附錄 3、2015 Annual Summary

National Atmospheric Deposition Program

2015 Annual Summary



Percentage of total nitrogen deposition as dry, 2013-2015



Percentage of total nitrogen deposition as reduced nitrogen, 2015



On the cover: NADP's Total Deposition (TDEP) Science Committee, produced a map summary for 2015. The cover shows the 3-year average annual percentage of total nitrogen deposition as dry for 2013 to 2015 (top), and the 2015 annual percentage of total nitrogen deposition as reduced nitrogen (bottom). The full TDEP report is available at http://nadp. isws.illinois.edu/committees/tdep.

When referencing maps or information in this report, please use the citation: National Atmospheric Deposition Program, 2016. National Atmospheric Deposition Program 2015 Annual Summary. NADP Data Report 2016-02. Illinois State Water Survey, University of Illinois at Urbana-Champaign, IL.

Contents

2015 Highlights	
NADP Background	6
About the Maps	
National Trends Network (NTN)	
Atmospheric Integrated Research Monitoring Network (AIRMoN)	20
Mercury Deposition Network (MDN)	22
Atmospheric Mercury Network (AMNet)	24
Ammonia Monitoring Network (AMoN)	26

2015 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 2015.

Summary of Network Measurements, 2015

Network	Measurements	Period	No. of sites
NTN	13,287	weekly	265
MDN	5,978	weekly	112
AIRMoN	799	daily	6
AMNet	60,954	hourly/	25
		2-hourly	
AMoN	2,400	two week	98

Highlights:

- NADP has been in operation for 38 years, and 31 individual NTN sites have operated continuously since the network was initiated.
- NADP data were used in:
 - 226 journal articles;
 - seven dissertations;
 - seven master's theses; and
 - three books: American Environmental Policy: The Failures of Compliance,

Abatement and Mitigation by Press & Griswold; Spatio-temporal Methods in Environmental Epidemiology by Shaddick and Zidek; and Air Pollutant Deposition and its Effects on Natural Resources in New York State by Sullivan.

For the full publications listing, see http://nadp. isws.illinois.edu/lib/bibliography.aspx.

- Thirty new AMON sites started (44% increase).
- The Spring Subcommittee Meeting was held in Pacific Grove, CA in April.
- The U.S. Geological Survey-led Mercury Litterfall Initiative completed its fourth year of operation. Eighteen sites collected litterfall (e.g., leaves, twigs, etc.) to measure mercury (http:// nadp.isws.illinois.edu/newissues/litterfall).
- The Critical Loads Atmospheric Deposition (CLAD) was renewed as a scientific subcommittee.
- The CLAD subcommittee published a map summary of critical load determinations for the continental United States. The report is



available from the Program Office.

- The NADP continued to convert its precipitation gages to an all-digital network, and 23 sites remain with Belfort mechanical precipitation gages.
- One NTN station began operation at urban locations in Massachusetts in support of the Subcommittee on Urban Atmospheric Monitoring.
- The NADP collaborated with U.S. Geological Survey scientists to measure atmospheric isotopes of mercury at ~20 NADP sites.

- The Total Deposition Science Subcommittee (TDEP) worked with U.S. Environmental Protection Agency (USEPA) scientists to estimate dry deposition of nitrogen and sulfur. They worked with Environment Canada to estimate dry deposition of mercury at each active AMNET site. (http://nadp.isws.illinois.edu/committees/ tdep/tdepmaps/).
- The NADP continued to collaborate with the USEPA to determine organic nitrogen concentrations in wet deposition samples (Coweeta, NC; NC25).
- NADP continued its international efforts:
 - NADP continues its partnership with Taiwan to establish the 12 country Asia Pacific Mercury Monitoring Network (APMMN). The APMMN systematically monitors mercury wet deposition and atmospheric concentrations at stations across East, Southeast, and South Asia. During the year, continuous monitoring was established in Vietnam and in Thailand (http://rsm2.atm. ncu.edu.tw/apmmn/).

- NADP collaborated with National Autonomous University of Mexico scientists to determine the feasability of cooperative sites along the Gulf Coast of Mexico with NADP operations.
- USGS and NADP began working with Cuban scientists to improve their analytical methods for NADP analytes. Currently, blind samples are provided for testing, with a goal to operate a small wet deposition network in Cuba.
- NADP hosted the 2015 international meeting of the Deposition of Biogeochemically Important Trace Species (DEBITS) group at the Fall 2015 NADP Meeting. This group is focused on deposition in Africa.
- NADP is part of the planning committee for the 13th International Conference on Mercury as a Global Pollutant (Mercury 2017) to be held in Providence, Rhode Island in July, 2017.

