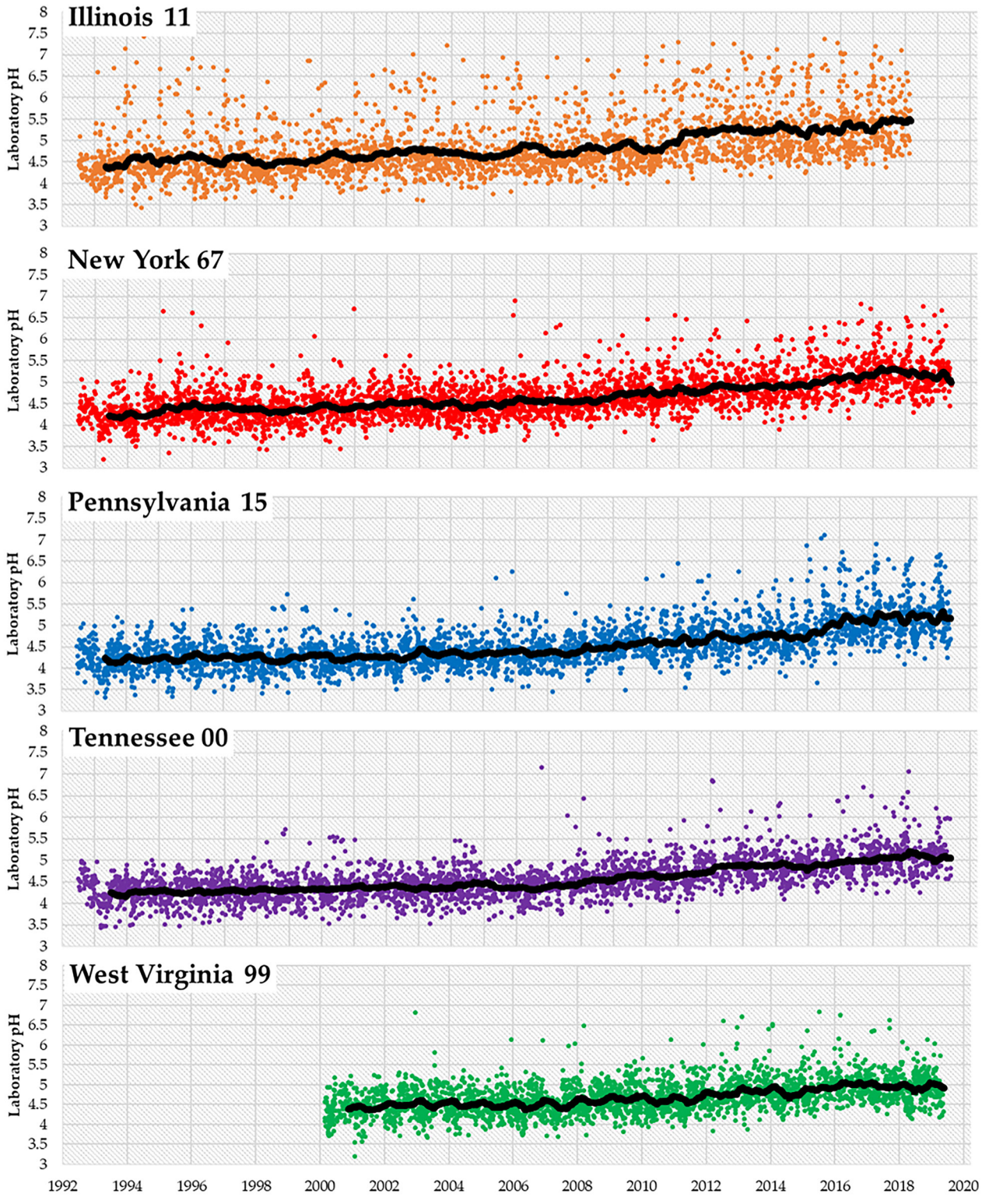
National Atmospheric Deposition Program

2019 Annual Summary

The Value of Long Term Monitoring

Atmospheric Integrated Research Monitoring Network (AIRMoN), 1992 - 2019



On the cover: As the current measurement period of the Atmospheric Integrated Research Monitoring Network (AIRMoN) ends, we thought it appropriate to show the entire record of pH ('potential of hydrogen' is a scale used to specify the acidity or basicity of an aqueous solution) measurement, with most observations beginning in 1992 and extending through September, 2019. Plotted are all precipitation pH measurements at the five final AIRMoN locations (e.g., 3,300 separate precipitation events at NY67). The black line is the 90-point moving average of the pH value. These measurements show the steady increase of pH over the years, and its dramatic rise at most of these sites.

When referencing maps or information in this report, please use the citation: National Atmospheric Deposition Program, 2020. National Atmospheric Deposition Program 2019 Annual Summary. Wisconsin State Laboratory of Hygiene, University of Wisconsin-Madison, WI.

Contents

2019 Highlights

The National Atmospheric Deposition Program (NADP) provides high-quality, robust measurements that support informed decisions about environmental and public health issues as they relate to atmospheric deposition chemistry, and advance our understanding of atmospheric processing through the measurement of gaseous ammonia and mercury. NADP data is relevant to scientists, educators, policymakers, and the public. All data is available without charge on the NADP website (http://nadp.slh.wisc.edu).

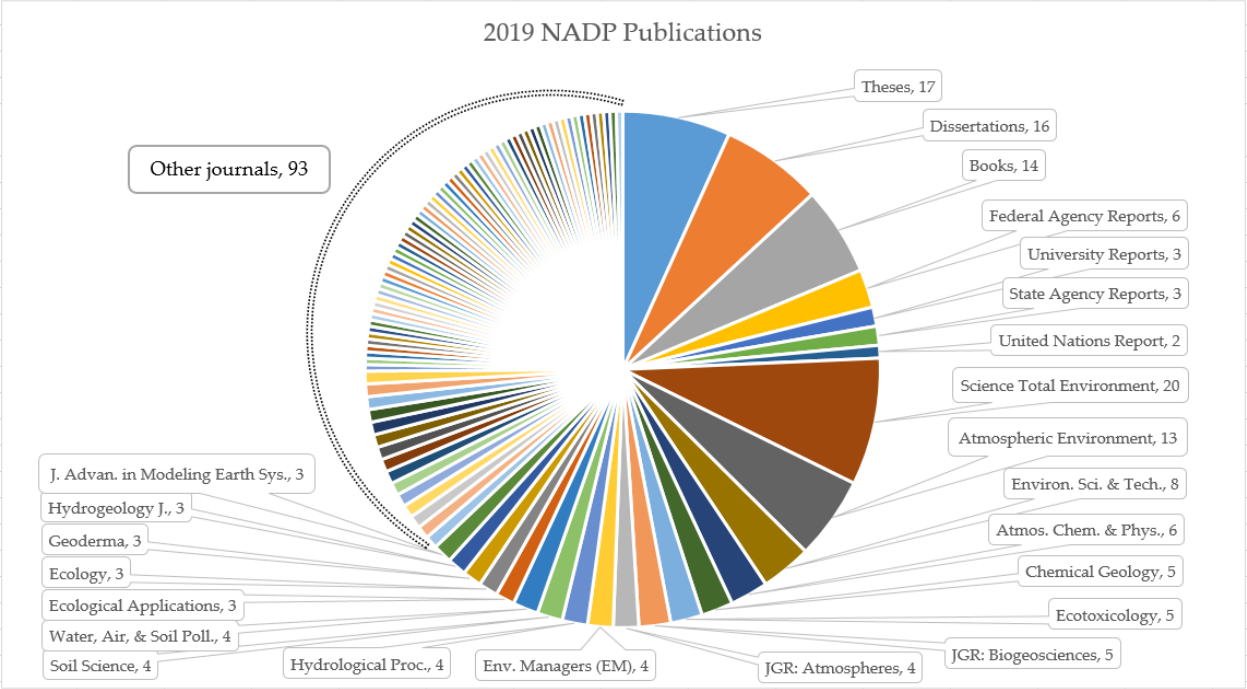
The NADP is composed of five networks, including the National Trends Network (NTN), the Atmospheric Integrated Research Monitoring Network (AIRMoN; stopped September 2019), the Mercury Deposition Network (MDN), the Atmospheric Mercury Network (AMNet), and the Ammonia Monitoring Network (AMoN). The table below summarizes the number of measurements from each network in 2019.

Summary of 2019 Network Measurements

Network	Measurements	Period	No. of sites
NTN	13,149	weekly	262
MDN	4,430	weekly	93
AIRMoN	183	daily	4
AMNet	65,026	hourly/ 2-hourly	15
AMoN	2,648	two week	107

Highlights:

- The successful transition of the Mercury Analytical Laboratory (HAL) from the Eurofins-Frontier Global Sciences to the University of Wisconsin-Madison's Wisconsin State Laboratory of Hygiene (WSLH) began in early 2019, with first samples arriving at WSLH in June, 2019. The transition included restructuring the WSLH facilities, transferring glassware, records, and some supplies from Seattle, WA, purchase of all new and dedicated analytical equipment, and completing a laboratory intercomparison evaluation (2020).
- The final Atmospheric Integrated Research Monitoring Network (AIRMoN) sample was collected on September 2nd, 2019 at New York 67 (Ithaca, by long-term operator Tom Butler). This completes a long-term operation of this network under the NADP "umbrella" of networks, starting with two samples collected on October 5, 1992 (two samples, TN00-Walker Branch and DE02-Lewes). Over the 29 years of operation, 29,337 daily precipitation samples were collected at 12 locations. The network was supported principally by the National Oceanic and Atmospheric Administration. NOAA and other agencies had operated the network previous to NADP participation. Its daily precipitation chemistry results will remain available on the NADP website, and samples collected prior to NADP involvement (MAP3S) will also remain available here: http://nadp.slh.wisc.edu/dl/map3s/.
- NADP data were used in 248 publications during the year. See the chart on page 5 for more detail of the publication types and publishing journals. Publications included:
    - 16 Doctoral Dissertations
    - 17 Master's Theses
    - 14 books
    - 14 government and university reports
    - 187 journal articles
- The Mercury Litterfall Initiative with U.S. Geological Survey (USGS) scientists completed its sixth year of operation. Progress toward making the initiative a formal NADP Network continues. Analysis and processing was transferred to the WSLH during the year, with full initiative operation to begin in 2020.
- **Fall Scientific Symposium and TDEP Workshop:** The Fall Scientific meetings were held in Boulder, CO (Nov. 4-8) with 36 oral presentations and 42 posters. Along with the general scientific presentations, the NADP also held the Total Deposition Science Committee (TDEP)



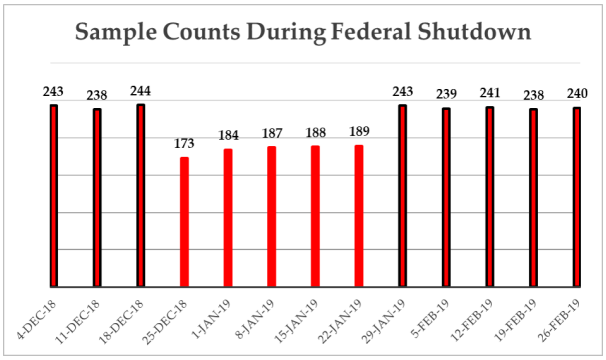
Workshop "Connecting Stakeholder and Science Perspectives to Better Understand the Linkages Between Agriculture and Reactive Nitrogen Deposition" with over 100 participants, 12 individual speakers, and multiple panel discussions.

- During the year, NADP purchased additional precipitation gages to replace the *final 14 Belfort gages* in the network. Movement of these gages to the sites is ongoing. Further, older android phones were purchased and are currently being used to transfer precipitation data from the gage to computers. These phones were selected to replace personal digital assistants (PDAs) still being used at some sites.

- The year started with the United States federal government shutdown occurred from midnight on December 22, 2018, until January 25, 2019 (35 days). It was the longest U.S. government shutdown in history. During the shutdown, the typical sample count was down by 50-55 samples per week, or approximately 25% (see chart at right).

- NADP continued to collaborate with Utah State University scientists to develop methods to monitor dry deposition accurately and correctly, as part of a pilot study. This study continues to expand and will generate valuable dry deposition data (see Brahney, et al., 2020, A new sampler for the collection and retrieval of dry dust deposition, Aeolian Research 45, 100600).

- Through extensive review with the Quality Assurance Advisory Group (QAAG) the NADP CAL documented that the web-published bromide data from January 2012 through June 2018 has known or suspected bias caused by the presence of oxalate. Motions to remove this data from the NADP website and discontinue bromide determination (due to >80% non-detects) was approved by NADP Executive Committee on May 17, 2019.



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. The NADP's primary charge was to provide data on the temporal trends and geographic distribution of the atmospheric deposition of acids, nutrients, and base cations by precipitation. 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 at Urbana-Champaign and the Program Coordinator was housed at Colorado State University.

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 the National Research Support Project No. 3 (NRSP-3), which it remains to this day. 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 (NIFA) and other universities, institutions, and agencies.

