

# 2011 Annual Summary





**On the cover:** The gradient maps represent (top) relative nitrogen (N) plus sulfur (S) wet deposition in 2011 as a percentage of the average annual wet deposition from 2006 to 2010, and (bottom) total precipitation in 2011 as a percentage of the average annual precipitation from 1981 to 2010. Nitrogen species include ammonium and nitrate ions; sulfur includes sulfate ion. See map on the bottom of page 15 for the 2011 N + S annual precipitation-weighted mean, and the map on the bottom of page 7 for the 2011 total precipitation.

# 2011 Highlights

The National Atmospheric Deposition Program (NADP) provides fundamental measurements that support informed decisions on environmental issues related to precipitation and deposition chemistry, as well as atmospheric mercury and ammonia. NADP data are relevant to scientists, educators, policymakers, and the public. All data are available free of charge 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 measurements made by each network.

Network	Measurements	Period	No. of sites
NTN	13,033	weekly	257
MDN	6,259	weekly	110
AIRMoN	1,152	daily	7
AMNet	50,022	hourly	21
AMoN	1,137	two week	54

Summary of	i Network	Measurements, 2011
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The NADP website is the primary tool for disseminating data from the five NADP networks. In 2011, there were more than 26,000 registered users. Data were downloaded nearly 28,000 times by agencies, universities, and K-12 schools.

#### Highlights:

 The USGS and NADP collaborated on the measurement of radionuclides (Iodine-131, Cesium-134, and Cesium-137) in wet-deposition samples following the incident at the Fukushima Dai-ichi nuclear power plant in March. Results of the study were published in the journal *Environmental Science & Technology* and in a USGS report. Further information regarding the study is available on both the USGS and NADP websites. See http://bqs.usgs.gov/fukushima/ and http://nadp.isws.illinois.edu/fukushima/.

- The 2011 National Acid Precipitation Assessment Program (NAPAP) Report: An Integrated Assessment was presented to the U.S. Congress. This report featured data from the NADP networks.
- Bromide was approved as a new analyte for NTN and AIRMoN. Data will be available in 2012.
- NADP data and maps were used in more than 170 scientific publications.
- NADP was represented at the "World Acid Rain Conference" in Beijing, China. This conference is held every five years.
- NADP attended the "Mercury 2011" conference in Halifax, Nova Scotia, Canada. This international conference is held biannually and focuses on mercury as a global pollutant.
- 33 new sites were added to the AMoN.
- The NADP continued its support of the European directed Global Mercury Observation System (GMOS), and supported a new East Asia initiative for atmospheric mercury monitoring. NADP procedures for both field operations and data quality were adopted by GMOS. NADP serves on the Scientific Advisory Board of GMOS.
- Installation of electronic precipitation raingages at NADP wet-deposition sites continued (see map on page 4). At the end of 2011, 251 sites out

of 290 total sites were operating with the new raingage. This represents 80% of the wet-deposition network.

• NADP participated in the Prairie Research Institute's Naturally Illinois Expo at the University of Illinois. The Expo is attended by K-12 students throughout Illinois.



The distribution of operating digital precipitation gages at NADP wet deposition sites, as of December 31, 2011.

## 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 - Cooperative State Research, Education, and Extension Service (now 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. NAPAP continues under Title IX of the federal Clean Air Act Amendments of 1990.

In October 1992, the AIRMoN joined the NADP. AIRMoN sites collect samples daily when precipitation occurs. AIRMoN samples 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.

The map on the next page shows the location and the longevity of measurements at each of the NADP wet deposition networks (NTN, AIRMoN, and MDN). Longevity of continuous measurement is a goal of the NADP.

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.

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.



Site longevity of NADP sites, in years (NTN, AIRMoN, and MDN).

### **ABOUT THE MAPS**

This annual report and 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 are available on the NADP website. Black dots mark site locations that meet NADP completeness criteria (see the NADP website for details). Open circles designate urban sites, defined as having at least 400 people per square kilometer (km<sup>2</sup>) within a 15-km radius of the site.

Colors are assigned by using site values to compute grid-point values across the nation. Sites within 500 km of each grid point 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, July 2012). 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 figure below 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 0.0 centimeters (cm) ranging to over 200 cm/ year (dark red). The remaining 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.



Precipitation for 2011, 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 located away from urban areas and point sources of pollution. 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<sup>+</sup> as pH), specific conductance, and calcium (Ca2+), magnesium  $(Mg^{2+})$ , sodium  $(Na^{+})$ , potassium  $(K^{+})$ , sulfate  $(SO_{4}^{2-})$ , nitrate (NO<sub>2</sub>), 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 freely available from the NADP website (http://nadp.isws.illinois.edu/ntn/).

## **NTN MAPS**

The maps on pages 9 through 15 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 2011, 194 of the 257 active sites met NADP completeness criteria. Concentration and deposition maps are included for  $NO_3^-$ ,  $NH_4^+$ ,  $SO_4^{-2-}$ ,  $Ca^{2+}$ ,  $Cl^-$ , and pH. Maps of  $Mg^{2+}$ , Na<sup>+</sup>, and K<sup>+</sup> 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).





Nitrate ion concentration (top) and wet deposition (bottom), 2011.





