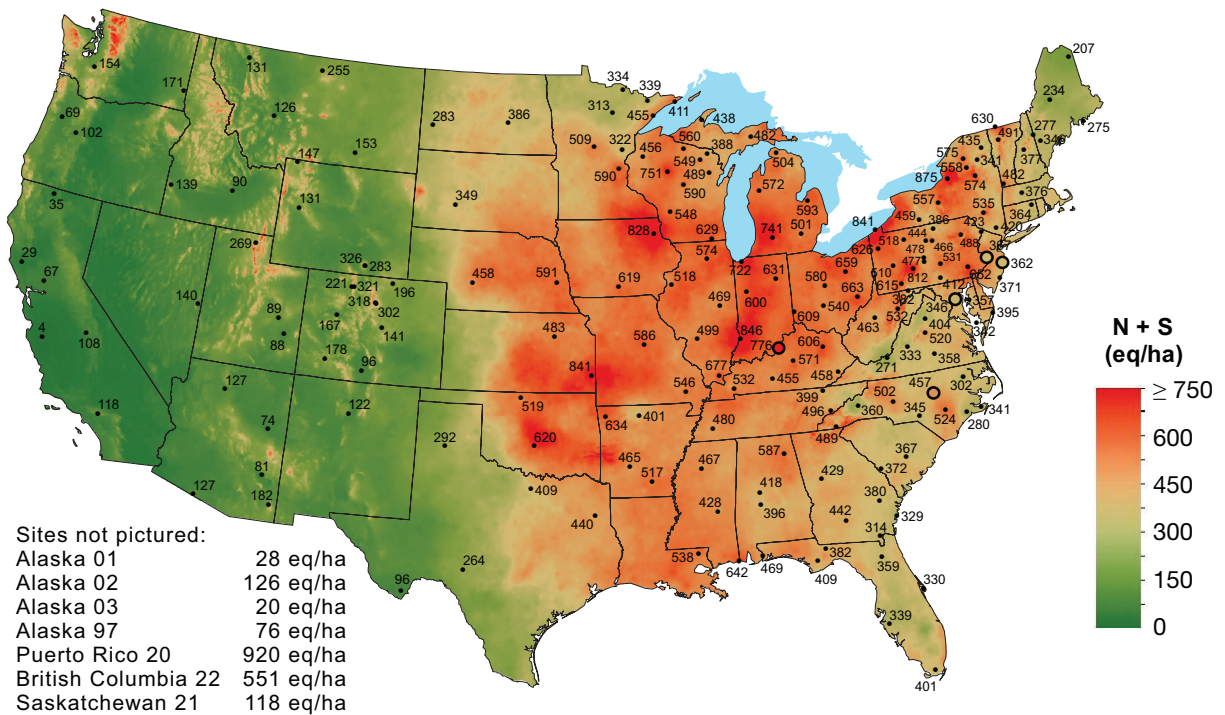
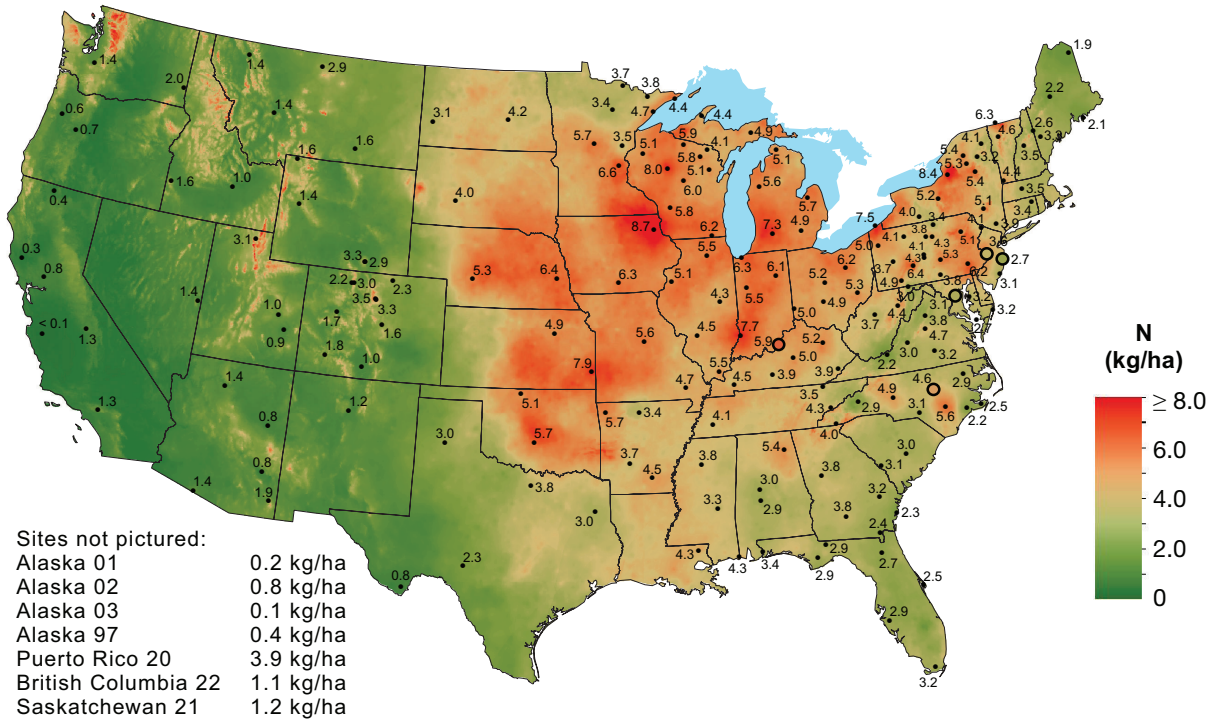
Sulfate ion concentration (top) and wet deposition (bottom), 2013.



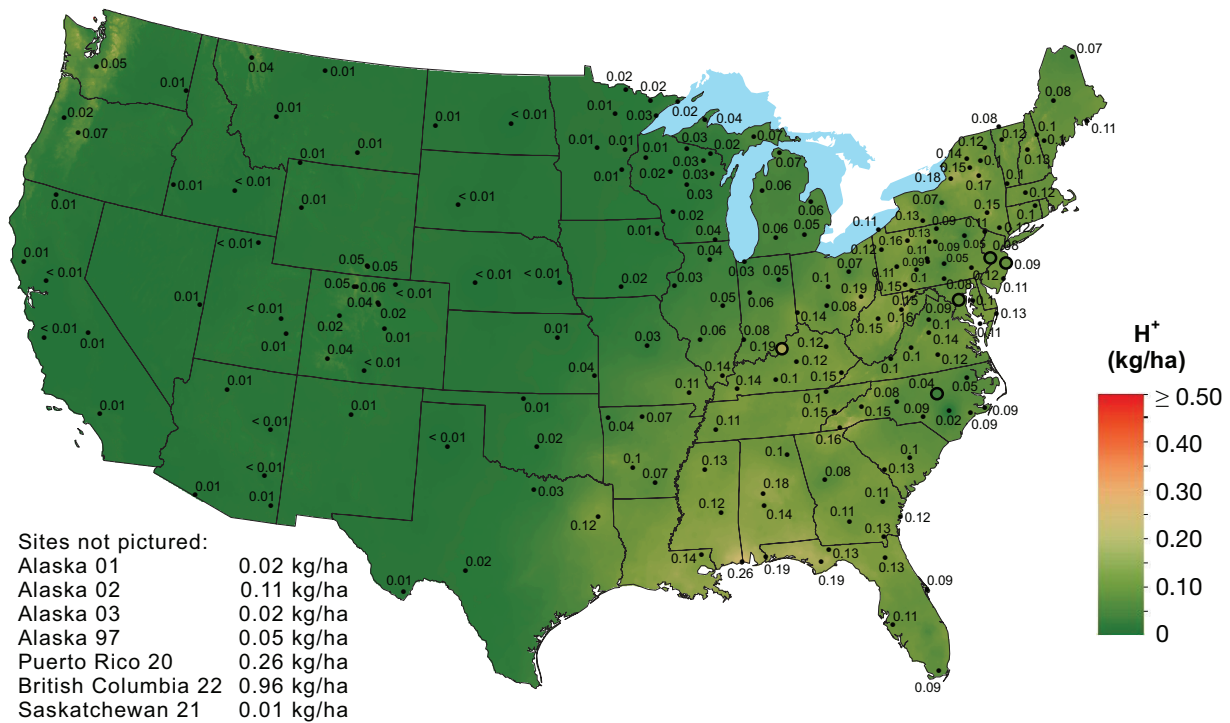
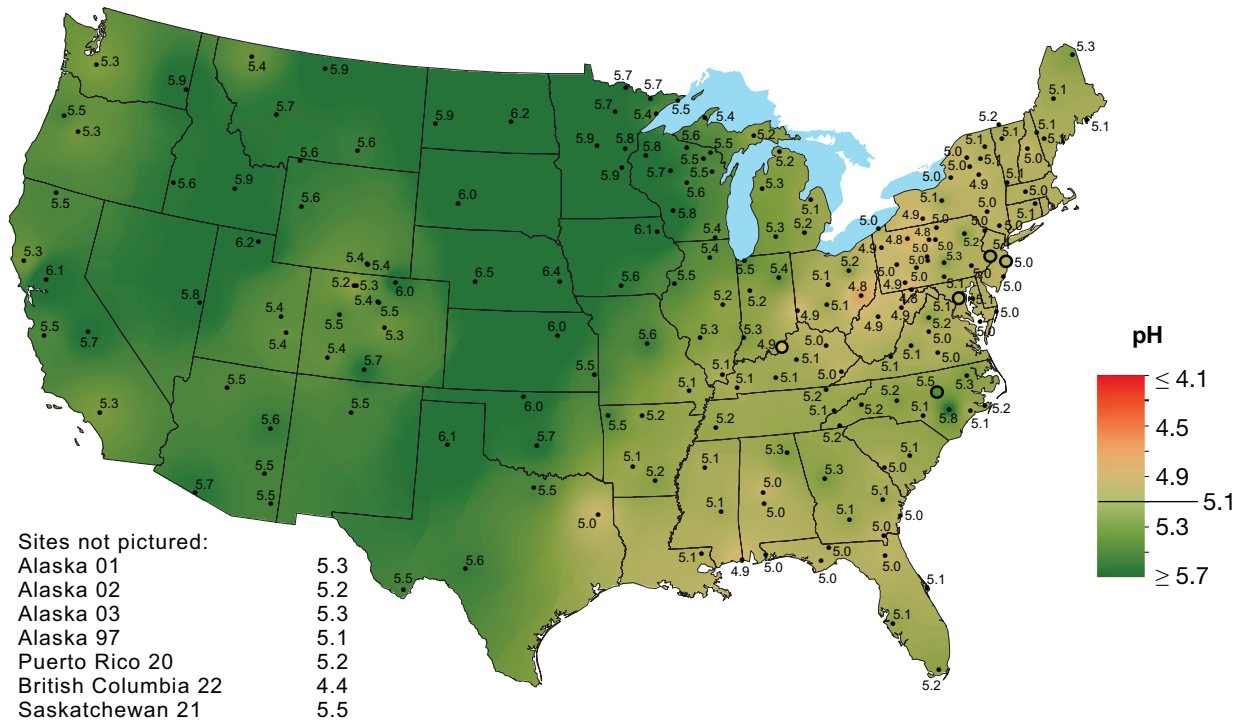
Nitrate ion concentration (top) and wet deposition (bottom), 2013.



