

2016 Annual Summary

21 Years of MDN





On the cover: 2016 represents the 21st year of Mercury Deposition Network operation. The cover shows the annual MDN mercury deposition map for each year of network operation (no map was produced for 1996). Rapid growth occurred in the network from 2000 to 2011, allowing the map to expand from values to the first partial contour map in 2003, to a map covering the majority of the US and southern Canada in 2009.

When referencing maps or information in this report, please use the citation: National Atmospheric Deposition Program, 2017. National Atmospheric Deposition Program 2016 Annual Summary. NADP Data Report 2017-01. Illinois State Water Survey, University of Illinois at Urbana-Champaign, IL.

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2016 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 on 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 from each network in 2016.

Network	Measurements	Period	No. of sites
NTN	13,758	weekly	274
MDN	5,617	weekly	115
AIRMoN	856	daily	6
AMNet	65,240	hourly/	22
		2-hourly	
AMoN	2,590	two week	104

Summary of Network Measurements, 2016

Highlights:

- NADP data were used in:
 - 248 journal articles;
 - six dissertations;
 - five master's theses; and
 - twelve agency reports.

The full publications list is available at: http:// nadp.isws.illinois.edu/lib/bibliography.aspx.

- The Mercury Litterfall Initiative with U.S. Geological Survey (USGS) scientists completed its fifth year of operation. Twenty-six sites collected litterfall (e.g., leaves, twigs, etc.) to measure mercury.
- NADP continued its collaboration with USGS scientists to measure atmospheric isotopes of mercury at ~20 NADP sites.
- The Total Deposition Science Subcommittee (TDEP) continued its work with U.S.
 Environmental Protection Agency (USEPA) scientists to estimate dry deposition of nitrogen, sulfur, and other analytes.

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- TDEP published a Map Summary for 2015.
- TDEP continued to collaborate with Environment Canada to estimate mercury dry deposition using AMNet data.
- TDEP was renewed as a Science Subcommittee for an
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Total Deposition 2015

Subcommittee for an additional four years.

- NADP collaborated with Utah State University to monitor dry deposition as part of a pilot study.
- The OTT Pluvio²-L raingage was accepted for network use.
- The Aeroallergen Monitoring Science Committee was established.
- NADP continued to work with the Council of State and Territorial Epidemiologists (CSTE) on a possible monitoring network for airborne allergen tracking. Airborne allergens are important as they contribute to allergic rhinitis (i.e., hay fever) and asthma. Other participants in this

work include National Oceanic and Atmospheric Administration (NOAA), USEPA, and the Centers for Disease Control and Prevention.

 The Ecological Response and Outreach Subcommittee (EROS) published the Nitrogen From the Atmosphere booklet. This educational resource focuses on nitrogen within the atmospheric environment and the nitrogen cycle.



- NADP was part of the planning committee for the 13th International Conference on Mercury as a Global Pollutant (Mercury 2017) held in Providence, RI in July 2017.
- NADP began work with the USEPA Office of Research & Development to coordinate atmospheric deposition monitoring with water quality monitoring networks around the U.S.



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 at 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 the National Research Support Project No. 3 (NRSP-3), which it remains to this day. The latest renewal was in Federal Year 2015. 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 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. Because of 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 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.

In October 2009, AMNet joined the NADP as its fourth network. AMNet measures the concentration of atmospheric mercury using on-site instrumentation.

In October 2010, AMoN joined the NADP. Atmospheric ammonia concentrations are measured every two weeks using passive samplers.

As of December 2016, 31 NTN sites have operated continuously since January 1980. The map on the facing page shows active sites in each of the five networks and the length of time that each site has been operating.



Site longevity of active NADP sites in each network.

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.

All map products are restricted to sites that meet completeness criteria (see the NADP website for details). Black dots mark site locations that met NADP completeness criteria in 2016. Open circles designate urban sites, defined as having at least 400 people per square kilometer (km²) 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, Sept. 2017). 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 (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 this format from the NADP website.



Total annual precipitation for 2016, 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 participate. 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 (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), sulfate (SO₄²⁻), nitrate (NO3⁻), chloride (Cl⁻), bromide (Br⁻), and ammonium (NH₄⁺) ions. The CAL analyzes inorganic orthophosphate ions (PO₄³⁻) for quality assurance purposes. It is used 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 regional and national scales. In 2016, 226 of the 274 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.

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).



Inorganic nitrogen wet deposition from nitrate and ammonium (top) and nitrogen plus sulfur wet deposition from nitrate, ammonium, and sulfate (bottom), 2016.