Ammonium ion concentration (top) and wet deposition (bottom), 2011.





Sulfate ion concentration (top) and wet deposition (bottom), 2011.





Calcium ion concentration (top) and wet deposition (bottom), 2011.





Chloride ion concentration (top) and wet deposition (bottom), 2011.





Hydrogen ion concentration as pH (top) and wet deposition (bottom), 2011. Typically, a precipitation pH of less than 5.1 is considered acidic.





Inorganic nitrogen wet deposition from nitrate and ammonium (top) and nitrogen plus sulfur wet deposition from nitrate, ammonium, and sulfate (bottom), 2011.

## 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 wetonly deposition collector used at NTN sites. Each site also has a standard stick-type precipitation gage for reporting total precipitation. 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  $NH_4^+$  and  $PO_4^{-3-}$ . Chemical analyses and data screening procedures for AIRMON and NTN are similar.

Ternary (or triangle) plots on this page illustrate the relative equivalence ratios for  $SO_4^{2^-}$ ,  $NO_3^{-}$  and  $NH_4^{+}$ , expressed as a percentage of the sum of these species on an annual precipitation-weighted mean basis. Lines representing an equivalence ratio of 50% are darkened. Data for 1996 and 2011 are shown together to illustrate the temporal change in the relative contribution of each of these species, and their dominance at each AIRMoN site.

The ternary plots on page 17 illustrate the relative equivalence ratios for  $SO_4^{2-}$ ,  $NO_3^{-}$  and  $NH_4^{+}$ for all valid samples at each of the AIRMoN sites. These plots compare data for meteorological winter (e.g., December, January, and February) and summer (June, July, and August). Seasonally-distinct patterns of the species are apparent at each site.





Ternary plots comparing the annual relative equivalence ratios for  $SO_4^{2}$ ,  $NO_3^{-}$  and  $NH_4^{+}$  for 1996 and 2011 for each AIRMoN site.





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Ternary plots comparing winter and summer 2011 relative equivalence ratios for  $SO_4^{2-}$ ,  $NO_3^{-}$  and  $NH_4^+$  for individual samples collected at each of the AIRMoN 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 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 2011, the Devil's Lake site in south-central Wisconsin (WI31), the Underhill site in northern Vermont (VT99), 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 Frontier Global Sciences, Inc., Bothell, Washington.

All MDN samples are analyzed for total mercury concentration. In 2011, 19 MDN sites opted to measure methyl mercury 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 are made available on the NADP website (http://nadp.isws.illinois.edu/mdn).



#### **MDN MAPS**

The maps on page 19 show spatial variability in the precipitation-weighted mean concentration and wet deposition of total mercury. Only sites meeting NADP completeness criteria are included. In 2011, 99 of 110 active sites met these criteria.



Total mercury concentration (top) and wet deposition (bottom), 2011.

## Atmospheric Mercury Network (AMNet)

The AMNet was established in 2009. AMNet sites measure atmospheric mercury fractions that contribute to mercury deposition. Sites measure concentrations of atmospheric mercury species (gaseous oxidized, particulate-bound, and elemental) using automated, continuous measuring systems. Measurements are made using standardized methods, and are quality assured.

AMNet data are available on the NADP website at http://nadp.isws.illinois.edu/amn/. 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<sub>2,c</sub>).

The figures on page 21 show the average atmospheric mercury concentrations for each site in 2011. Figure a shows the distribution of GEM in nanograms per cubic meter (ng/m<sup>3</sup>). Figure b shows the distribution of two-hourly atmospheric concentrations of GOM, and PBM<sub>2.5</sub> in picograms per cubic meter (pg/m<sup>3</sup>). Included as part of figure b is the number of valid GOM and PBM<sub>2.5</sub> observations that exceed 40 pg/m<sup>3</sup>, the upper limit shown with the box plots.





a) Hourly GEM concentrations in ng/m<sup>3</sup> for each AMNet site and b) 2-hour GOM and PBM<sub>2.5</sub> concentrations in pg/m<sup>3</sup> for each AMNet site in 2011. The bubble chart indicates the number of valid observations for both GOM and PBM<sub>2.5</sub> above 40 pg/m<sup>3</sup>, the upper limit shown with the box plots.

# Ammonia Monitoring Network (AMoN)

The AMoN was established in 2010, and 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 will be used to assess long-term  $NH_3$  trends, provide necessary information for model development and verification, and to assess changes in atmospheric chemistry.

At the end of 2011, there were 53 AMoN sites. Data are available on the NADP website at http://nadp.isws.illinois.edu/amon/.

The figures on page 23 show the distribution and seasonality of gaseous ammonia concentrations for each site meeting completeness criteria. In 2011, 38 of 54 active sites met these criteria. Circles in figure a represent annual average concentrations in micrograms per cubic meter ( $\mu$ g/m<sup>3</sup>) at each site. In figure b, 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. Variability is substantial across the sites and the quarters.







a) Average 2011 ammonia concentrations as measured by AMoN (in μg/m<sup>3</sup>), and b) quarterly relative percentage (Q1 = January, February, March, etc.) for each AMoN site. Size of symbol is relative to the annual concentration.
\* indicates the use of substitute data as the site operated for only a portion of the year



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