In October 1981, the federally-supported National Acid Precipitation Assessment Program (NAPAP) was established to increase our 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. Building on its experience in organizing and operating a national-scale network, the NADP agreed to coordinate operation of NAPAP's National Trends Network. Later, to benefit from identical siting criteria, 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.

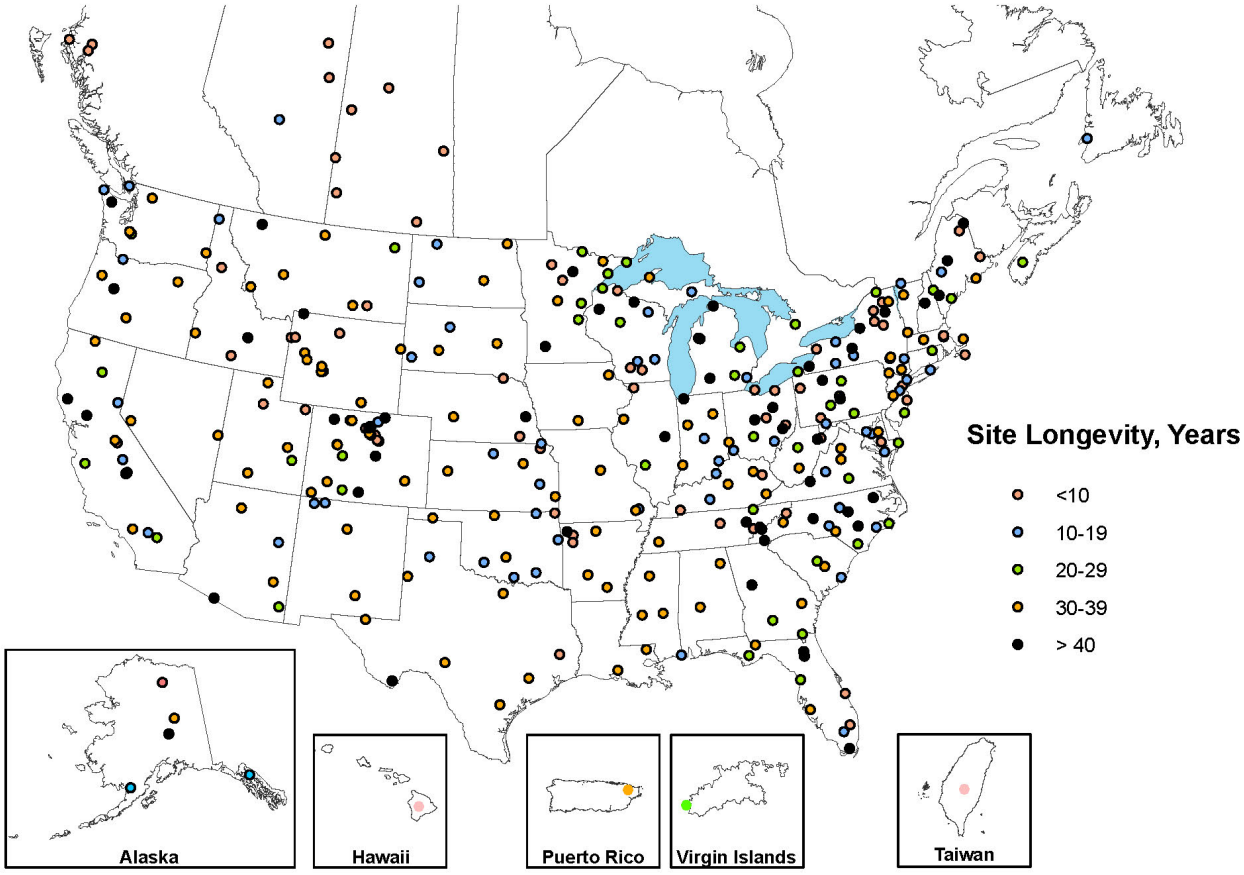
In October 1992, the AIRMoN was formed from the Multistate Atmospheric Power Production Pollution Study (MAP3S), which was operated by the Department of Energy and NOAA. MAP3S measured wet deposition and estimated dry deposition (later discontinued) for the same analytes. AIRMoN sites collect samples 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. MDN samples, like NTN samples, are weekly collections.

In October 2009, AMNet joined the NADP as its fourth network. AMNet measures the concentration of atmospheric mercury at high-time resolution using on-site, real-time analyzers.

In October 2010, AMoN joined the NADP. Atmospheric ammonia concentrations are measured every two weeks using passive samplers. The AMoN furthers the understanding of wet and dry deposition and ammonia partitioning in the atmosphere, allowing better assessment of ecosystem impacts and secondary air pollution formation.

Beginning in late 2017 and completed in mid-2018, the NADP PO and CAL moved from the University of Illinois at Urbana-Champaign to the University of Wisconsin–Madison, and in June 2019 the HAL moved to the University of Wisconsin–Madison.



Global distribution and longevity of NADP sites.

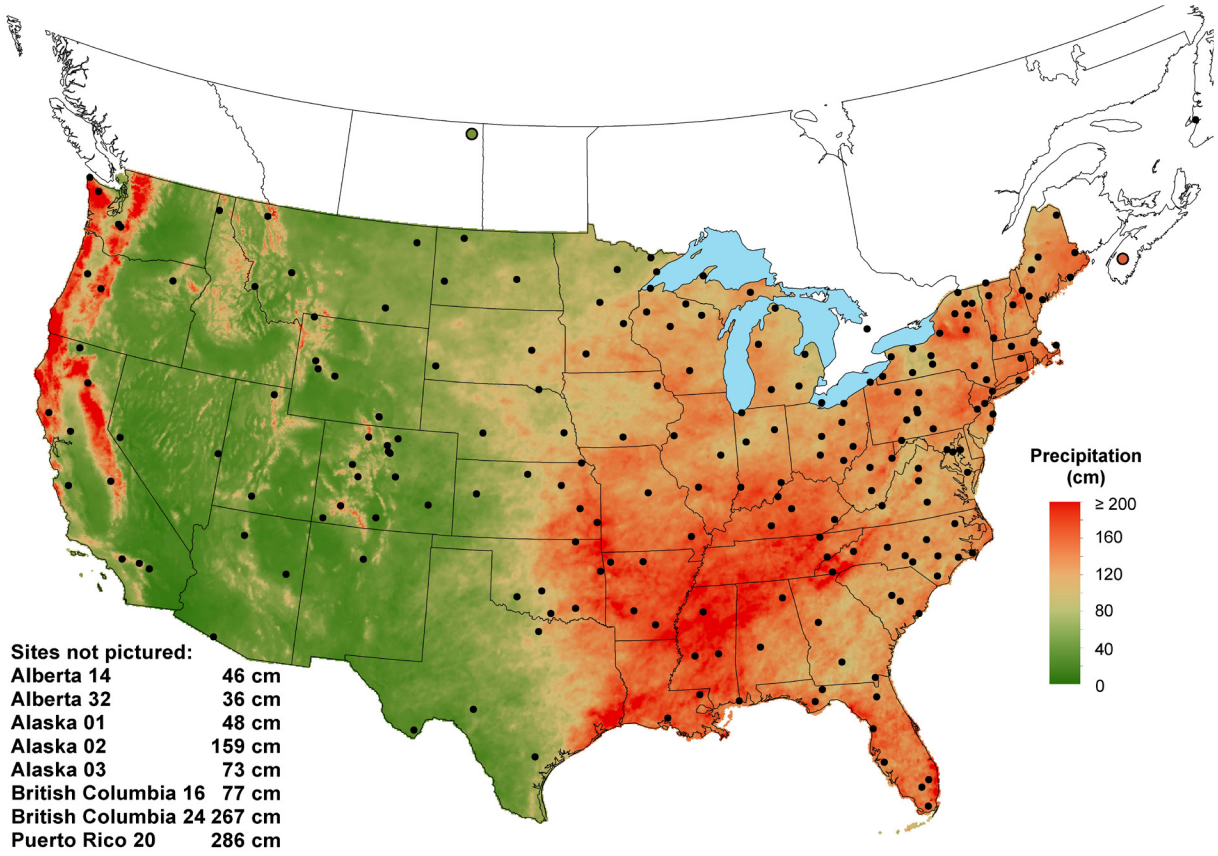
About the Maps

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 graphical form. Additional maps, related geographic information, and reviewed analytical results are available on the NADP website.

To be included in a map product, site data must meet strict data completeness criteria (see the NADP website for details). Black dots mark site locations that met NADP completeness criteria in 2019. 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. Sites (e.g., Canadian sites) that are too far removed from other observations to extend the contour surface are represented as color-filled circles.

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. The precipitation surface is a modified version of the U.S. precipitation grid developed by the PRISM Climate Group ("Parameter-elevation Regressions on Independent Slopes Model," http:// prism.oregonstate.edu, data downloaded September 2020). 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 within a 20 km radius of each NADP site (see the NADP website for specific information). The resulting precipitation map is used to generate the deposition maps.

The precipitation figure on the next page has a continuous gradient of color from dark green (0 cm of precipitation) to yellow to dark red (greater than 200 cm of precipitation). Concentration and deposition maps follow this same format, with specified units on each map. All maps back to 1985 follow this schema and are available in multiple formats from the NADP website (http://nadp.slh.wisc.edu).



Total annual precipitation for 2019, using precipitation measurements from the NADP and PRISM (in cm).

National Trends Network (NTN)

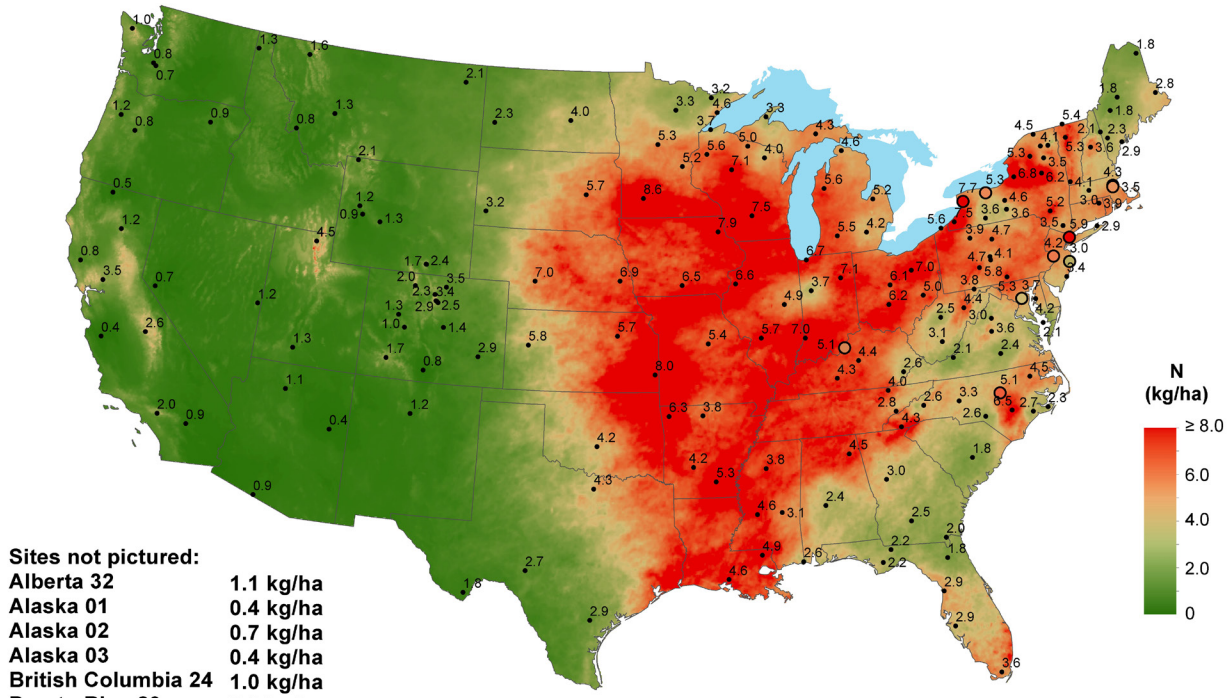
The NTN is the largest North American network that provides a long-term record of precipitation chemistry. Most sites are located away from urban areas and point sources of pollution, although urban sites do participate. Each site has a precipitation collector and rain gage. The automated collector ensures that sampling only occurs during precipitation events. 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, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), and ammonium (NH_4^+) ions. The CAL quantifies orthophosphate for quality assurance purposes, as an indicator of potential field 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.slh.wisc.edu/ntn/).