Nitrate ion concentration (top) and wet deposition (bottom), 2016.



Ammonium ion concentration (top) and wet deposition (bottom), 2016.









Hydrogen ion concentration as pH (top) and wet deposition (bottom), 2016. Typically, a precipitation pH of less than 5.1 is considered acidic.













Chloride ion concentration (top) and wet deposition (bottom), 2016.







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. 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.

AIRMON sites are equipped with the same wet-only deposition collector used at NTN sites. All AIRMON sites operate digital raingages 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, such as with H⁺, NH₄⁺, and PO₄³⁻. 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 back trajectory plots on page 21 (using NOAA's HYSPLIT model {February 2017 revision 854}) are back trajectories for the six AIRMoN sites (DE02, IL11, NY67, PA15, TN00, and WV99), suggesting the general pathways for air reaching the individual sites that resulted in each site's five lowest pH values during 2016. Back trajectory analysis is commonly used to determine the origin of air reaching the sampling sites. Measurements of observed surface and upper air flow are used to model the movement of an air parcel from air pollutant sources to a



point of interest. In this case, the point of interest is the AIRMoN site, where these pollutants are measured in precipitation samples. By establishing this "source-receptor relationship," back trajectories establish the possible source location of pollutants found in NADP samples.

Samples were limited to valid samples with at least 5 mm of precipitation depth. Sample pH values ranged from 4.43 to 4.78 pH units. The back trajectories were 72-hour back trajectories originating at 1000 meters above each station, and beginning approximately twelve hours before the sample was collected and precipitation ended. The back trajectories were based upon the Global Data Assimilation System (GDAS) meteorological data for calculations.



72-hour back trajectory pathways originating at 1000 meters above each AIRMoN station 12 hours before the sample was removed. Trajectories represent air flow resulting in the lowest 5 pH values measured in all valid samples with at least 5 mm precipitation depth. Sample pH values ranged from 4.43 to 4.78 pH units.

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 2016, 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. 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). Subsamples of MDN precipitation were analyzed for methyl mercury (MeHg) at 11 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. Only sites meeting NADP completeness criteria are included. In 2016, 96 of 115 active sites met these criteria. Spatial variability of total mercury can be seen on regional and national scales. The graph below shows the distribution of methyl mercury concentrations (shaded boxes) as a percentage of total mercury. The precipitation-weighted mean of the methyl mercury concentrations in ng/L is represented by the red dot.







Total mercury concentration (top) and wet deposition (bottom), 2016.

Atmospheric Mercury Network (AMNet)

Atmospheric mercury contributes to mercury deposition. AMNet sites measure this mercury using automated, continuous measurement systems. Quality-assured measurements are made using NADP standardized methods.

AMNet measurements are made continuously (fiveminute 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}). As of December 2016, there were 22 AMNet sites. 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 meeting completeness criteria in 2016. The top figure shows the distribution of GEM for all sites meeting criteria, in nanograms per cubic meter (ng/m³). In the bottom figure, circles represent the quarterly relative percentage (i.e., Q1 = January, February, March, etc.) for each AMNet site in 2016. GOM concentrations are on the left, and PBM_{2.5} concentrations are on the right. Both are represented in picograms per cubic meter (pg/m³). The size of the wedge is the relative percentage for the quarter, and the area of the symbol is proportional to the annual average concentration for the site. Note that GOM for HI01 is scaled differently.





Hourly GEM concentration ranges in ng/m³ for each AMNet site (top), and quarterly relative percentage (Q1 = January, February, March, etc.) for each AMNet site (bottom), with GOM concentrations on the left, and PBM_{2.5} concentrations on the right, for 2016. Size of the symbol in each plot is relative to the annual concentration in pg/m³.

Ammonia Monitoring Network (AMoN)

The AMoN measures atmospheric concentrations of ammonia (NH_3) gas. The network uses a passive diffusion-type sampler. 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 both long-term NH_3 trends and changes in atmospheric chemistry and provide information for model development and verification.

As of December 2016, there were 104 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 2016, 96 of 104 active sites met these criteria. In the top figure, circles represent annual average concentrations in micrograms per cubic meter (μ g/m³) 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), 2016. Size of the symbol in the bottom plot is relative to the annual concentration.



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http://nadp.isws.illinois.edu

All NADP data and information, including color contour maps in this publication, are available free of charge from the NADP website: http://nadp.isws.illinois.edu. Alternatively, contact: NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820, Tel: (217) 333-7871, Fax: (217) 333-0249, E-mail: nadp@isws.illinois.edu.

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