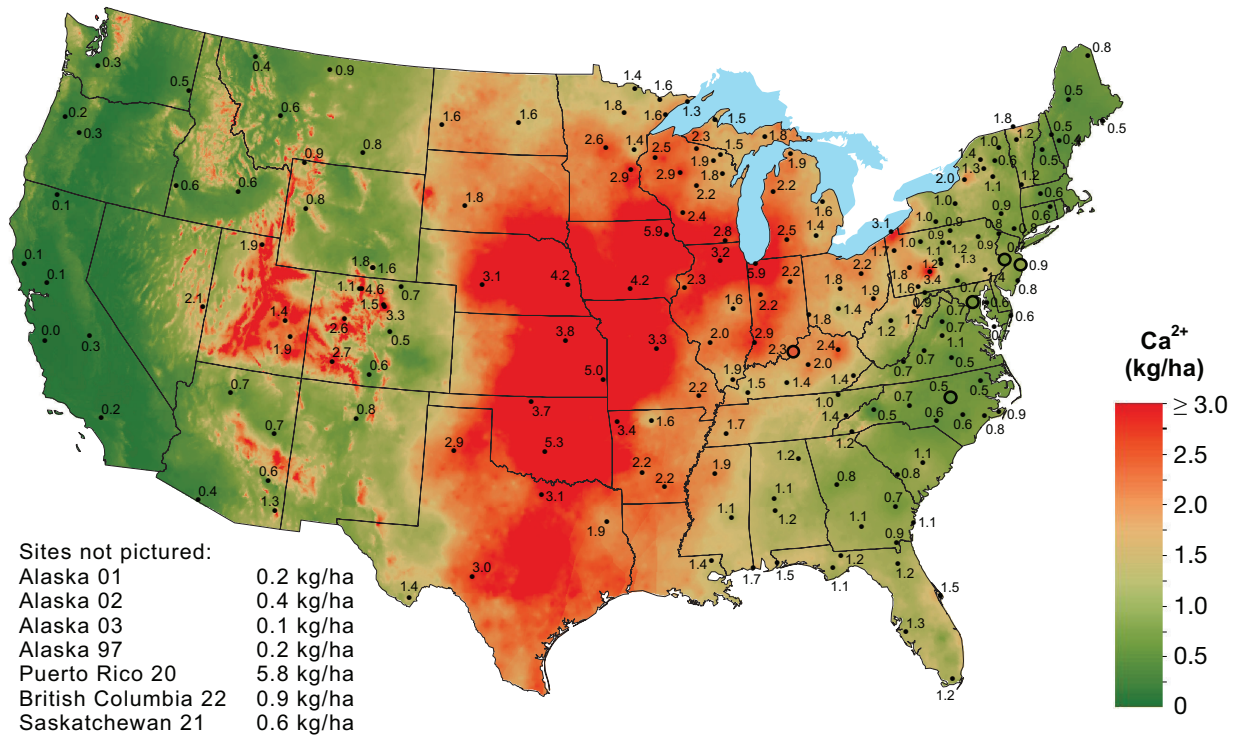
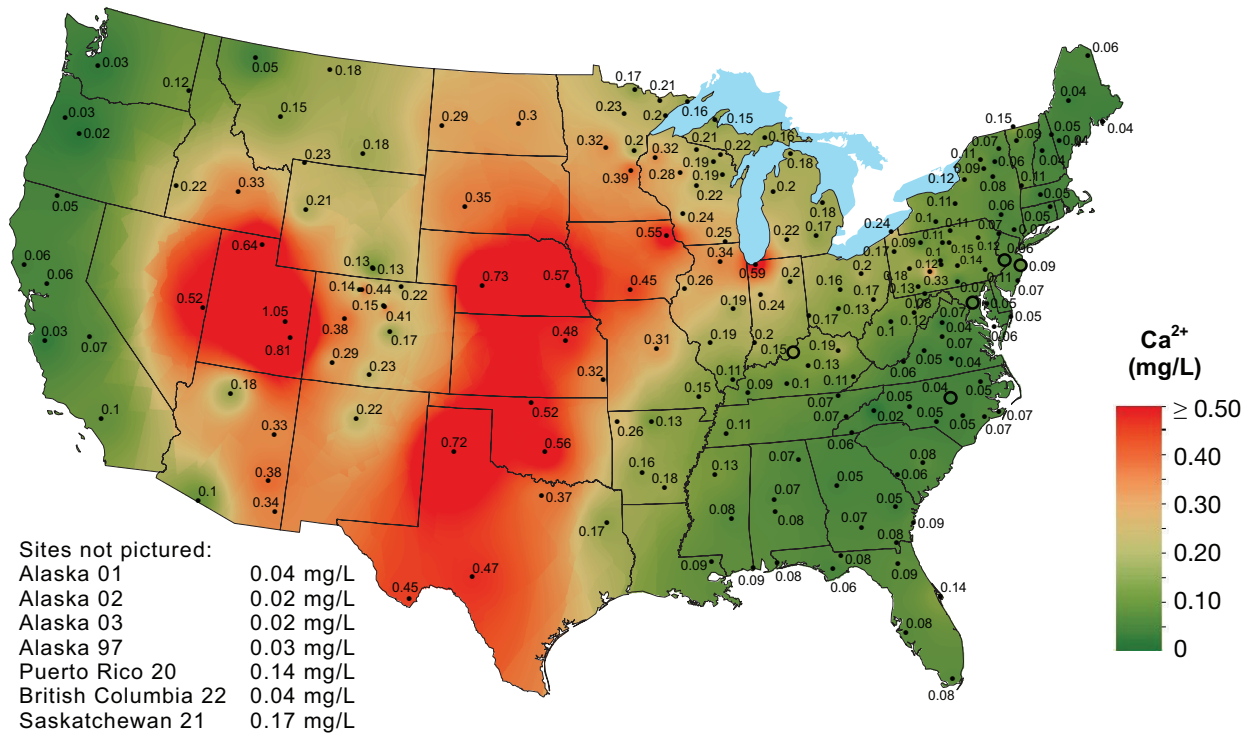
Ammonium ion concentration (top) and wet deposition (bottom), 2013.