NTN Maps

The maps on pages 11 through 19 show precipitation-weighted mean concentration and annual wet deposition for select acid anions, nutrients, and base cations. Substantial spatial heterogeneity across the nation is apparent for all measured species. In 2019,

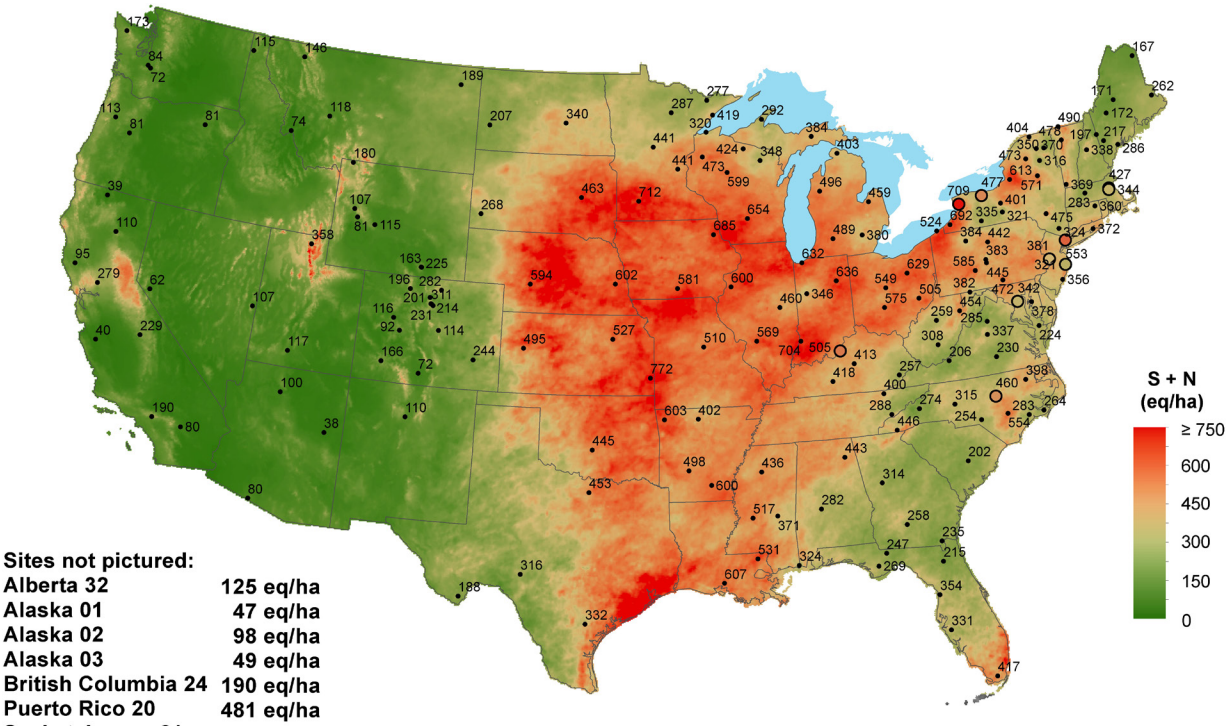
190 of the 262 active sites met NADP completeness criteria. Concentration and deposition maps are included for SO_4^{2-}, NO_3^-, NH_4^+, pH, Ca^{2+}, Mg^{2+}, Cl^-, and Na^+. Maps of K^+ are not included in this report, but are available from the NADP website. Bromine ion data is no longer reported by NADP.

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



Sites not pictured:

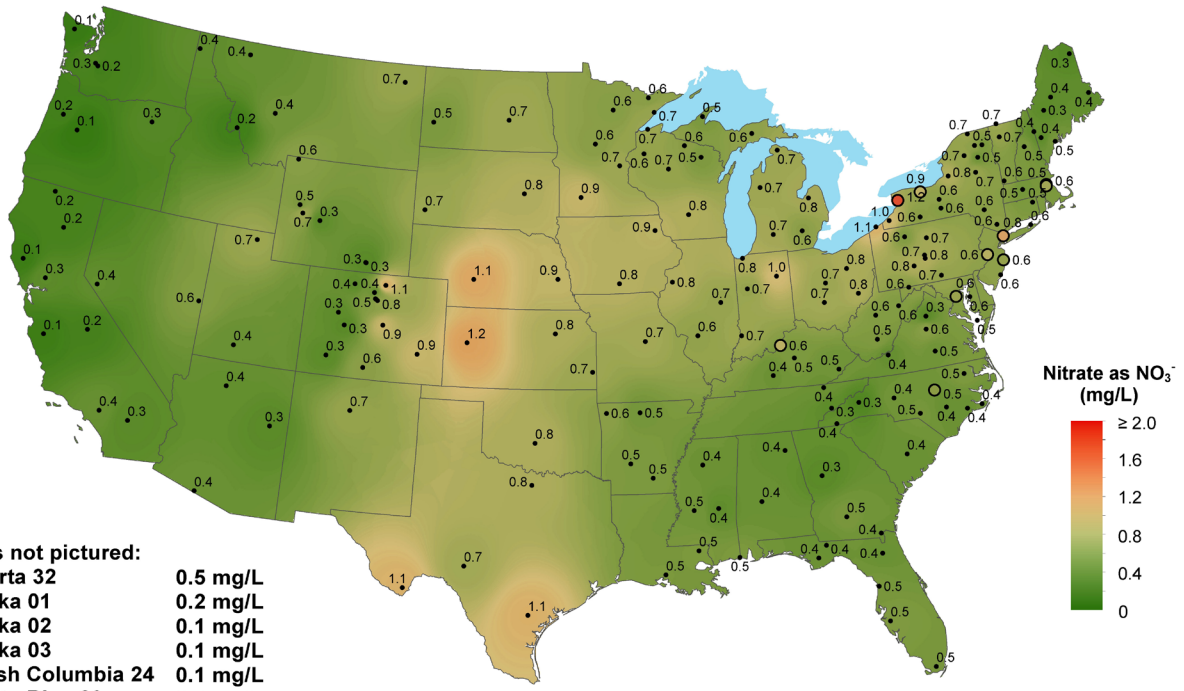
Alberta 32	1.1 kg/ha
Alaska 01	0.4 kg/ha
Alaska 02	0.7 kg/ha
Alaska 03	0.4 kg/ha
British Columbia 24	1.0 kg/ha
Puerto Rico 20	2.2 kg/ha
Saskatchewan 21	1.5 kg/ha



Sites not pictured:

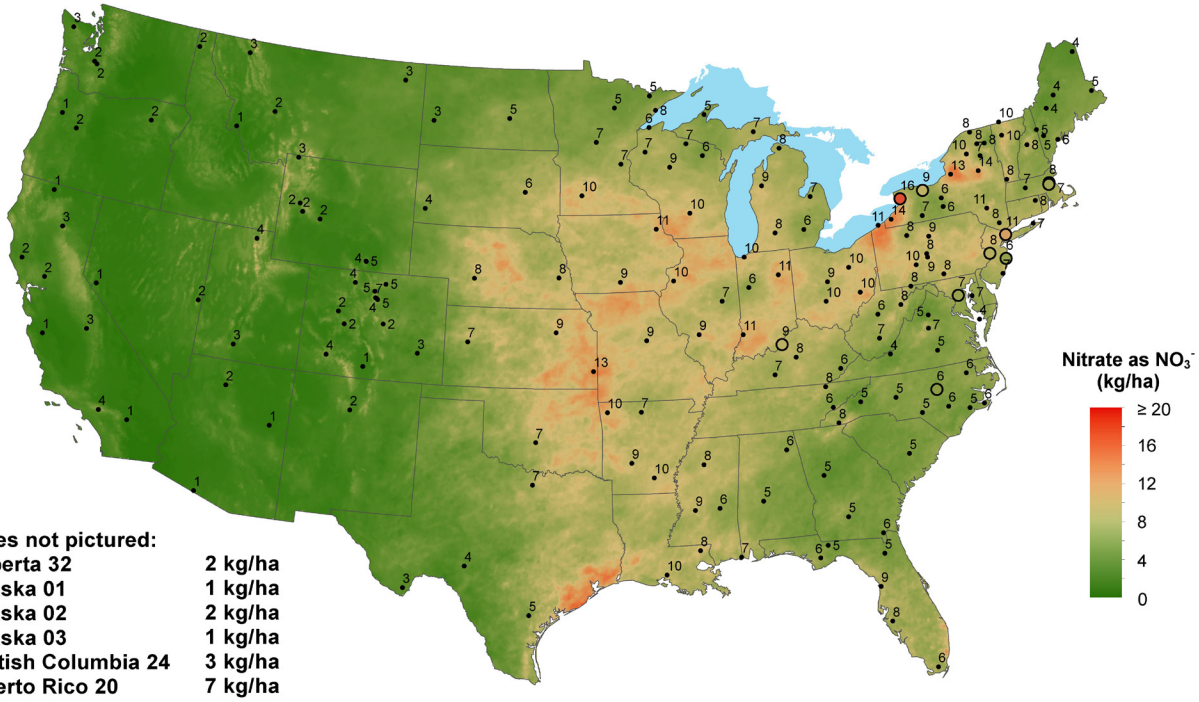
Alberta 32	125 eq/ha
Alaska 01	47 eq/ha
Alaska 02	98 eq/ha
Alaska 03	49 eq/ha
British Columbia 24	190 eq/ha
Puerto Rico 20	481 eq/ha
Saskatchewan 21	140 eq/ha

Inorganic nitrogen wet deposition from nitrate and ammonium (top) and nitrogen plus sulfur wet deposition from nitrate, ammonium, and sulfate (bottom), 2019.



Sites not pictured:

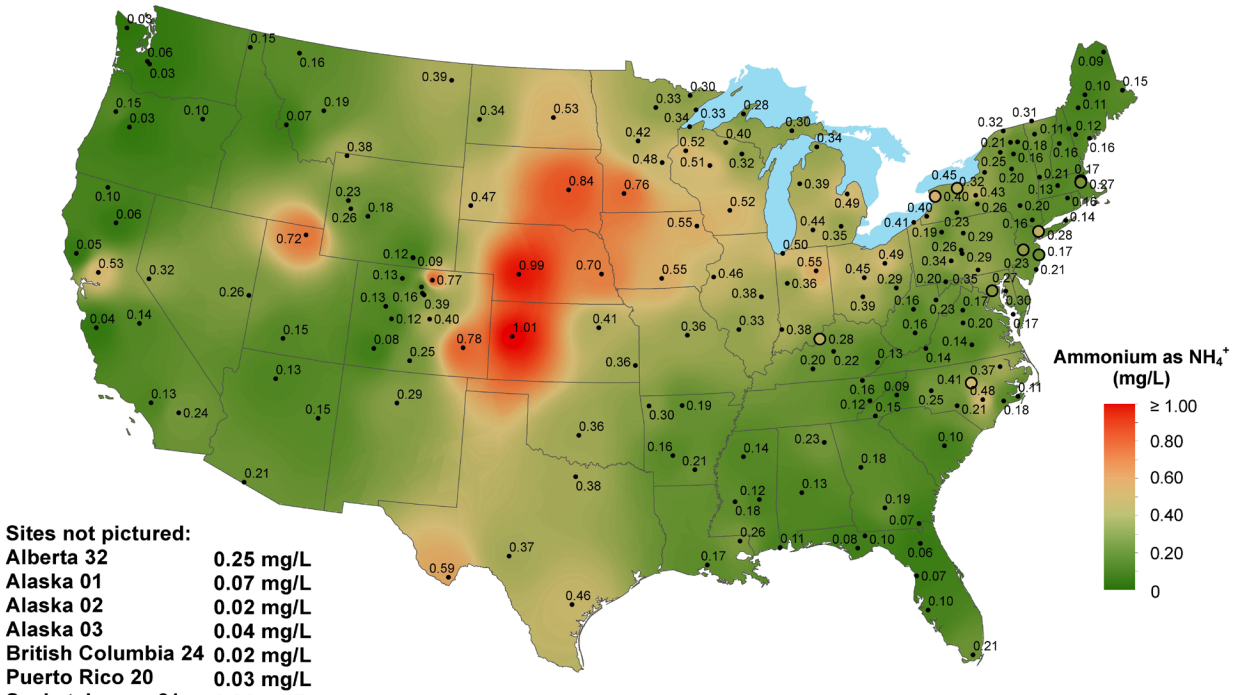
Alberta 32	0.5 mg/L
Alaska 01	0.2 mg/L
Alaska 02	0.1 mg/L
Alaska 03	0.1 mg/L
British Columbia 24	0.1 mg/L
Puerto Rico 20	0.2 mg/L
Saskatchewan 21	0.5 mg/L



Sites not pictured:

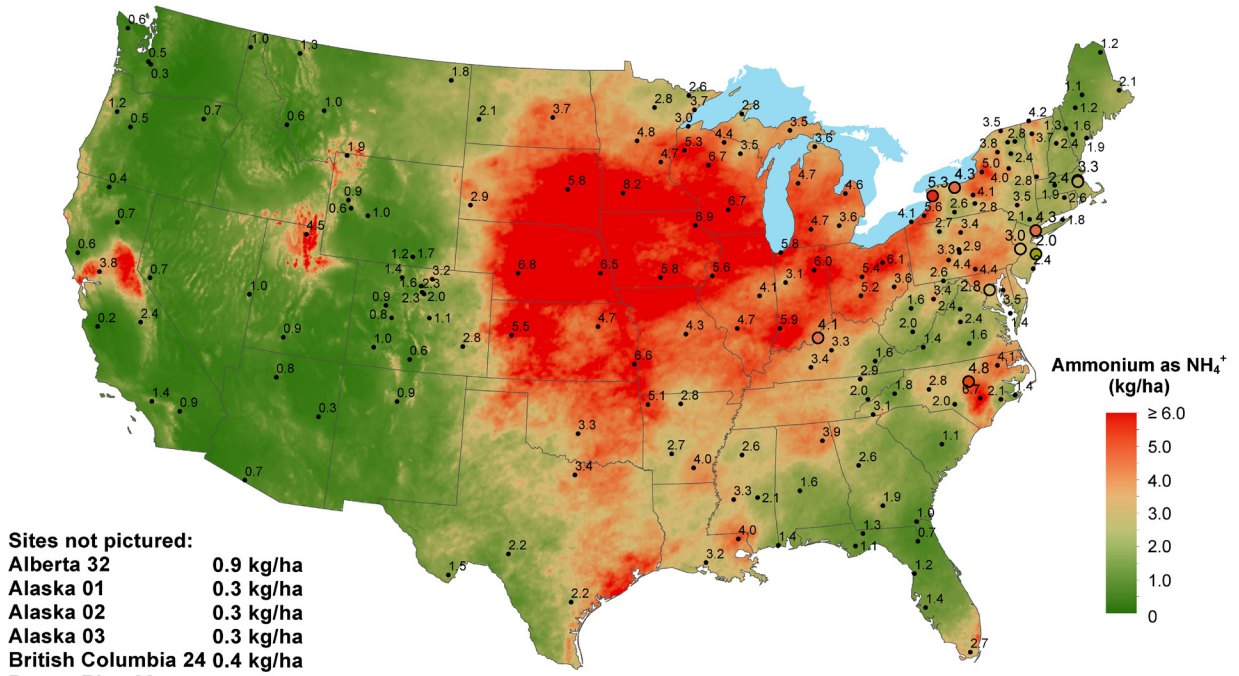
Alberta 32	2 kg/ha
Alaska 01	1 kg/ha
Alaska 02	2 kg/ha
Alaska 03	1 kg/ha
British Columbia 24	3 kg/ha
Puerto Rico 20	7 kg/ha
Saskatchewan 21	3 kg/ha

Nitrate ion concentration (top) and wet deposition (bottom), 2019.



Sites not pictured:

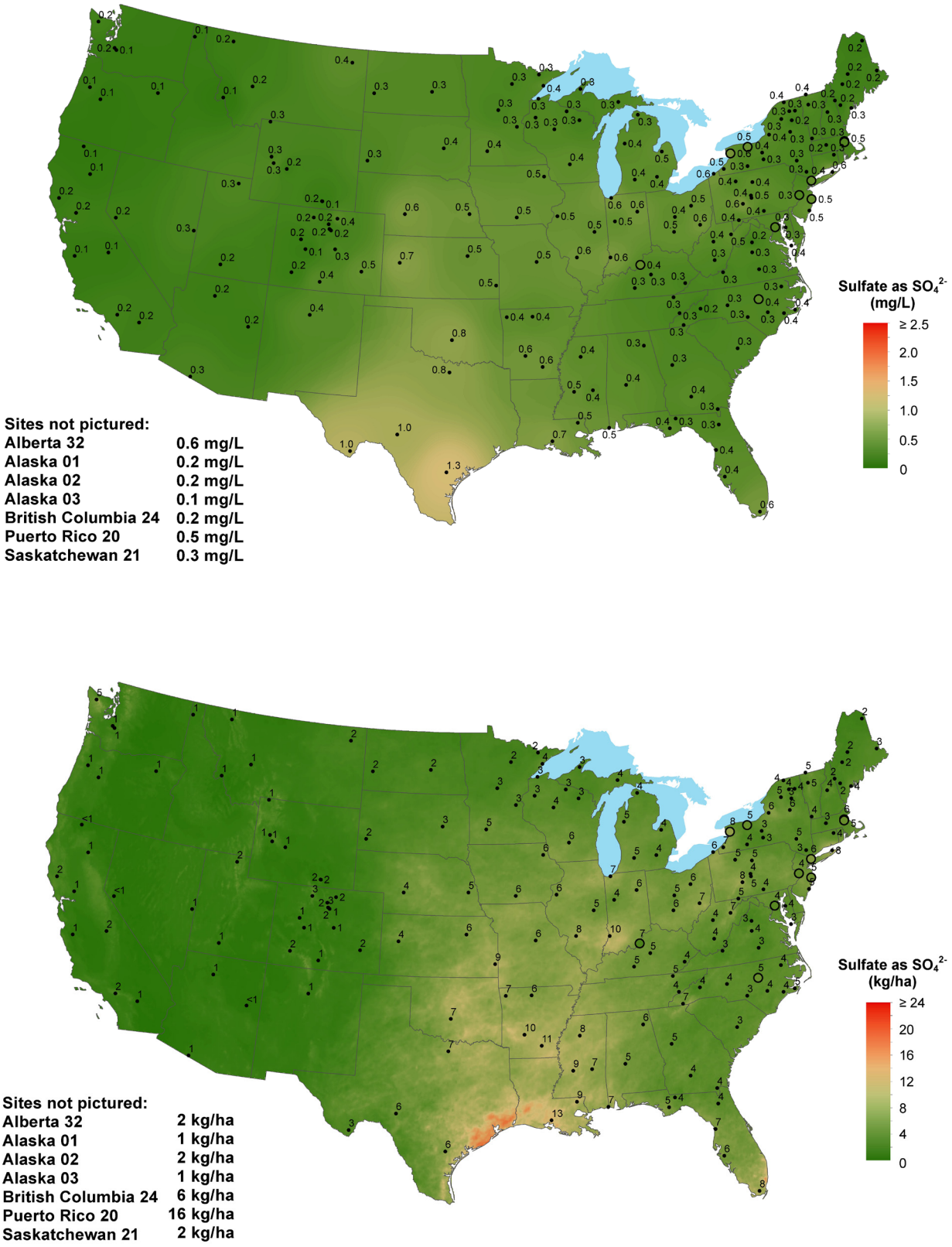
Alberta 32	0.25 mg/L
Alaska 01	0.07 mg/L
Alaska 02	0.02 mg/L
Alaska 03	0.04 mg/L
British Columbia 24	0.02 mg/L
Puerto Rico 20	0.03 mg/L
Saskatchewan 21	0.26 mg/L



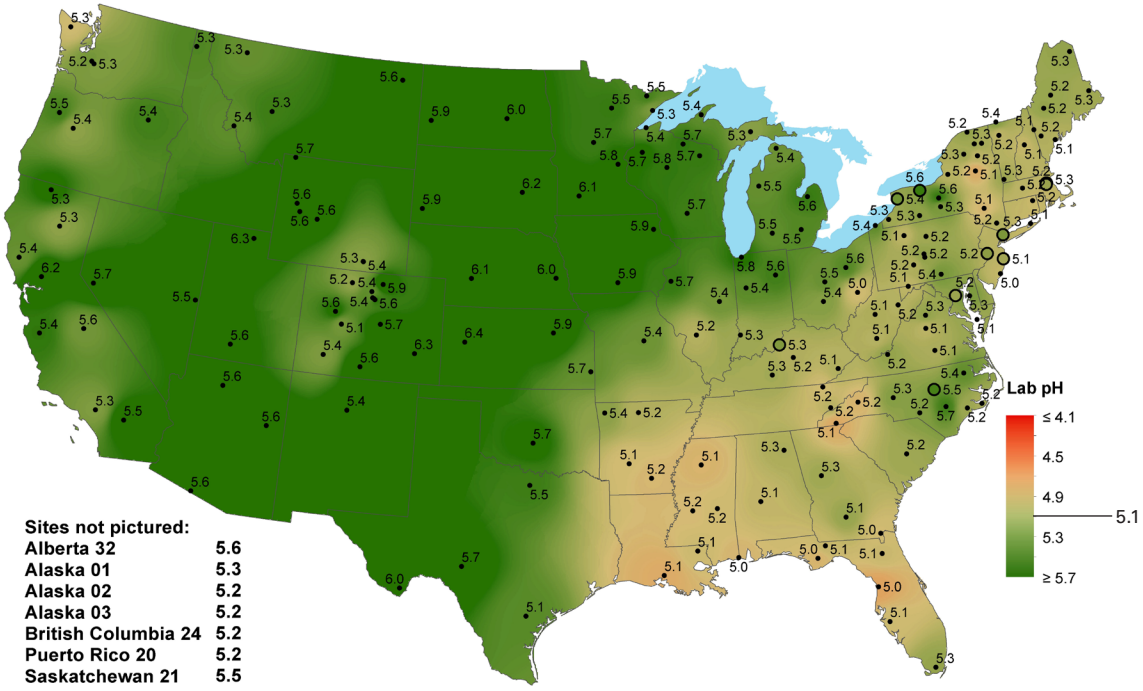
Sites not pictured:

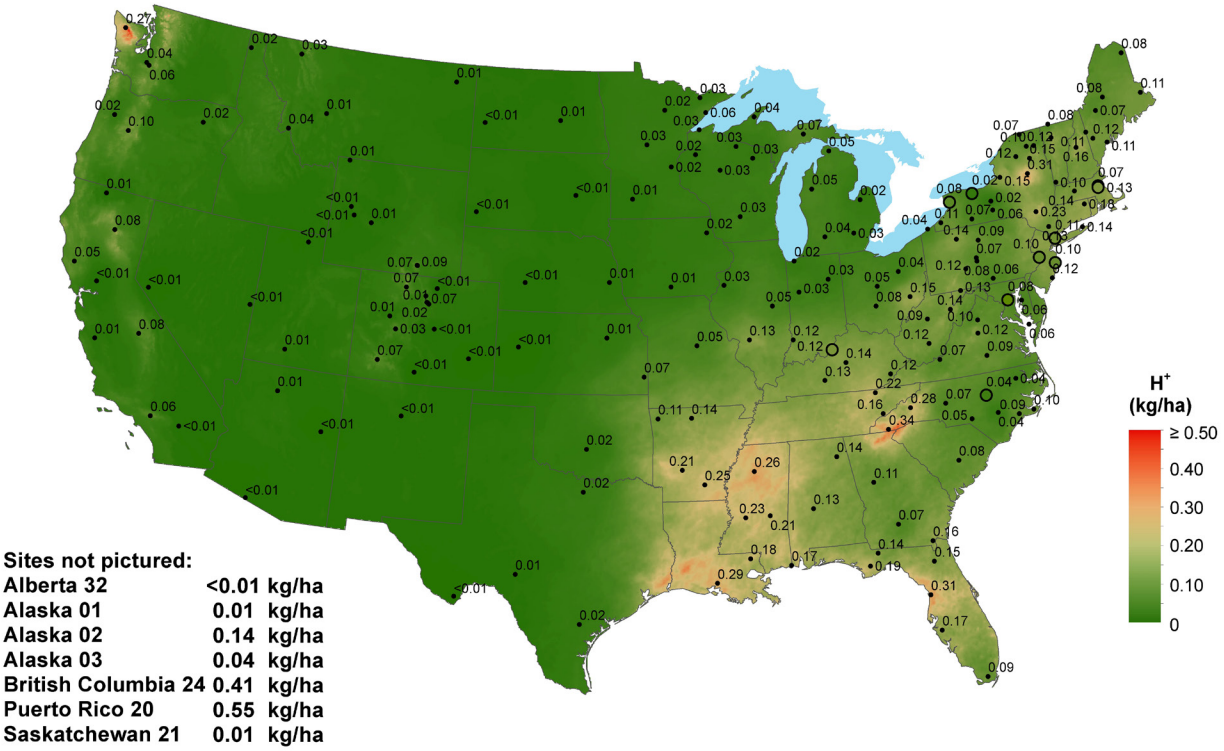
Alberta 32	0.9 kg/ha
Alaska 01	0.3 kg/ha
Alaska 02	0.3 kg/ha
Alaska 03	0.3 kg/ha
British Columbia 24	0.4 kg/ha
Puerto Rico 20	0.7 kg/ha
Saskatchewan 21	1.2 kg/ha

Ammonium ion concentration (top) and wet deposition (bottom), 2019.