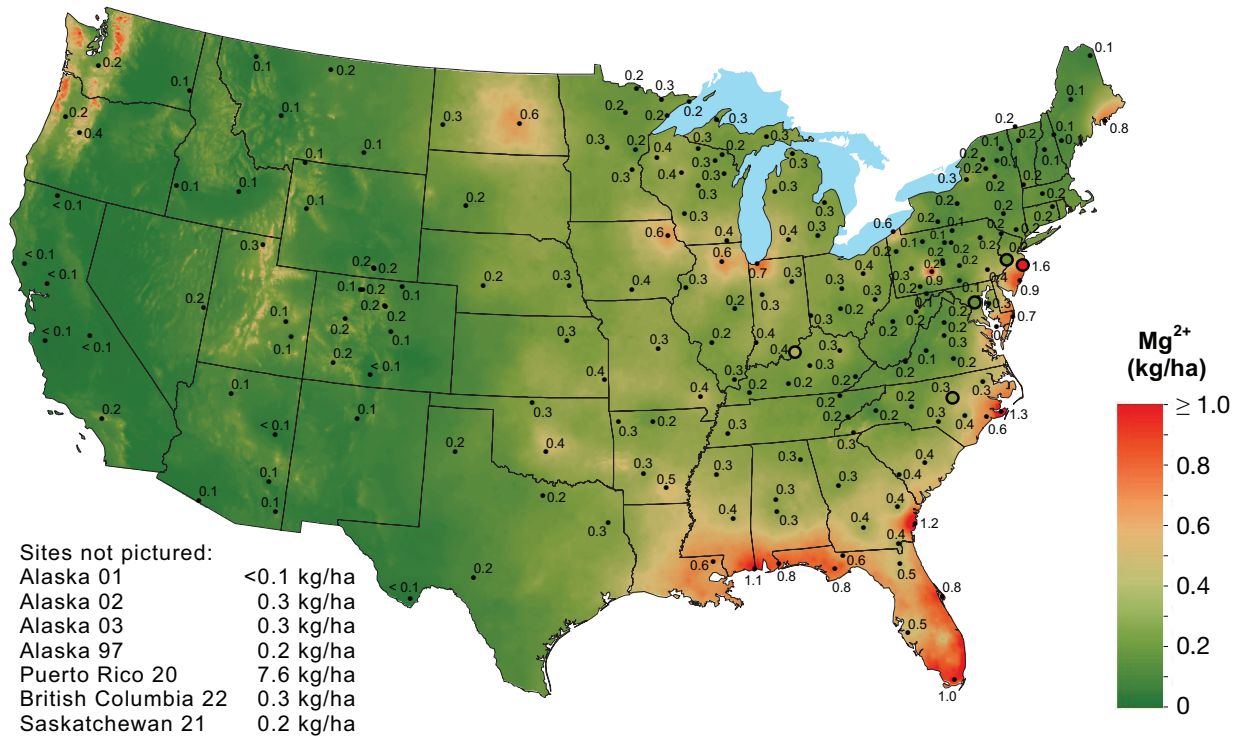
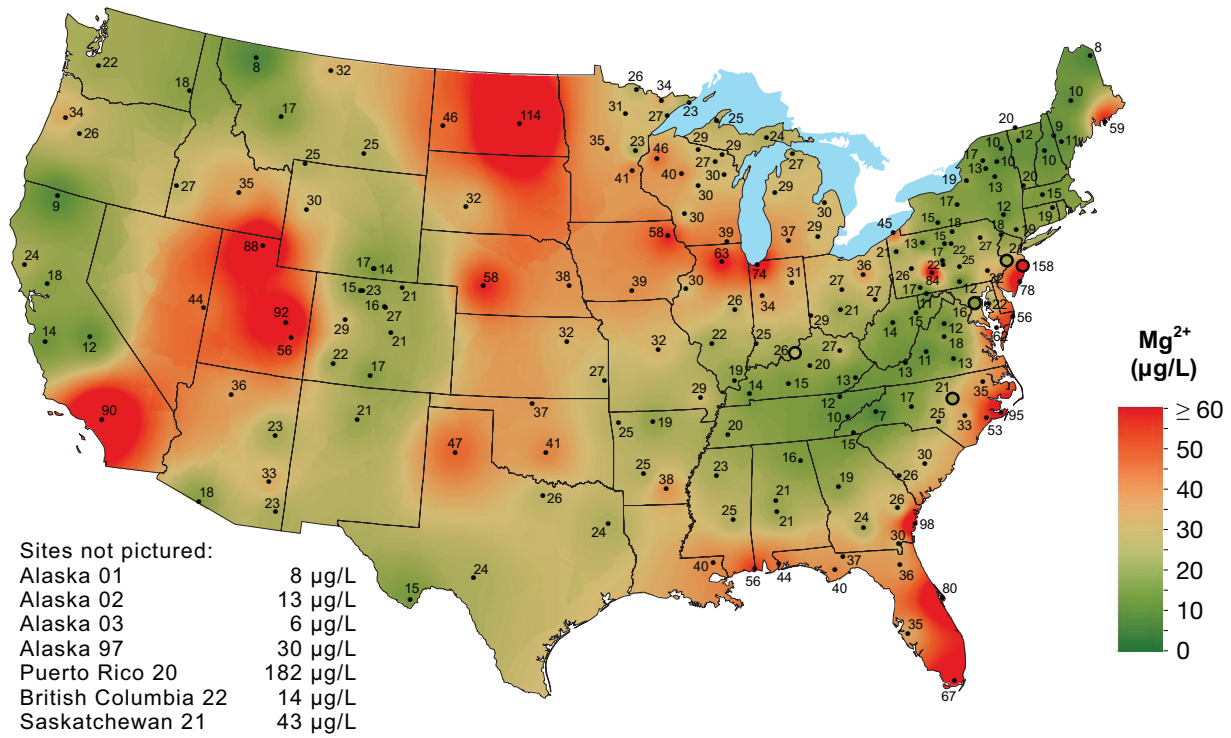
**Inorganic nitrogen wet deposition from nitrate and ammonium (top)
and nitrogen plus sulfur wet deposition from nitrate, ammonium, and sulfate (bottom), 2013.**