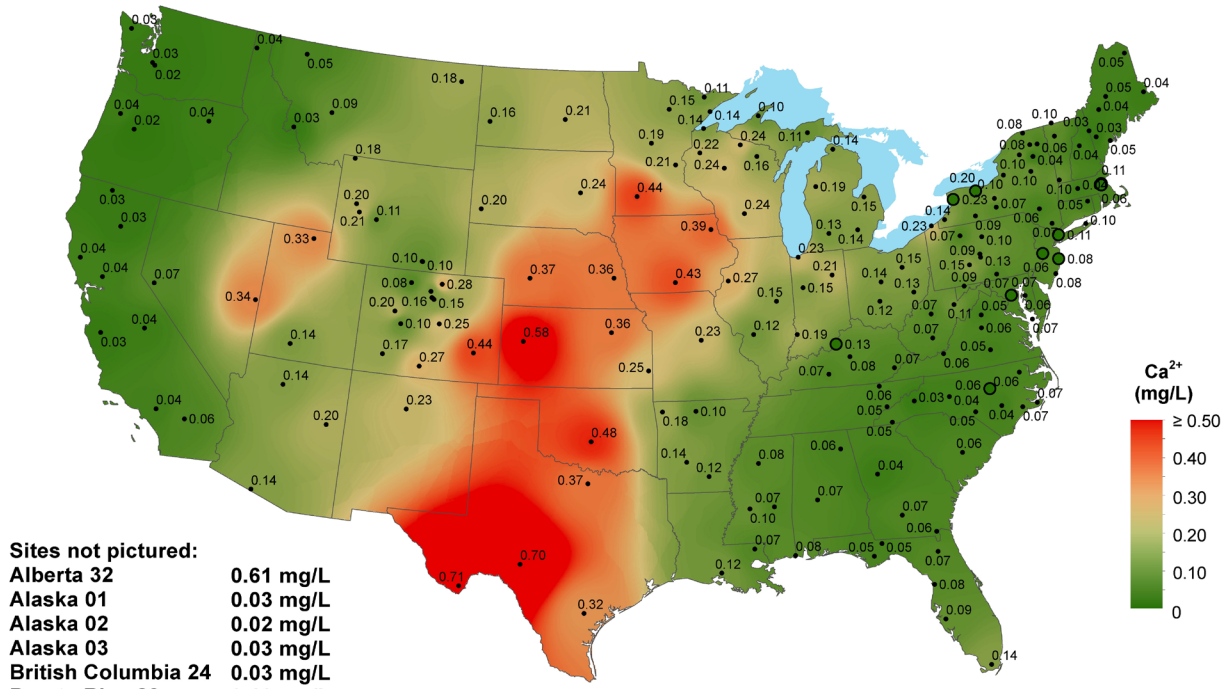


Sulfate ion concentration (top) and wet deposition (bottom), 2019.



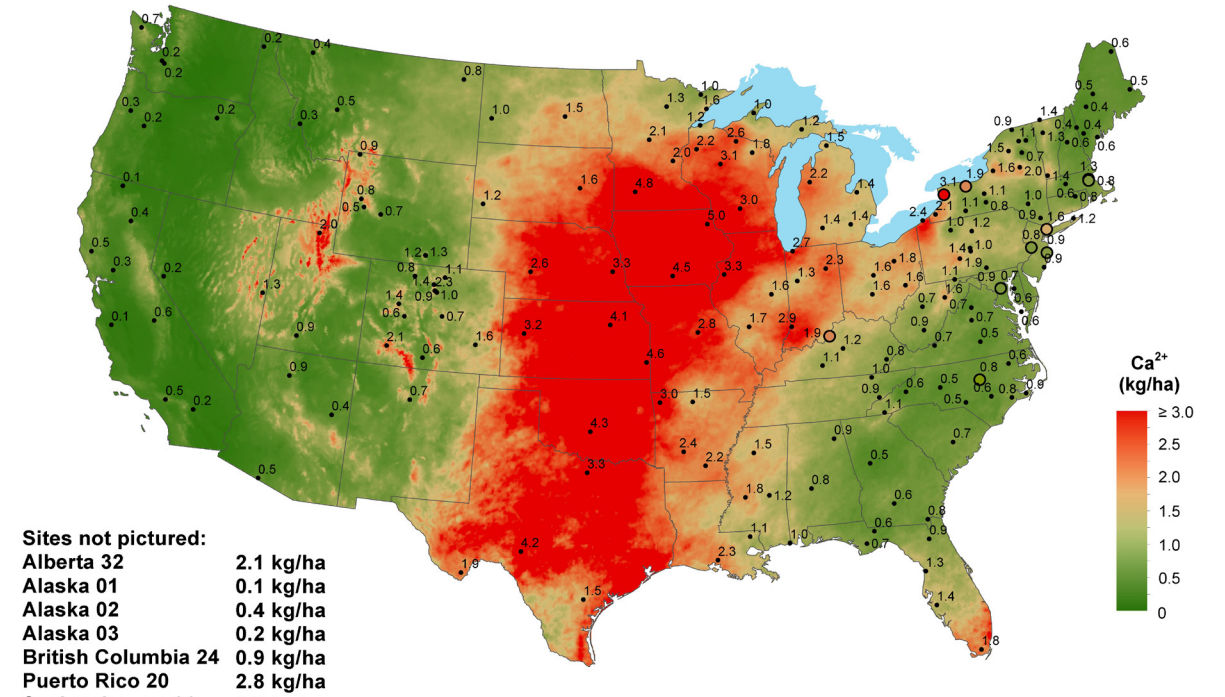


Hydrogen ion concentration as pH (top) and wet deposition (bottom), 2019.
Typically, a precipitation pH of less than 5.1 is considered acidic precipitation.



Sites not pictured:

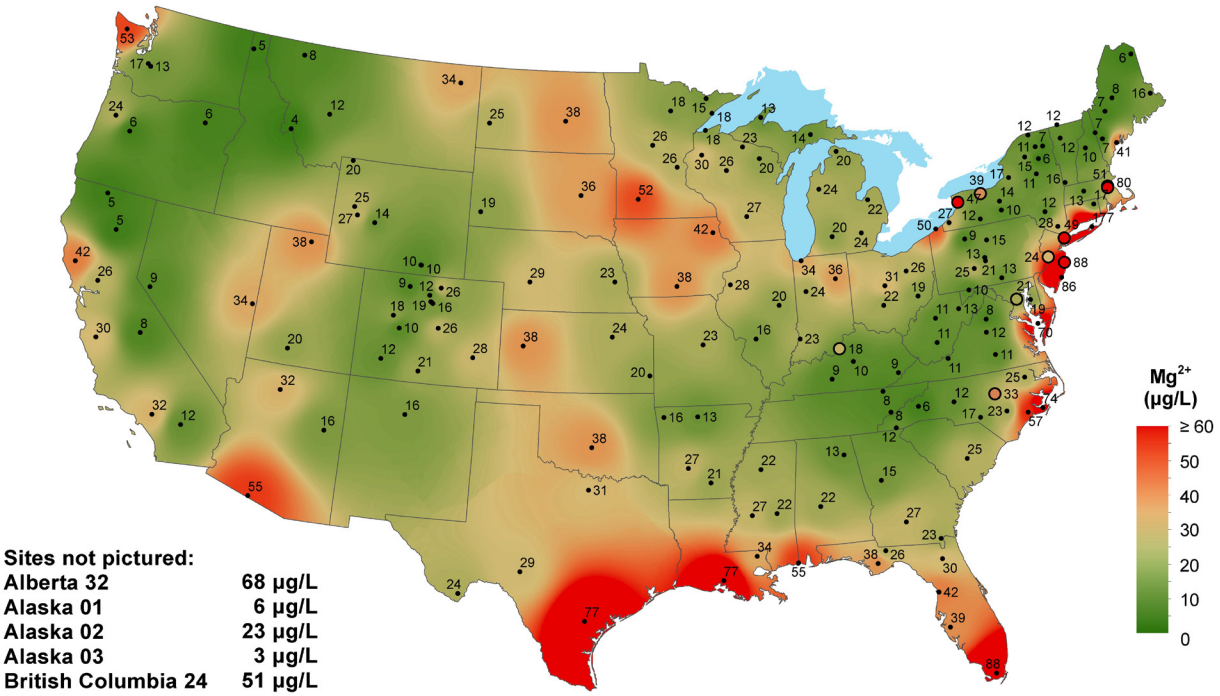
Alberta 32	**0.61 mg/L**
Alaska 01	**0.03 mg/L**
Alaska 02	**0.02 mg/L**
Alaska 03	**0.03 mg/L**
British Columbia 24	**0.03 mg/L**
Puerto Rico 20	**0.10 mg/L**
Saskatchewan 21	**0.20 mg/L**



Sites not pictured:

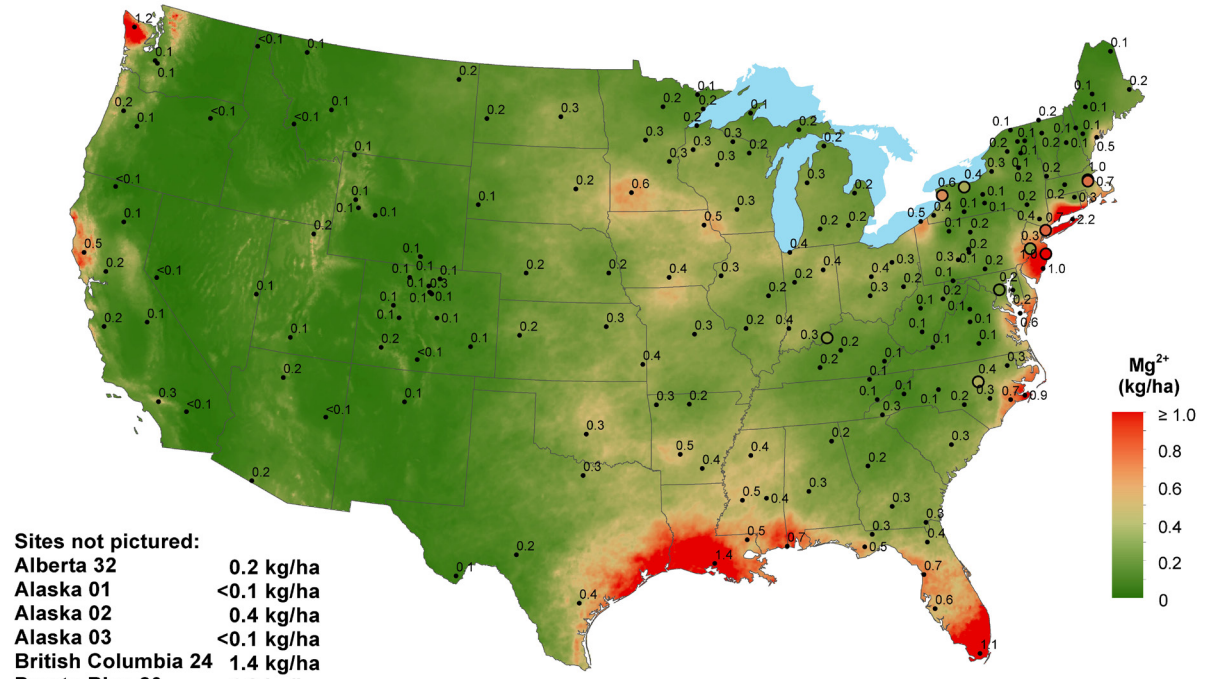
Alberta 32	**2.1 kg/ha**
Alaska 01	**0.1 kg/ha**
Alaska 02	**0.4 kg/ha**
Alaska 03	**0.2 kg/ha**
British Columbia 24	**0.9 kg/ha**
Puerto Rico 20	**2.8 kg/ha**
Saskatchewan 21	**0.9 kg/ha**

Calcium ion concentration (top) and wet deposition (bottom), 2019.



Sites not pictured:

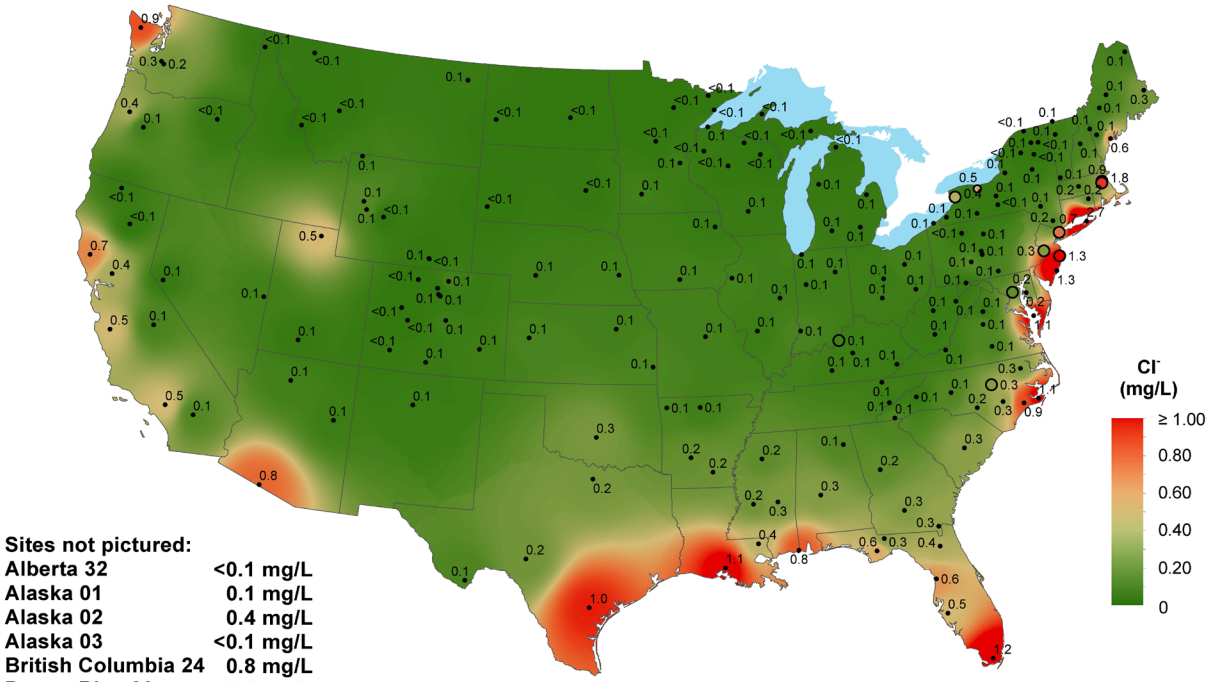
Alberta 32	68 µg/L
Alaska 01	6 µg/L
Alaska 02	23 µg/L
Alaska 03	3 µg/L
British Columbia 24	51 µg/L
Puerto Rico 20	139 µg/L
Saskatchewan 21	53 µg/L