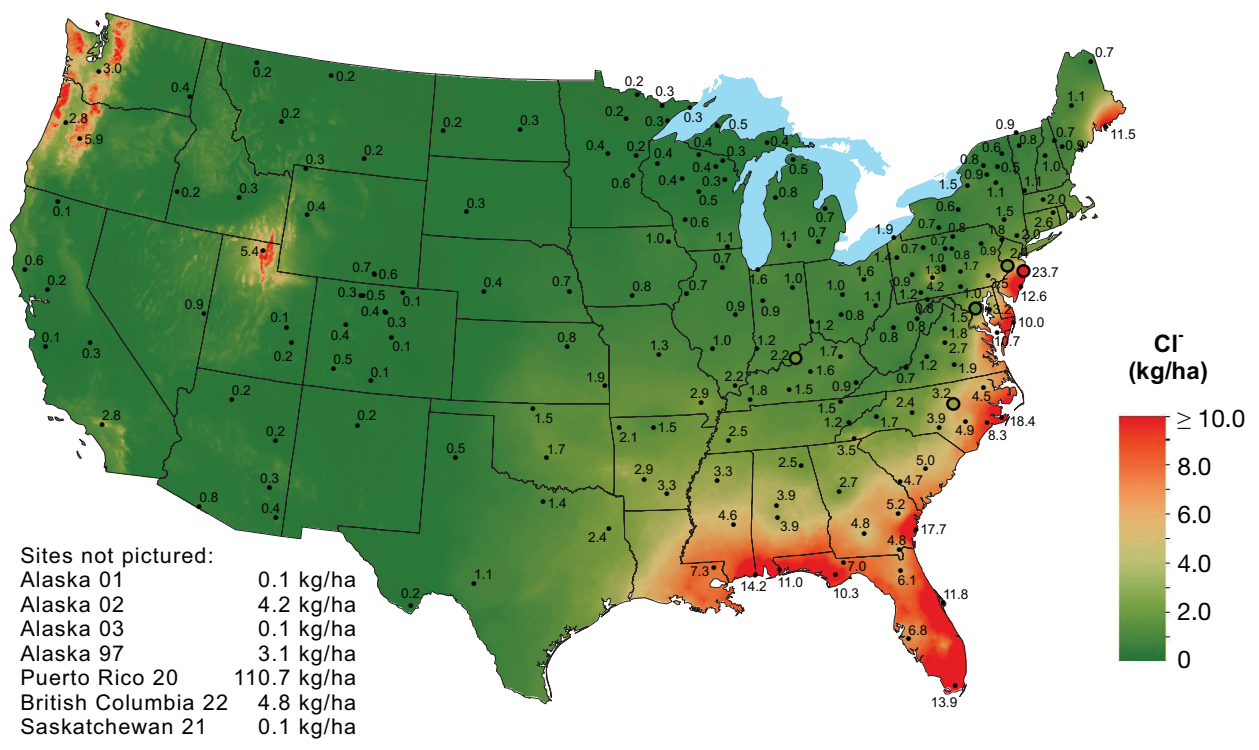
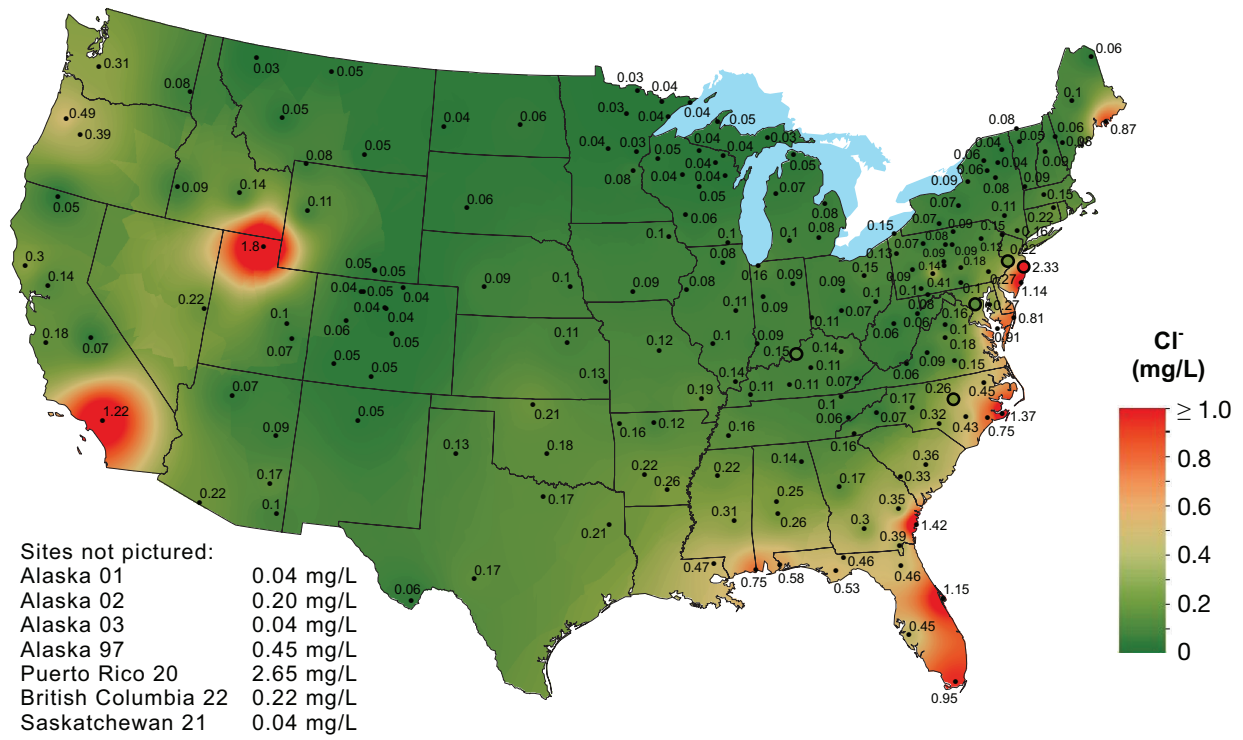
Hydrogen ion concentration as pH (top) and wet deposition (bottom), 2013.
Typically, a precipitation pH of less than 5.1 is considered acidic.



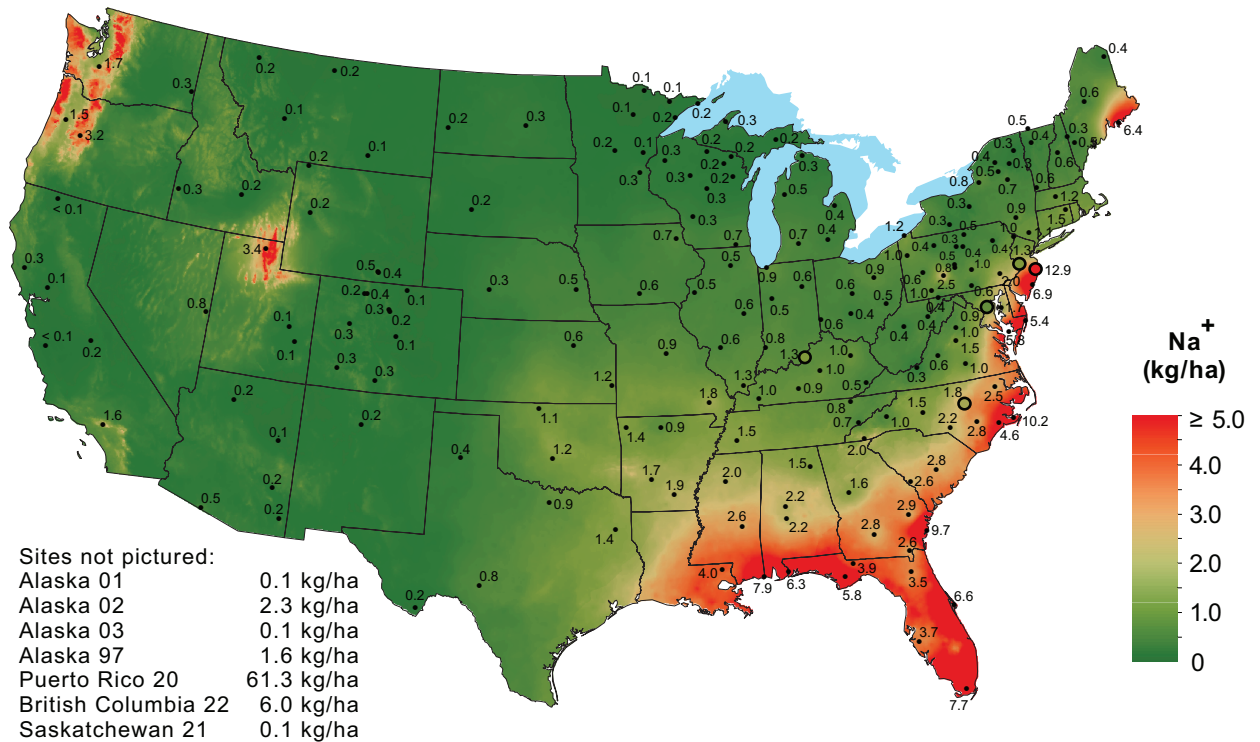
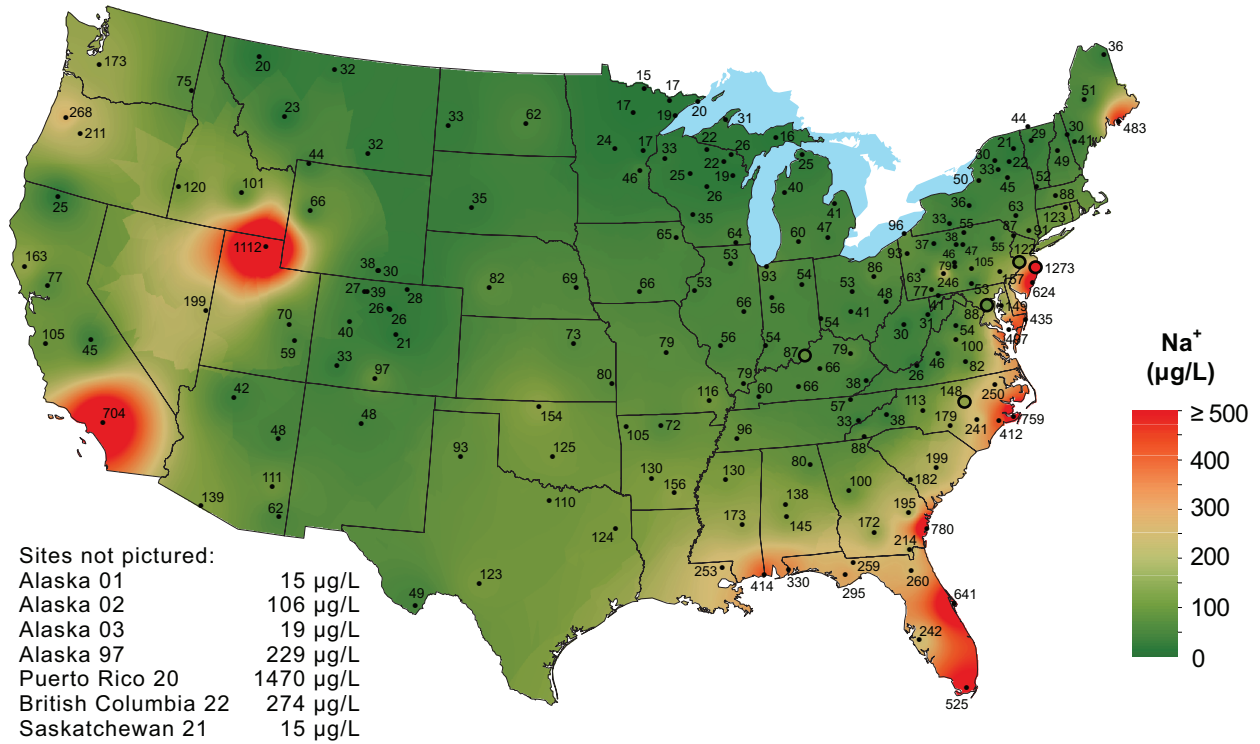
Calcium ion concentration (top) and wet deposition (bottom), 2013.