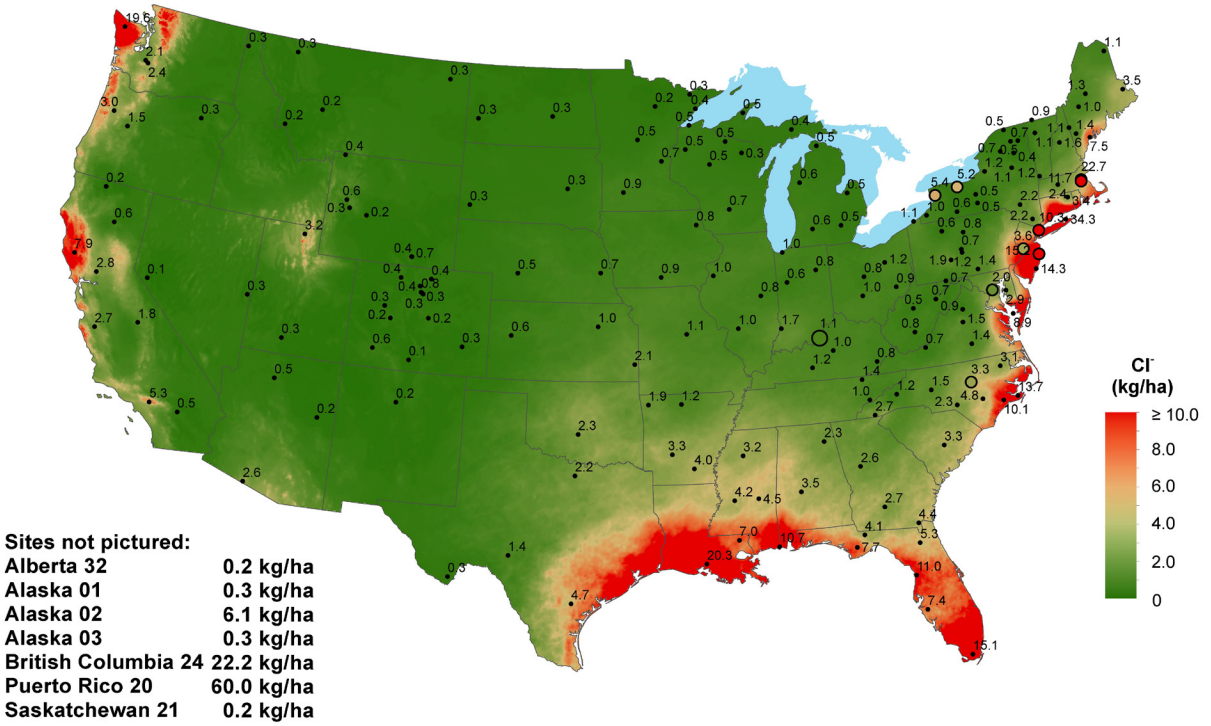


Sites not pictured:

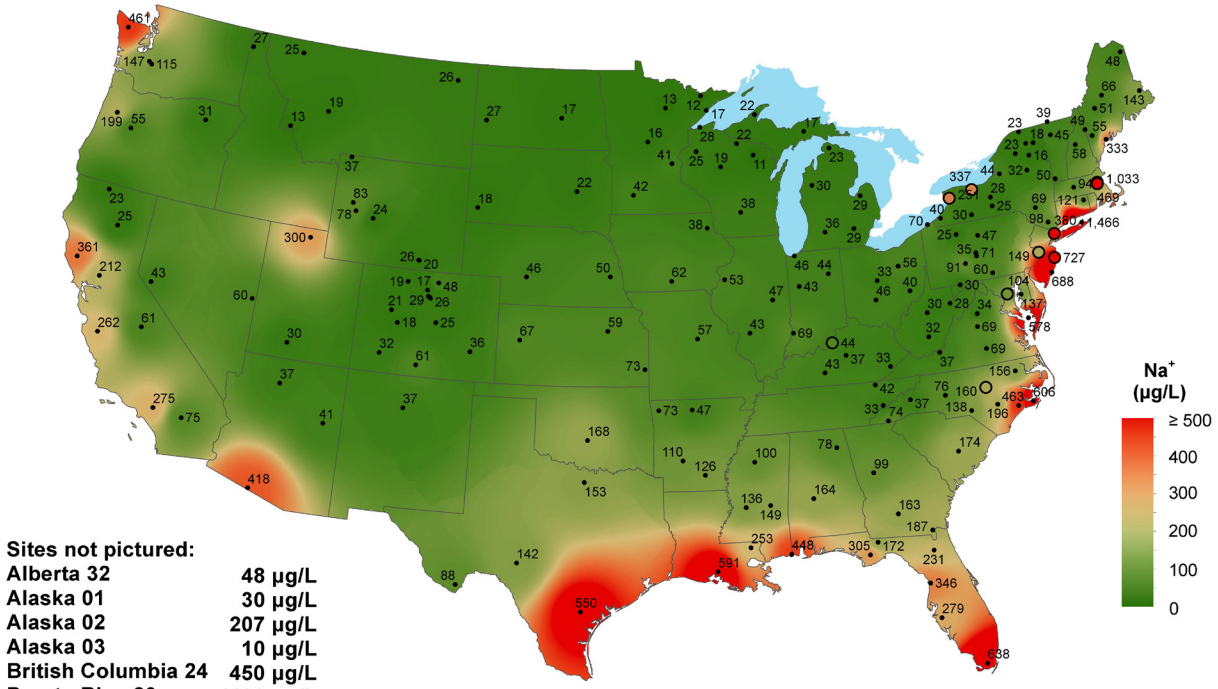
Alberta 32	0.2 kg/ha
Alaska 01	<0.1 kg/ha
Alaska 02	0.4 kg/ha
Alaska 03	<0.1 kg/ha
British Columbia 24	1.4 kg/ha
Puerto Rico 20	4.0 kg/ha
Saskatchewan 21	0.3 kg/ha

Magnesium ion concentration (top) and wet deposition (bottom), 2019.



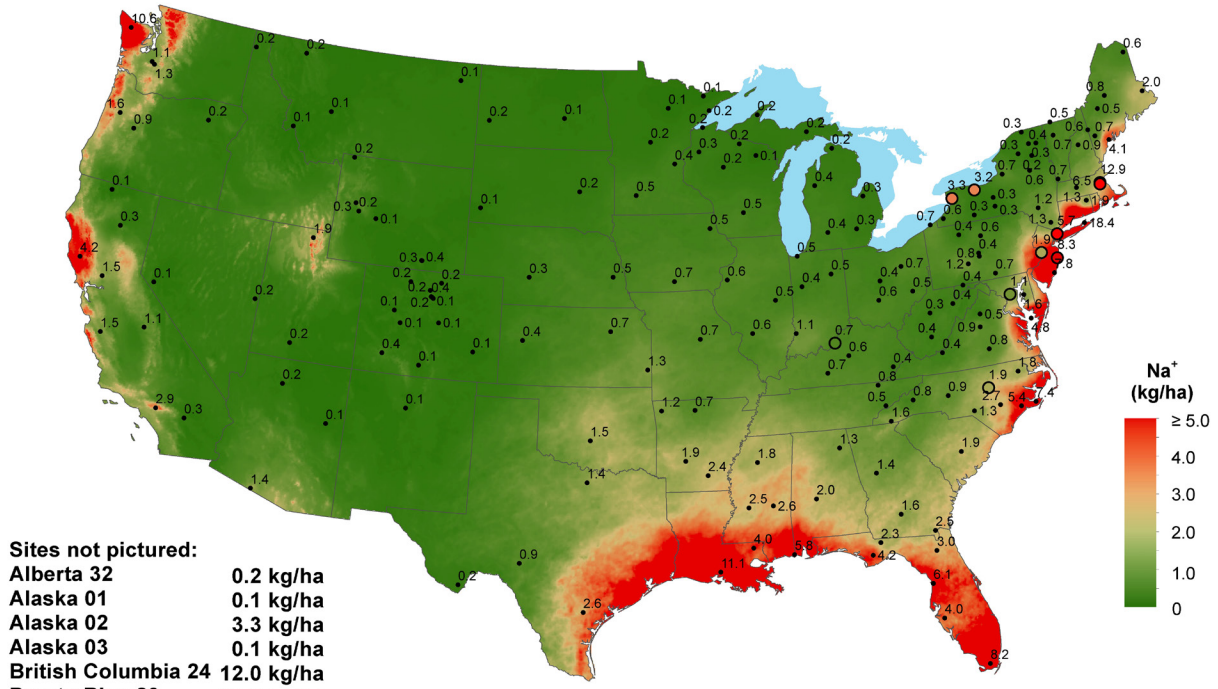


Chloride ion concentration (top) and wet deposition (bottom), 2019.



Sites not pictured:

Alberta 32	48 µg/L
Alaska 01	30 µg/L
Alaska 02	207 µg/L
Alaska 03	10 µg/L
British Columbia 24	450 µg/L
Puerto Rico 20	1138 µg/L
Saskatchewan 21	12 µg/L



Sites not pictured:

Alberta 32	0.2 kg/ha
Alaska 01	0.1 kg/ha
Alaska 02	3.3 kg/ha
Alaska 03	0.1 kg/ha
British Columbia 24	12.0 kg/ha
Puerto Rico 20	32.6 kg/ha
Saskatchewan 21	0.1 kg/ha

Sodium ion concentration (top) and wet deposition (bottom), 2019.

Atmospheric Integrated Research Monitoring Network (AIRMoN)

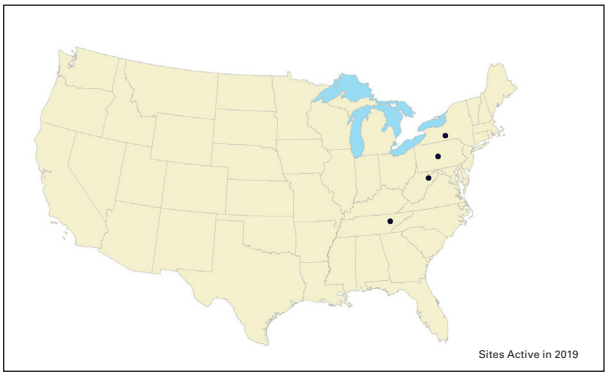
AIRMoN samples are collected daily within 24 hours of the start of precipitation, often providing data for individual storm events. Event-based data facilitate studies of atmospheric processes, give insight to wet deposition data quality sensitivity, and support the development and testing of atmospheric models such as the NOAA/HYSPLIT fate and transport model and Community Multiscale Air Quality (CMAQ) Modeling System.

AIRMoN sites are equipped with the same wet-only deposition collector used at NTN sites. All AIRMoN sites operate digital rain gages to report total precipitation. Each site also has a standard stick-type precipitation gage as a backup.

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 helps retard potential chemical changes. Chemical analyses and data screening procedures for AIRMoN and NTN are similar. Data from the AIRMoN are available on the NADP website (http://nadp.slh.wisc.edu/airmon/).

The AIRMoN network offers a unique set of data, with a significant increase in temporal resolution compared to the NTN.