Magnesium ion concentration (top) and wet deposition (bottom), 2013.



Chloride ion concentration (top) and wet deposition (bottom), 2013.



Sodium ion concentration (top) and wet deposition (bottom), 2013.

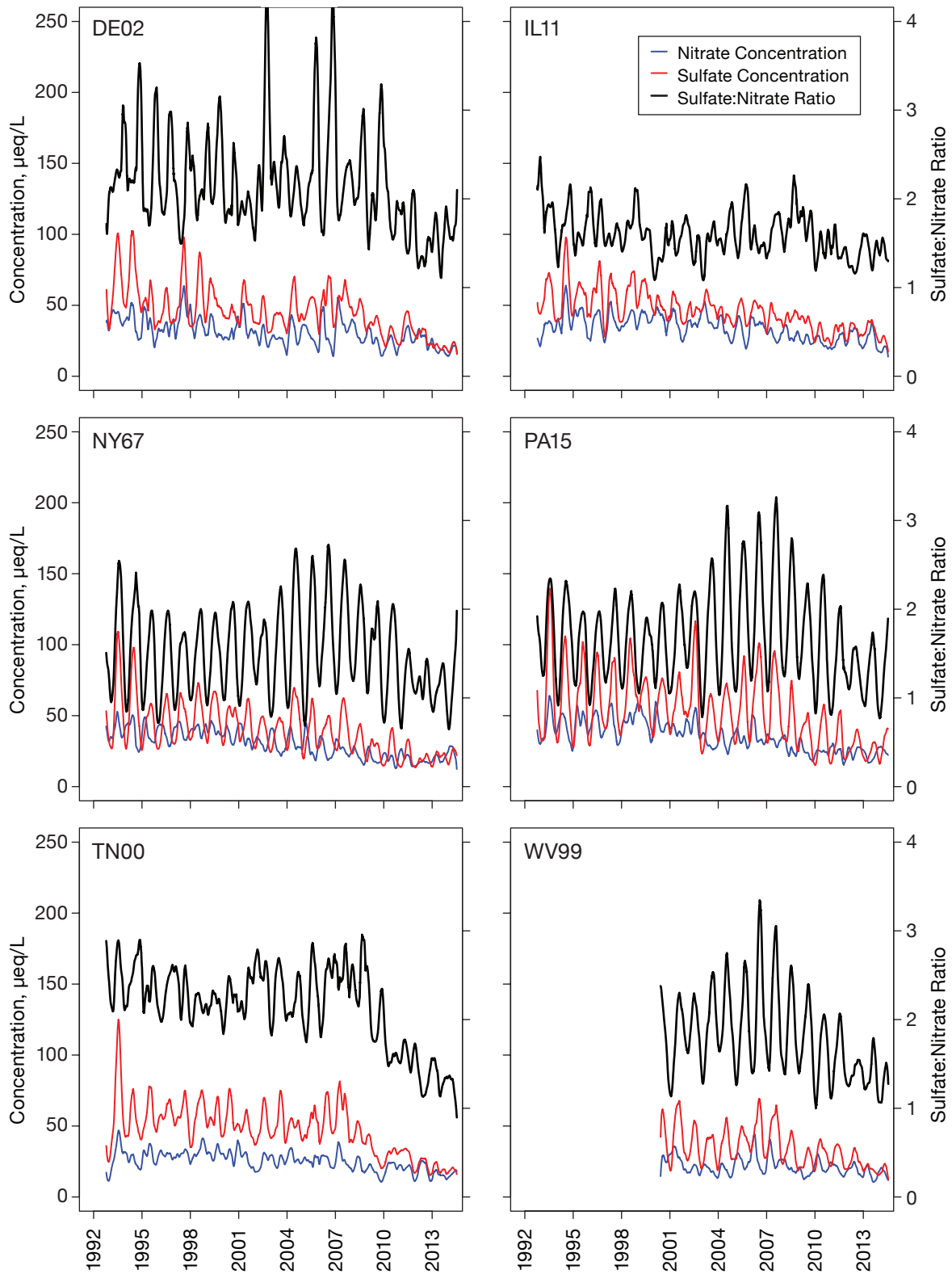
Atmospheric Integrated Research Monitoring Network (AIRMoN)

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, such as the NOAA/HYSPLIT fate and transport model. Back trajectories for all AIRMoN samples are provided at <http://nadp.isws.illinois.edu/AIRMoN>. Rapid release of data from this network is an AIRMoN goal.

AIRMoN sites are equipped with the same wet-only deposition collector used at NTN sites. By the end of 2013, all AIRMoN sites operated digital raingages for reporting total precipitation. Each site also has a standard stick-type precipitation gage. Samples are refrigerated after collection and are shipped in chilled, insulated containers to the CAL for analysis. Samples remain refrigerated until they are analyzed. Refrigeration retards potential chemical changes, such as with H^+ , NH_4^+ , and PO_4^{3-} . Chemical analyses and data screening procedures for AIRMoN and NTN are similar. Data from the AIRMoN are available on the NADP website (<http://nadp.isws.illinois.edu/airmon/>).



The figures on page 21 show the concentration of sulfate and nitrate ion for each of the AIRMoN sites from 1992 to 2013 on a hydrogen equivalents basis. The sulfate to nitrate ratio is also plotted. All sites indicate a decreasing sulfate to nitrate ratio over time, reflecting targeted reductions in sulfur air emissions versus nitrogen emissions.

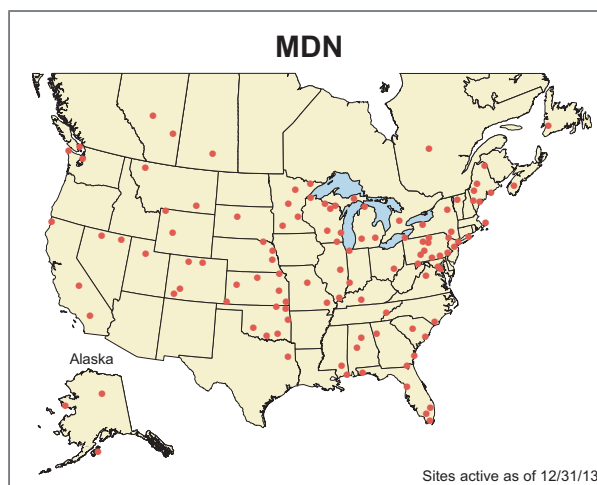


Concentration of sulfate and nitrate ion concentration in wet deposition samples as measured by AIRMoN, October 1992–December 2013. Lines indicate 180-day weighed smoothing of sulfate concentration (red), nitrate concentration (blue), and sulfate-to-nitrate ratio (black). Note: WV99 began measurements in June 2000.

Mercury Deposition Network (MDN)

The MDN is the only network providing a long-term record for the concentration of mercury (Hg) in precipitation in North America. MDN sites follow standard procedures and use approved precipitation collectors and raingages. The automated collector is similar to the NTN collector, but it is modified to preserve mercury. Site operators collect samples either every Tuesday morning or daily within 24 hours of the start of precipitation. In 2013, the Devil's Lake site in south-central Wisconsin (WI31), the Yorkville site in northwestern Georgia (GA40), the Birmingham site in Alabama (AL19), and the Pensacola, Florida site (FL96) collected daily samples. Chemical analysis of the MDN samples is performed by the Mercury Analytical Laboratory (HAL) at Eurofins Frontier Global Sciences, Inc., Bothell, Washington.

All MDN samples are analyzed for total mercury concentration. In 2013, 19 MDN sites opted to measure methyl mercury (MeHg) concentrations. The HAL reviews field and laboratory data for accuracy and completeness, and identifies samples that were mishandled, compromised by equipment failure, or grossly contaminated. Data from the MDN are available on the NADP website (<http://nadp.isws.illinois.edu/mdn>).



MDN Maps

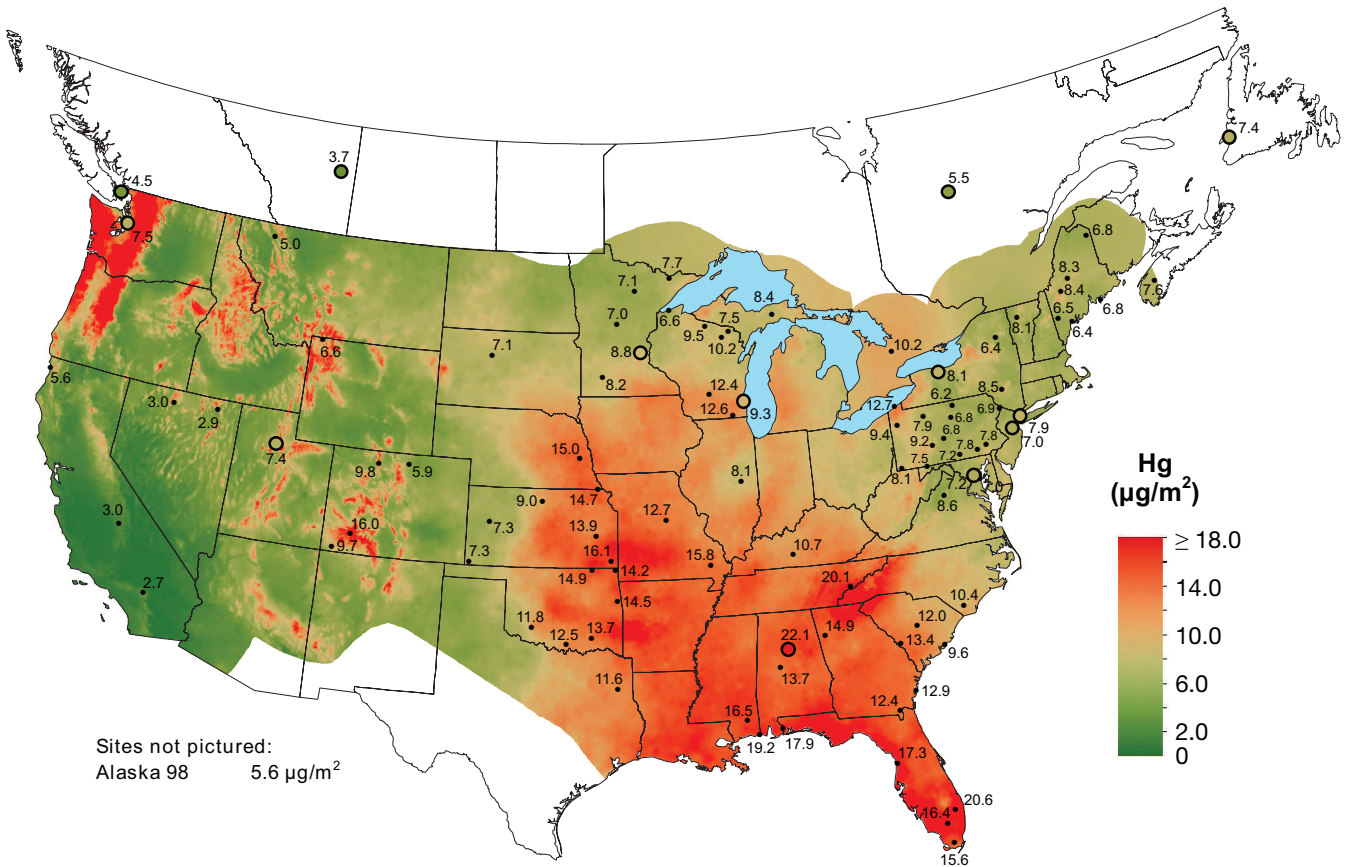
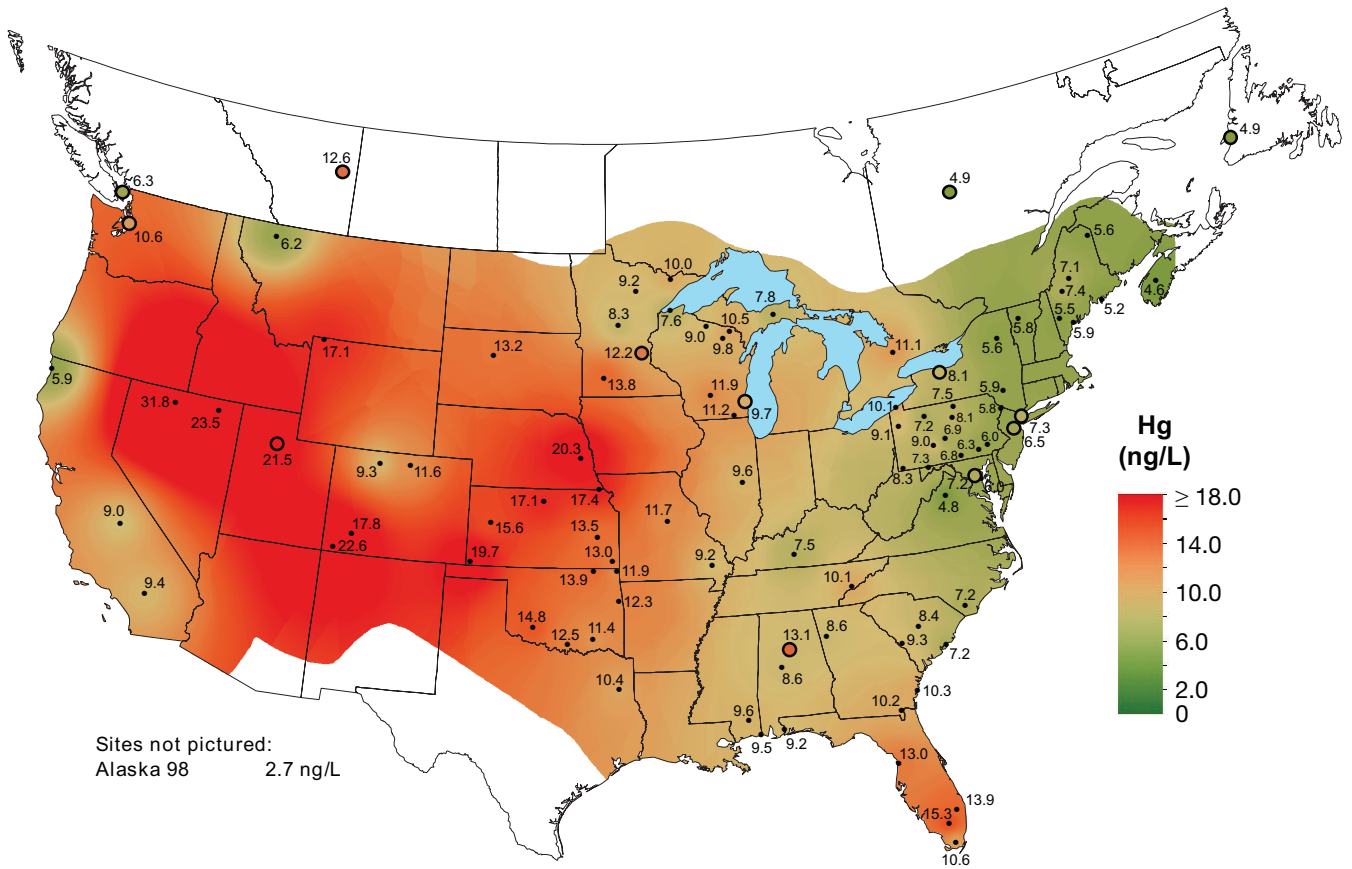
The maps on page 23 show spatial variability in the precipitation-weighted mean concentration and wet deposition of total mercury. Only sites meeting NADP completeness criteria are included. In 2013, 97 of 109 active sites met these criteria. Spatial variability of total mercury can be seen on a regional and a national scale.

Methyl Mercury

Since 1996, subsamples of MDN precipitation have been analyzed for methyl mercury (MeHg) at a subset of NADP sites. Data from late 2002 through 2013 will be released on the NADP website.