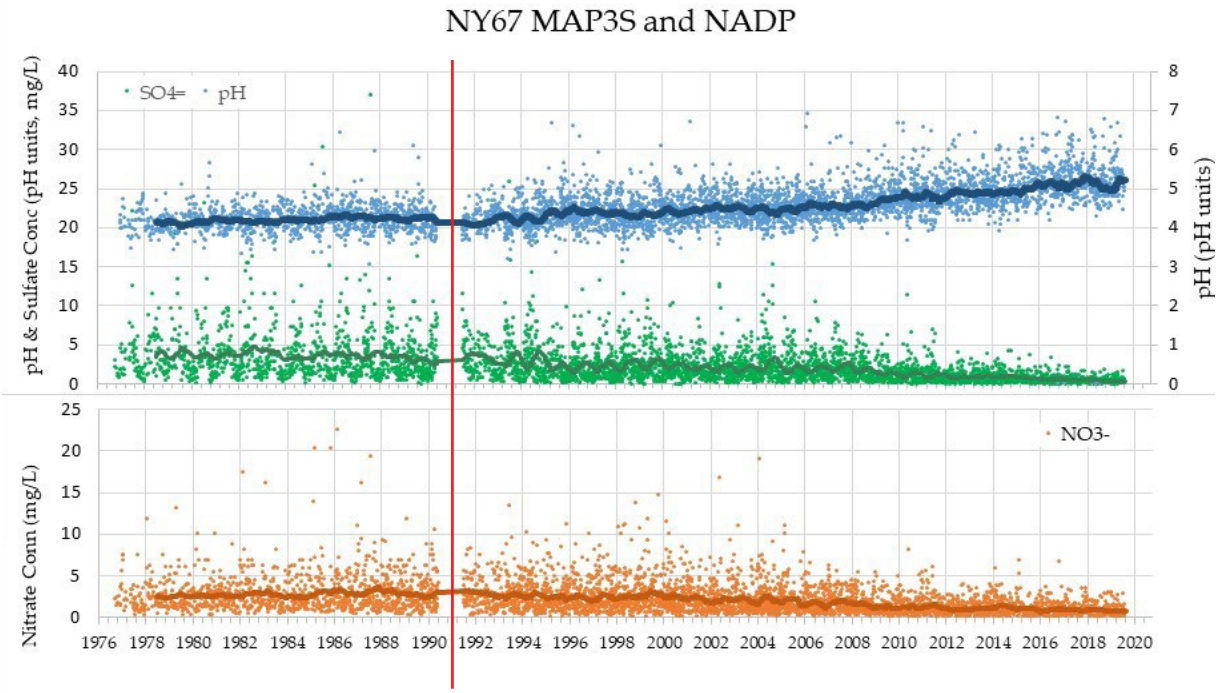
The figure below shows the combined record of NADP pH, sulfate and nitrate precipitation

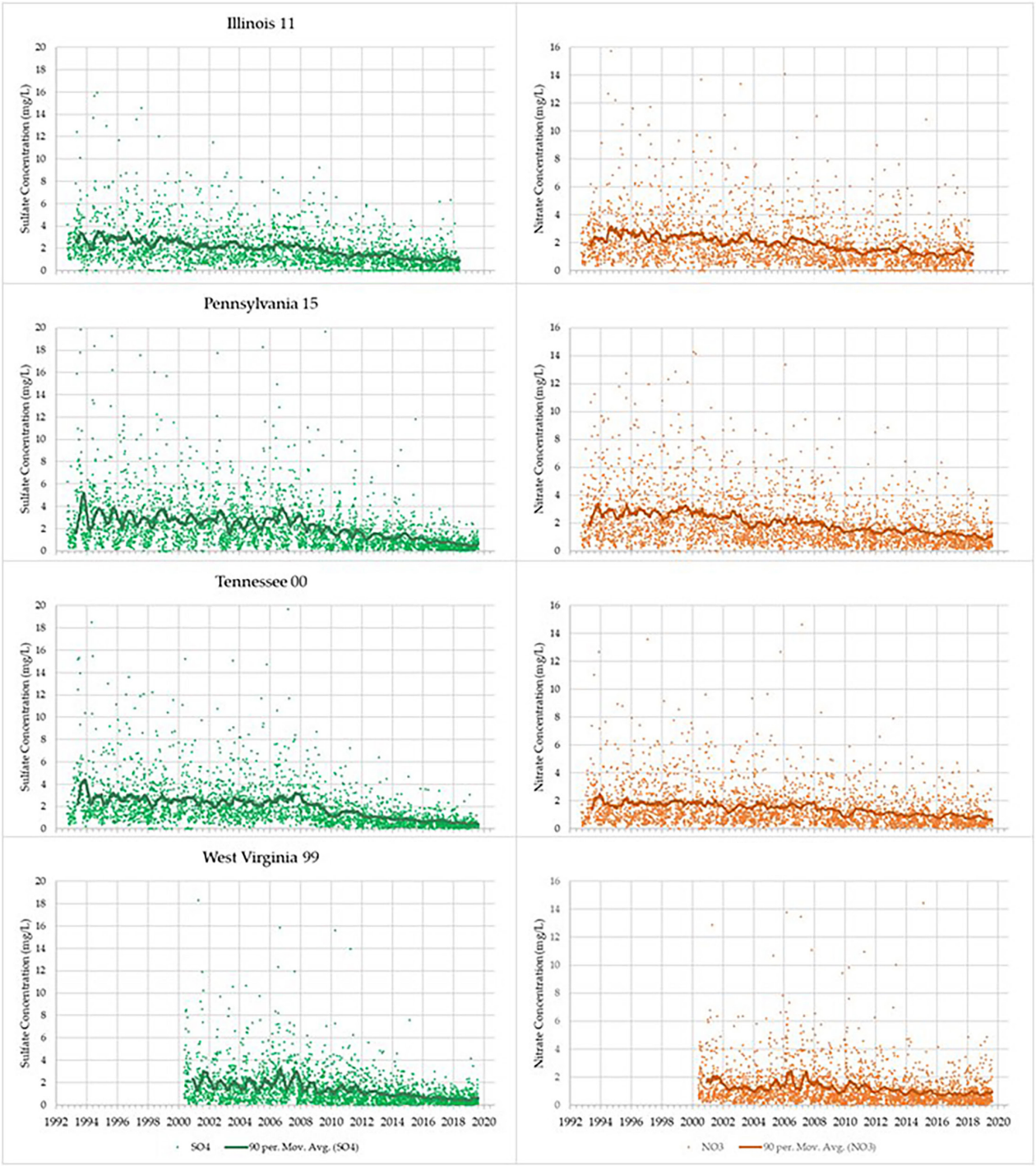


concentration as measured at NY67, and the pre-NADP chemical precipitation record as measured by the Multistate Atmospheric Power Production Pollution Study ("MAP3S"), the predecessor network and rough equivalent of the AIRMoN. These measurements began in October, 1976 at the same NY67 location. The red line shows the network separation point, when AIRMoN moved to NADP. The heavy lines are the 90-point moving average of the pH, sulfate, and nitrate measurements.

The figures on page 21 show the AIRMoN measurements of precipitation nitrate and sulfate for the other four final AIRMoN sites (IL11, PA15, TN00, WV99) from their NADP beginning. The heavy lines are the 90-point moving average of the sulfate and nitrate measurements.

Due to budget considerations, the AIRMoN was stopped in September 2019.





Time series of nitrate and sulfate concentrations (orange, green, in mg/L) at the last five AIRMoN sites, and the moving average concentration (heavy line). Note the axis differences between SO_4^{2-} and NO_3^-, and between NY67 (page to left) and other sites.

Mercury Deposition Network (MDN)

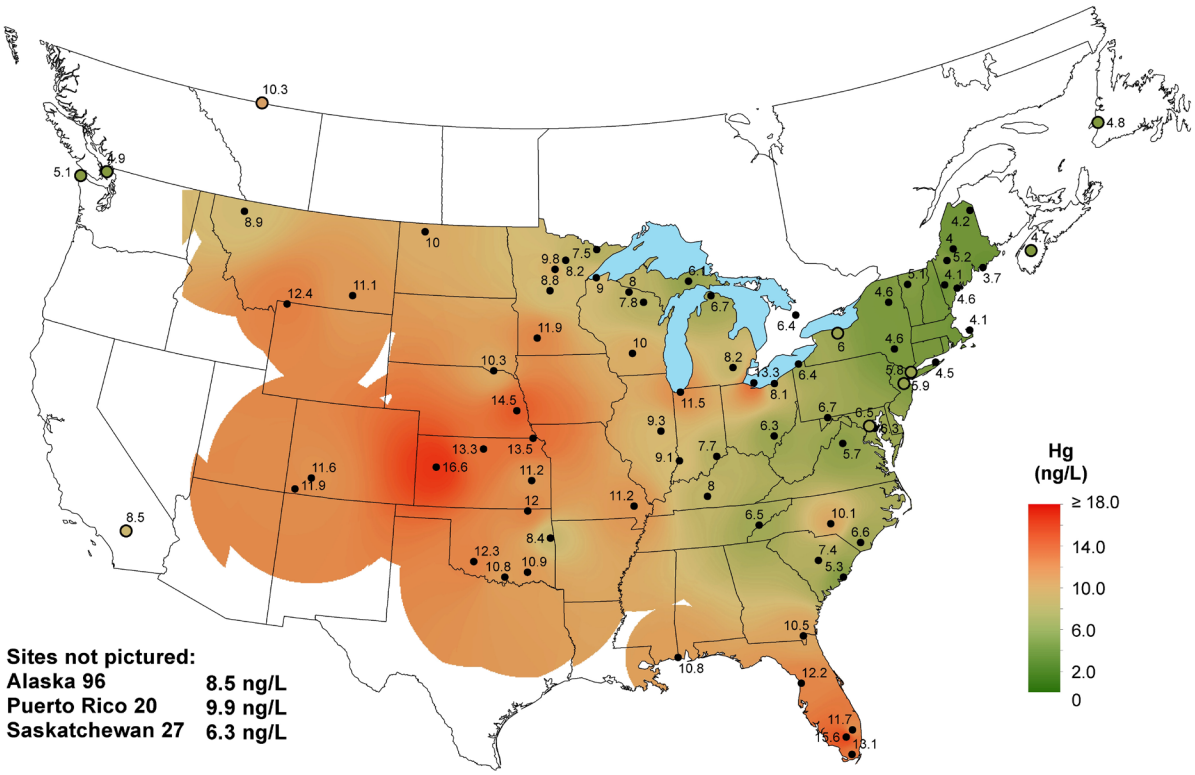
The MDN is the only network providing a long-term record for the concentration of mercury (Hg) in precipitation in North America. MDN sites follow standard procedures and use approved precipitation collectors and rain gages. The automated collector is similar to the NTN collector, but it is modified to preserve mercury. Site operators collect samples every Tuesday morning. Chemical analysis of the MDN samples was performed by the Mercury Analytical Laboratory (HAL) at Eurofins Frontier Global Sciences, Inc., Bothell, Washington, through June 2019; after this date the HAL was located at the WSLH in Madison, Wisconsin.

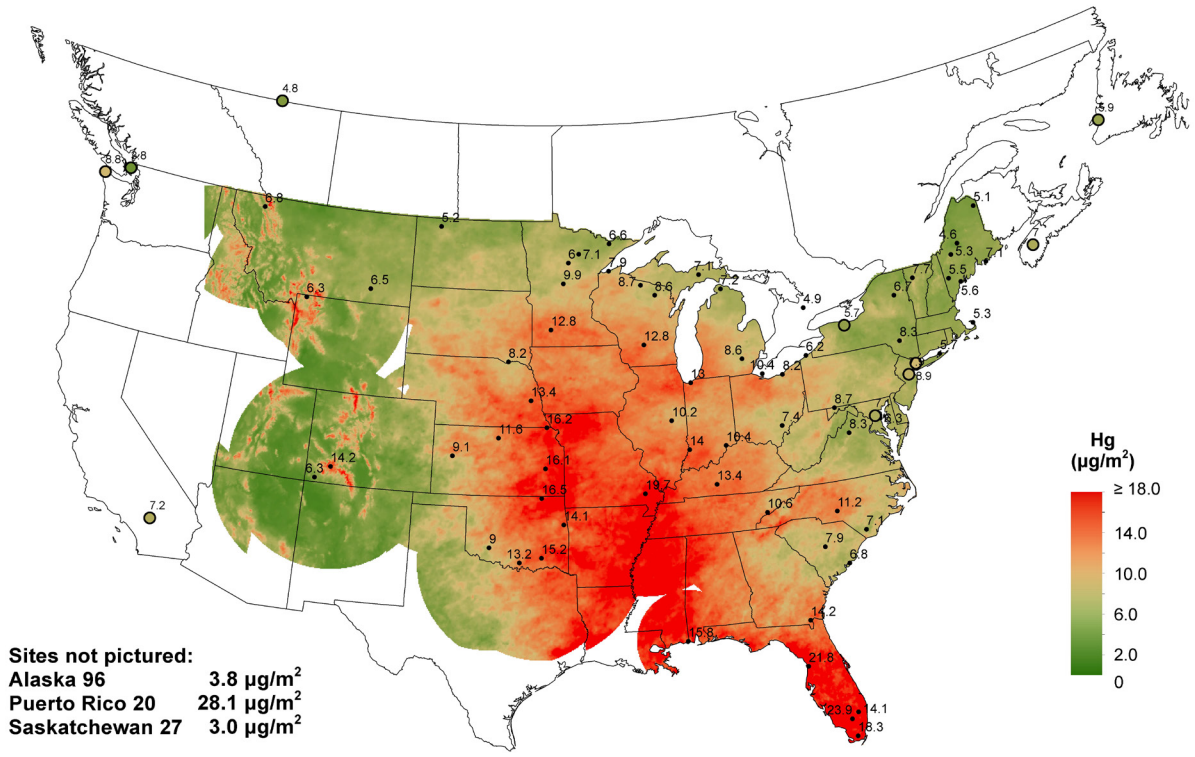
All MDN samples are analyzed for total mercury concentration. The HAL reviews field and laboratory data for accuracy and completeness, and identifies samples that were mishandled, compromised by equipment failure, or grossly contaminated. Data from the MDN is available on the NADP website (http://nadp.slh.wisc.edu/mdn/). Subsamples of MDN precipitation were analyzed for methyl mercury (MeHg) at 10 NADP sites. Details about sample collection and analysis are available on the NADP website.

MDN Maps and Graphs

The maps on page 23 show spatial variability in the precipitation-weighted mean concentration and wet deposition of total mercury across the United States.

Only sites meeting NADP completeness criteria are included. In 2019, 78 of 93 active sites met these criteria. Large variations in both mercury concentrations and wet-deposition are observed across the nation.





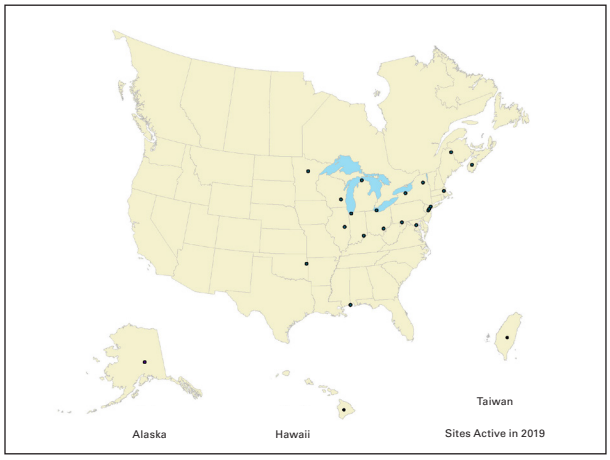
Total mercury concentration (top) and wet deposition (bottom), 2019.

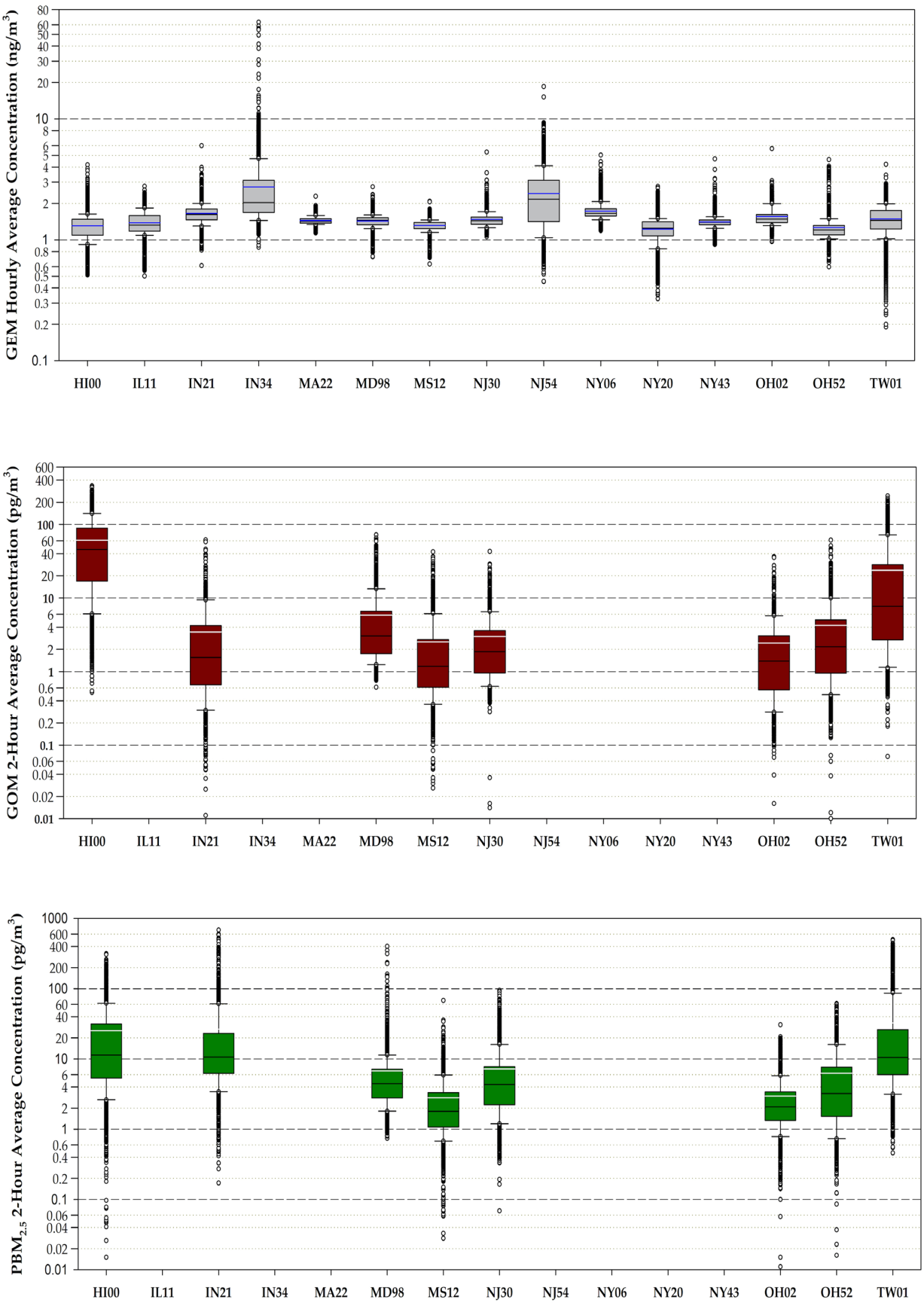
Atmospheric Mercury Network (AMNet)

AMNet sites measure ambient atmospheric mercury using automated, continuous measurement systems in order to understand the impact of atmospheric mercury on deposition. Quality-assured measurements are made using NADP standardized methods.

AMNet measurements are made continuously (five minute and two-hour averages). Data is qualified and averaged to one-hour (gaseous elemental mercury, GEM) and two-hour values (gaseous oxidized mercury, GOM, and particulate bound mercury, $PBM_{2.5}$). As of December 2019, there were 15 AMNet sites. Data from the AMNet are available on the NADP website (http://nadp.slh.wisc.edu/amnet/).

The figures on page 25 show the distribution of atmospheric mercury concentrations for each site. The top figure shows the distribution of GEM (shaded grey area), for all sites reporting data. GEM is reported in nanograms per cubic meter (ng/m^3). The middle figure shows the distribution of two-hour atmospheric concentrations of GOM (red shaded area) and the bottom figure shows $PBM_{2.5}$ (green shaded area) in picograms per cubic meter (pg/m^3); concentrations are plotted logarithmically, and with different scale ranges, to highlight the range of measured values for each site.





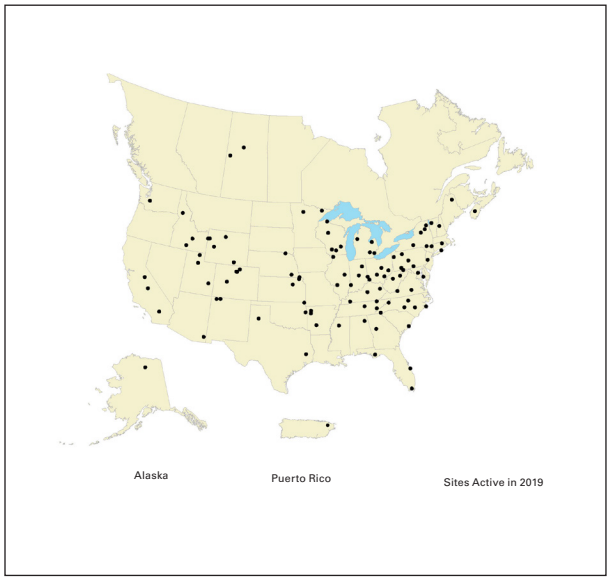
Hourly GEM concentration in ng/m³ for each AMNet site (top) and 2-hour GOM and $PBM_{2.5}$ concentrations in pg/m³ for each AMNet site (middle and bottom) in 2019. For each data set, the mean value is indicated as a blue (GEM) or white line (GOM and $PBM_{2.5}$) and the median is indicated as a black bar. Sites with no GOM and $PBM_{2.5}$ data shown did not monitor for speciated mercury.

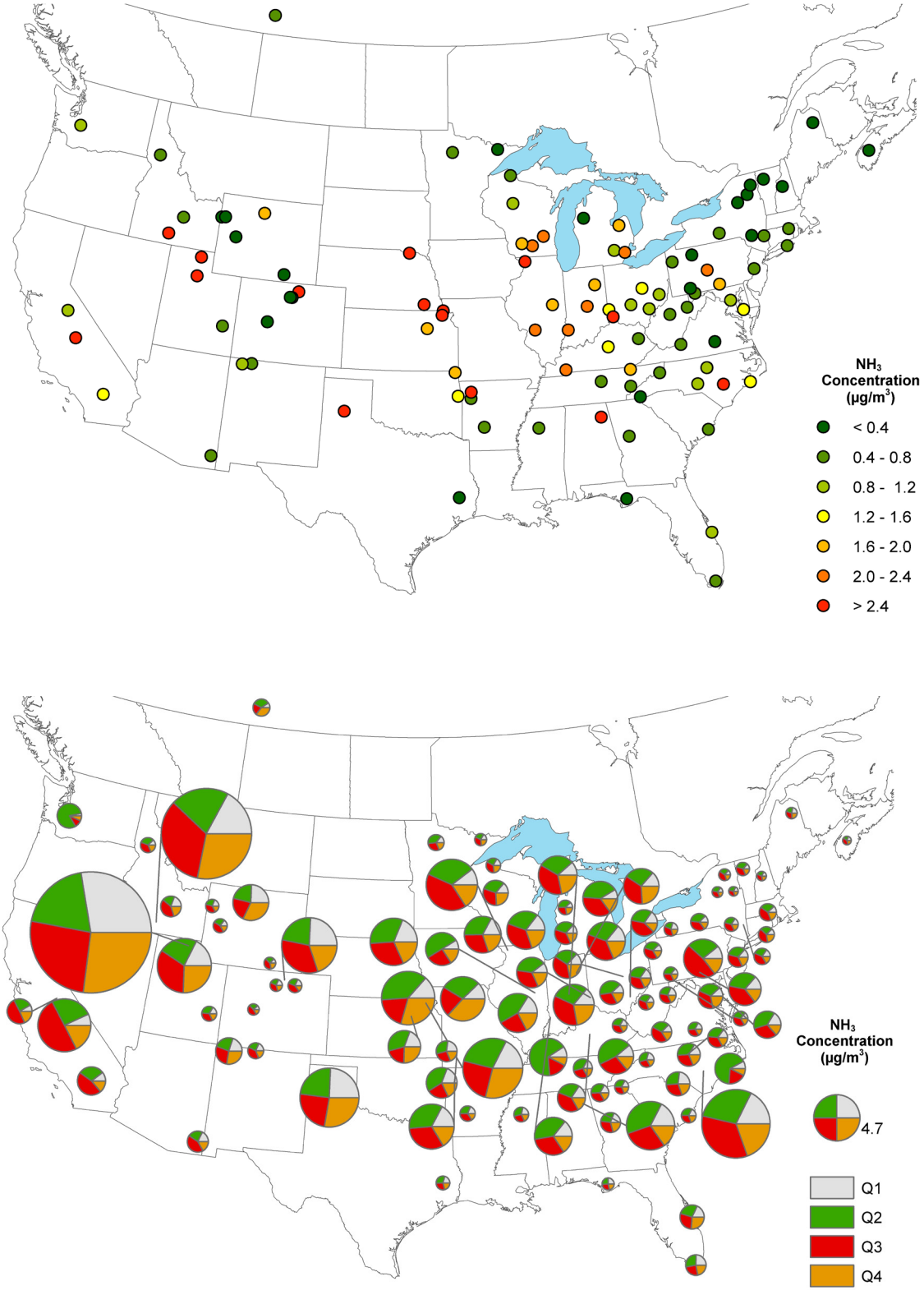
Ammonia Monitoring Network (AMoN)

The AMoN measures atmospheric concentrations of ammonia (NH_3) gas. The network uses a passive diffusion-type sampler that provides cost-effective, accurate and time-integrated measurements. Sampling occurs over a two-week period and all sites collect additional quality assurance samples on a rotating basis. This data is used to assess long-term NH_3 trends and changes in atmospheric chemistry, and to provide information for model development and verification.

As of December 2019, there were 107 AMoN sites. Data from the AMoN are available on the NADP website (http://nadp.slh.wisc.edu/amon/).

The figures on page 27 show the distribution and seasonality of gaseous ammonia concentrations for each site meeting completeness criteria. In 2019, 106 of 107 active sites met these criteria. In the top figure, circles represent annual average concentrations in micrograms per cubic meter ($\mu g/m^3$) 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 area 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), 2019. Size of the symbol in the bottom plot is relative to the annual concentration.

National Atmospheric Deposition Program

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All NADP data and information, including color contour maps in this publication, are available free of charge from the NADP website: http://nadp.slh.wisc.edu. Alternatively, contact: NADP Program Office, Wisconsin State Laboratory of Hygiene, 465 Henry Mall, Madison, WI 53706, Tel: (608) 263-9162, E-mail: nadp@slh.wisc.edu.

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