Samples for MeHg analysis were collected in two ways: split samples (or weekly) and composite samples (four week combined samples). For a split sample, an aliquot is taken from a single MDN total mercury sample for analysis. For a composite sample, a percentage of each weekly MDN sample is taken for four consecutive weeks, with the resulting composite sample analyzed.

All samples are preserved using 1% volume:volume HCl and are stored in a refrigerator (4°C) until analysis. MeHg concentrations are corrected for bubbler blanks, preparation blanks, and acid pre-charge preservative. A reporting limit is used based on the mass of methyl mercury that is measured in the sample aliquot. Samples that were analyzed prior to 18 April 2007 required a minimum mass of 0.0050 ng to be measured in the aliquot. Samples that were analyzed on 18 April 2007, or later, required a minimum mass of 0.0025 ng.



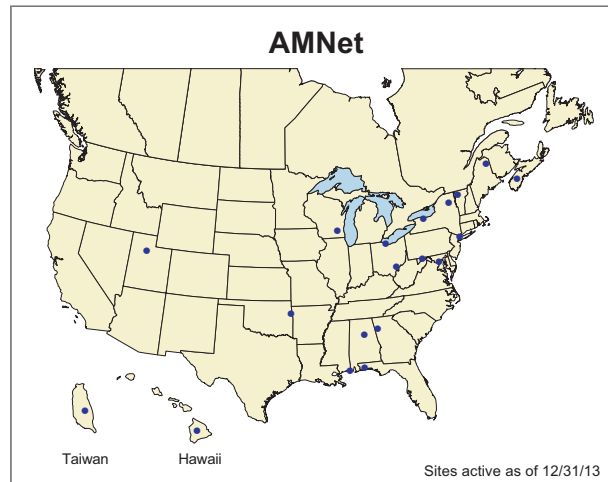
Total mercury concentration (top) and wet deposition (bottom), 2013.

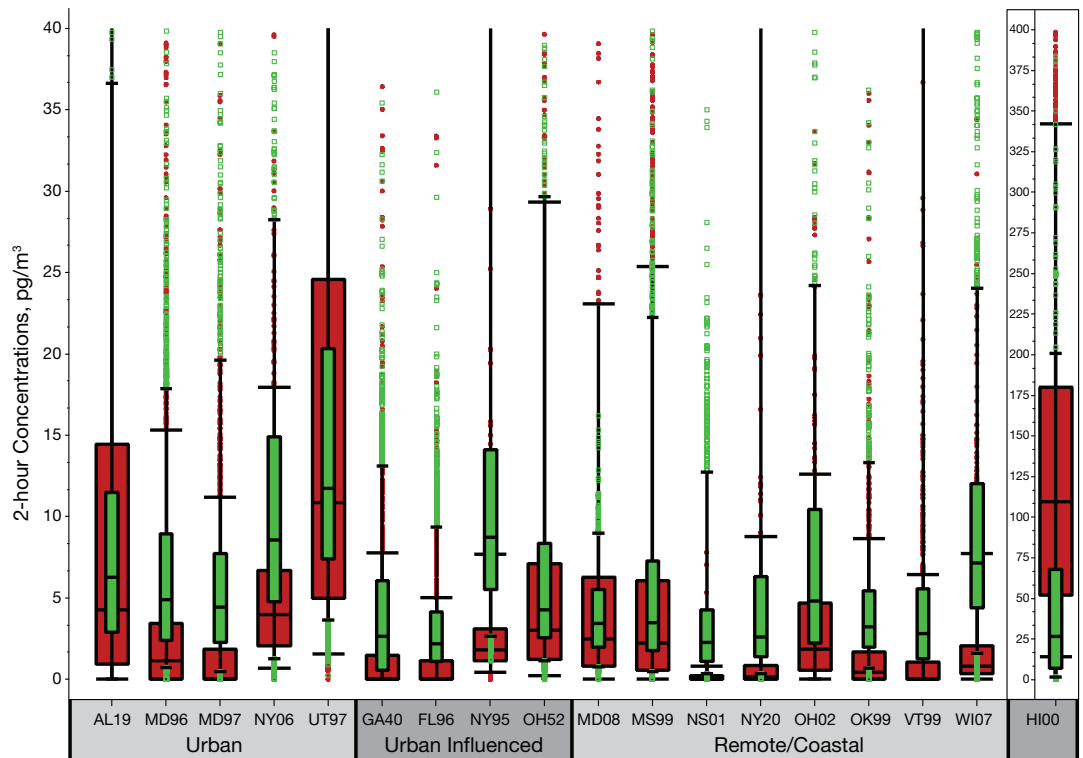
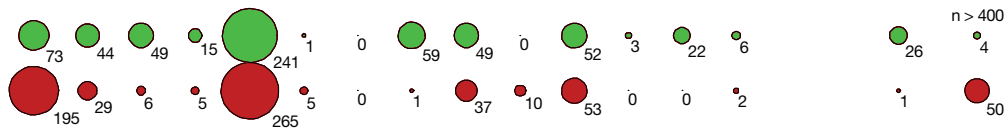
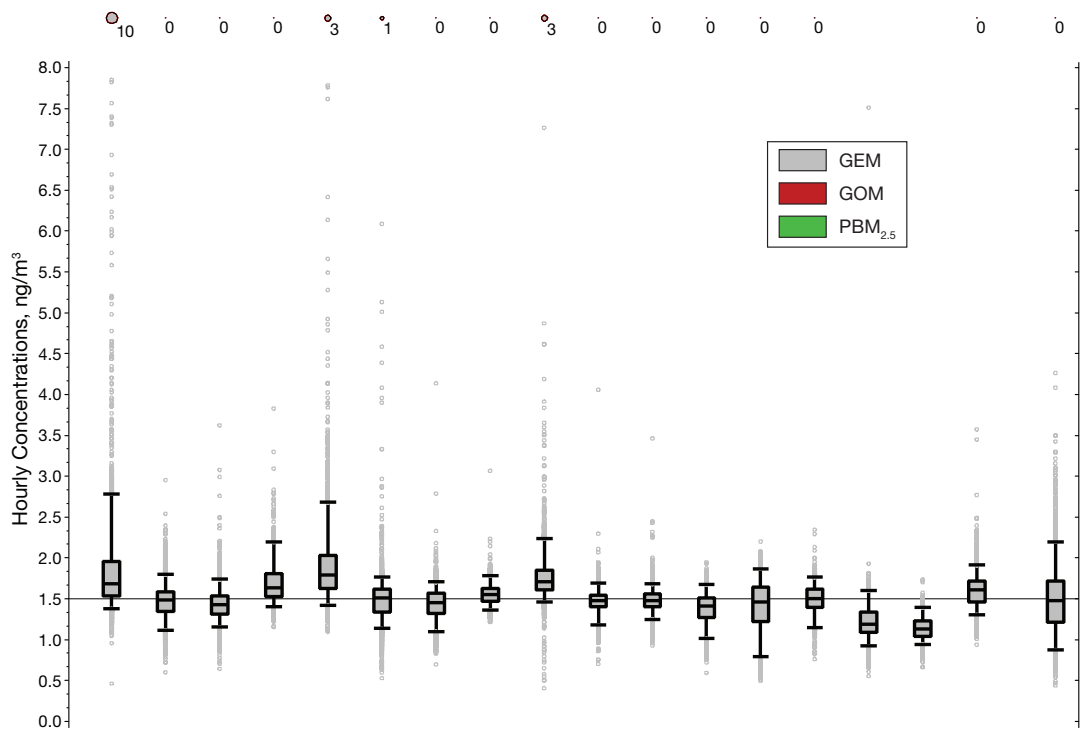
Atmospheric Mercury Network (AMNet)

AMNet sites measure atmospheric mercury fractions that contribute to mercury dry deposition. Sites measure concentrations of atmospheric mercury species (gaseous oxidized, particulate-bound, and elemental) using automated, continuous measurement systems. Measurements are made using NADP standardized methods, and are quality assured.

AMNet measurements are made continuously (five-minute and two-hour averages). Data are qualified and averaged to one-hour (gaseous elemental mercury, GEM) and two-hour values (gaseous oxidized mercury, GOM, and particulate bound mercury, $PBM_{2.5}$). Data from the AMNet are available on the NADP website (<http://nadp.isws.illinois.edu/amn/>).

The figures on page 25 show the distribution of atmospheric mercury concentrations for each site in 2013. The top figure shows the distribution of GEM (grey shaded area) in nanograms per cubic meter (ng/m^3). The bottom figure shows the distribution of two-hour atmospheric concentrations of GOM (red shaded area), and $PBM_{2.5}$ (green shaded area) in picograms per cubic meter (pg/m^3). Indicated above each plot is the number of valid GEM, GOM, and $PBM_{2.5}$ observations that exceed $8 ng/m^3$ and $40 pg/m^3$ respectively ($400 pg/m^3$ at HI00 GOM and $PBM_{2.5}$), the upper limit shown in the plots.





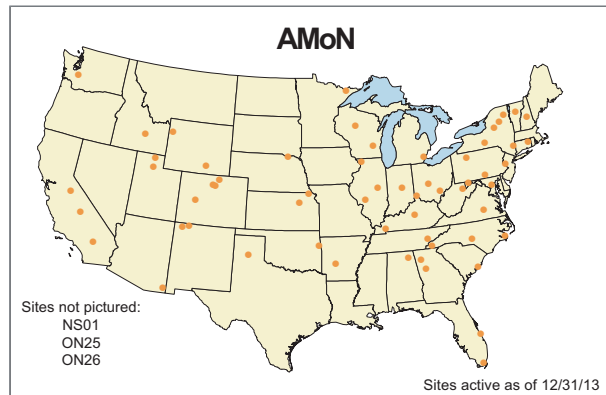
Hourly GEM concentrations in ng/m^3 for each AMNet site (top) and 2-hour GOM and $\text{PBM}_{2.5}$ concentrations in pg/m^3 for each AMNet site (bottom), 2013. The bubble charts indicate the number of valid observations for GEM values above $8 \text{ ng}/\text{m}^3$, and GOM and $\text{PBM}_{2.5}$ above $40 \text{ pg}/\text{m}^3$ ($400 \text{ pg}/\text{m}^3$ for HI00), the upper limit shown with the box plots. Note the different scale for HI00 in the bottom plot.

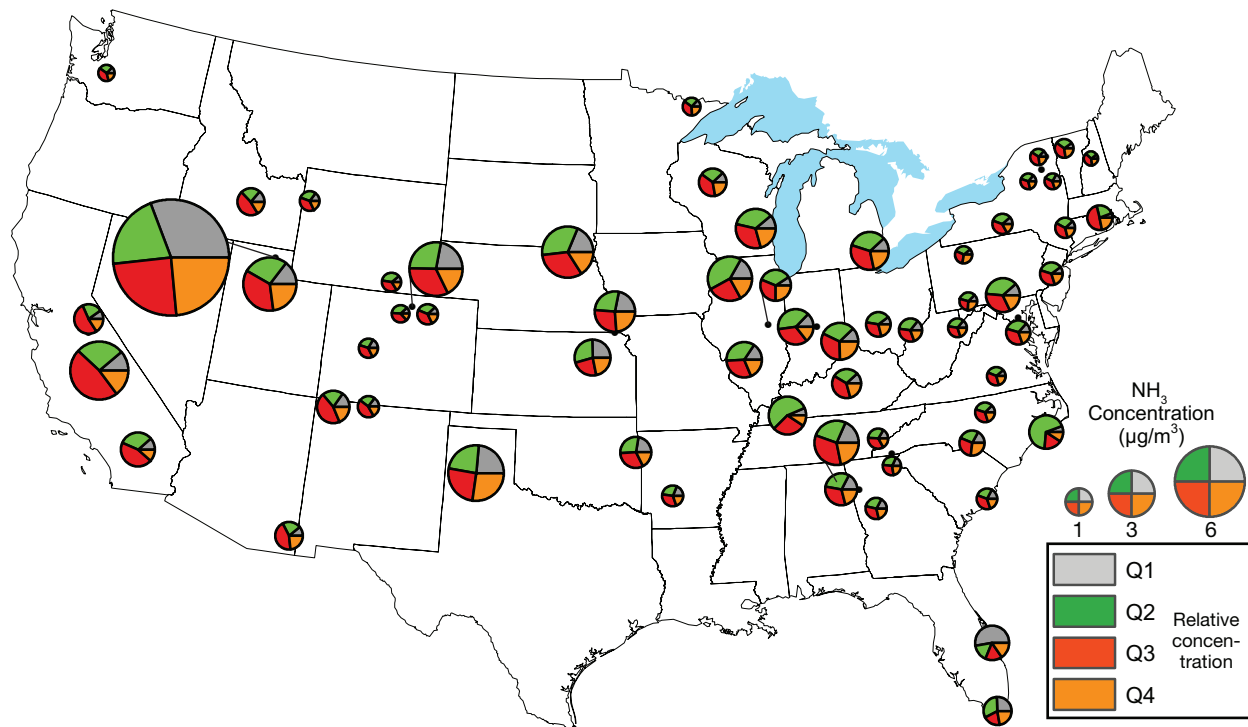
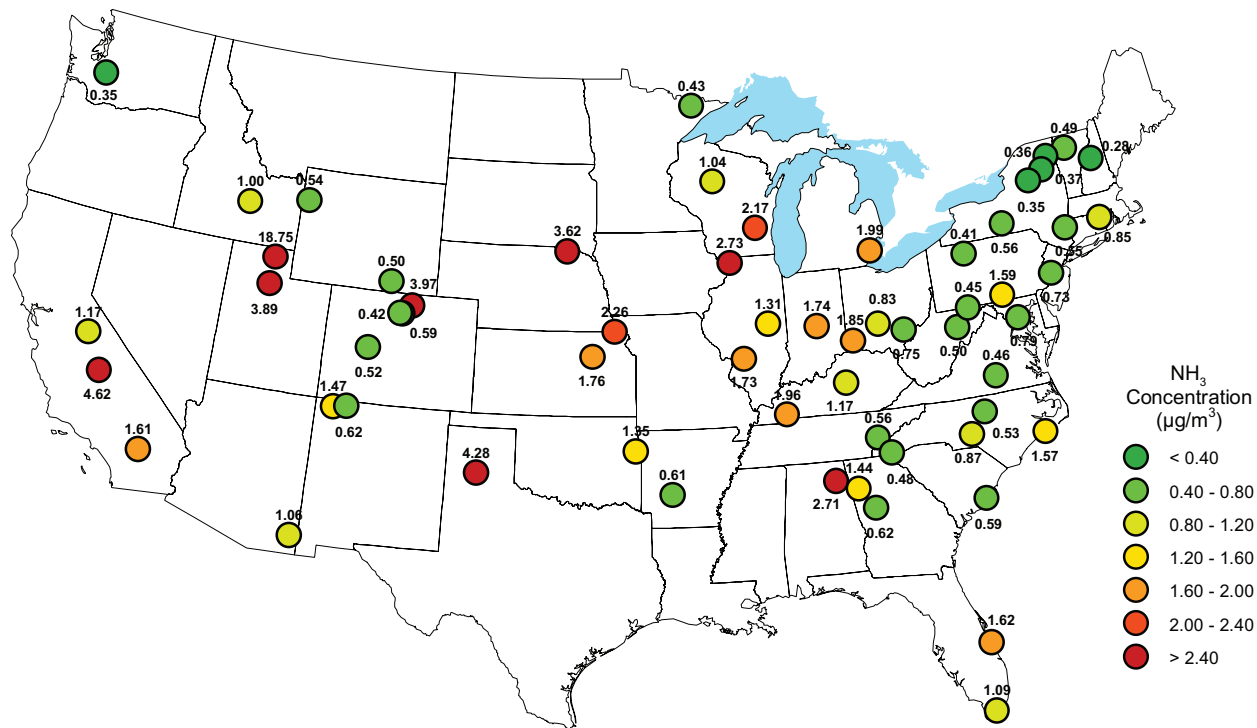
Ammonia Monitoring Network (AMoN)

The AMoN measures atmospheric concentrations of ammonia (NH_3) gas. The network uses passive diffusion-type samplers. This allows for cost-effective, straightforward, and simple measurements. Observations are made over a two-week period with some sites measuring in triplicate. This provides an integrated and quality-assured estimate of ammonia in the air. These data are used to assess long-term NH_3 trends, provide necessary information for model development and verification, and assess changes in atmospheric chemistry.

At the end of 2013, there were 64 AMoN sites. Data from the AMoN are available on the NADP website (<http://nadp.isws.illinois.edu/amon/>).

The figures on page 27 show the distribution and seasonality of gaseous ammonia concentrations for each site meeting completeness criteria. In 2013, 61 of 64 active sites met these criteria. In the top figure, circles represent annual average concentrations in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) at each site. In the bottom figure, the relative concentration for each site is shown for each calendar quarter. The size of the wedge is the relative percentage for the quarter. The size of the pie chart is proportional to the annual average for the site.





Average ammonia concentrations as measured by AMoN (top), and quarterly relative percentage (Q1 = January, February, March, etc.) for each AMoN site (bottom), 2013. Size of the symbol in the bottom plot is relative to the annual concentration.



National Atmospheric Deposition Program

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