The NADP planned and hosted Acid Rain 2015, the 9th International Conference on Acid Deposition. The conference was held in Rochester, NY in October with 350 global scientists and policy professionals from ~30 countries in attendance, and is held once every five years. There were 7 keynote addresses, 106 oral presentations, and 200 posters during five days. Videos of the keynote speakers and all presentations are available on the meeting website (http://acidrain2015.org/).

Continent	Attendees
Europe	62
Asia	62
South America	6
Africa	6
United States	194
Mexico and Canada	22
Total regular attendance	352





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. 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 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 2015, there are 31 NTN sites that have been in continuous operation 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 2015. 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 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. 2016). 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), extending above 200 cm (dark red). The concentration and deposition maps follow this same format, with specified units on each map. All maps back to 1985 follow the schema and are available in this format from the NADP website.



Total annual precipitation for 2015, 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 (NO₂⁻), chloride (Cl⁻), bromide (Br⁻), and ammonium (NH,+) ions. The CAL analyzes orthophosphate ions (PO, 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 regional and national scales. In 2015, 221 of the 265 active sites met NADP completeness criteria. Concentration and deposition maps are included for SO₄²⁻, NO₃⁻, NH₄⁺, pH, Ca²⁺, Mg²⁺, 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 (N, i.e., $NO_3^- + NH_4^+$) and nitrogen + sulfur (N + S) are also included. N + S (i.e., $NO_3^- + NH_4^+ + SO_4^{-2}$) 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), 2015.





Nitrate ion concentration (top) and wet deposition (bottom), 2015.



































Chloride ion concentration (top) and wet deposition (bottom), 2015.







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^+ , 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 back trajectory plots on page 21 (using NOAA's HYSPLIT model {February 2016 revision 802}) are clusters of back trajectories for the six AIRMoN sites (DE02, IL11, NY67, PA15, TN00, and WV99),



suggesting the general pathways of air reaching the individual sites that resulted in the highest 25% of S + N deposition (equivalents/hectare) during 2015. The cluster routine combines trajectories to five clusters.

The clustered trajectories were 48-hour back trajectories originating at 1000 meters above each station, and beginning at the midpoint of the precipitation event. The back trajectories were based upon the Global Data Assimilation System (GDAS) meteorological data for calculations. Clusters were produced using the 48th hour trajectory position and mean vector from this point. Total number of clusters used and unclustered are included for each site.



Clustered 48-hour back trajectory pathways originating at 1000 meters above each AIRMoN station at the time of precipitation. Trajectories represent air flow resulting in S + N depositions above the 75th percentile during 2015. The 5 pathways show a relative number and the percent of individual trajectories included in the trajectory cluster ("average" pathway). Heavy back trajectory lines represent the clustered trajectories that result in the two highest average depositions.

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 2015, 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 13 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 2015, 100 of 112 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.



Percent Total Mercury as Methyl Mercury by Site, 2015



Total mercury concentration (top) and wet deposition (bottom), 2015.

Atmospheric Mercury Network (AMNet)

AMNet sites measure atmospheric mercury that contributes to mercury deposition 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 2015, there were 25 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 2015. The top figure shows the distribution of GEM (grey shaded area) in nanograms per cubic meter (ng/m³). 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/m³).





Hourly GEM concentrations in ng/m³ for each AMNet site (top) and 2-hour GOM and PBM_{2.5} concentrations in pg/m³ for each AMNet site (bottom), 2015. The bubble charts indicate the number of valid observations for GEM values above 8 ng/m³, and GOM and PBM_{2.5} above 40 pg/m³, the upper limit shown with the box plots. Horizontal lines in each graph represent the respective 2015 median values.

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 2015, there were 98 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 2015, 91 of 98 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), 2015. Size of the symbol in the bottom plot is relative to the annual concentration.

National Atmospheric Deposition Program

The NADP is the National Research Support Project-3: A Long-Term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition. More than 250 sponsors support the NADP, including private companies and other non-governmental organizations, universities, local and state government agencies, State Agricultural Experiment Stations, national laboratories, Native American organizations, Canadian government agencies, the National Oceanic and Atmospheric Administration, the Environmental Protection Agency, the U.S. Geological Survey, the National Park Service, the U.S. Fish & Wildlife Service, the Bureau of Land Management, the U.S. Department of Agriculture - Forest Service, and the U.S. Department of Agriculture - National Institute of Food and Agriculture, under agreement no. 2012-39138-20273. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the program sponsors or the University of Illinois.

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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.

The NADP Program Office is located at the Illinois State Water Survey, a division of the Prairie Research Institute at the University of Illinois at Urbana-Champaign.

附錄4、Total Deposition 2015

National Atmospheric Deposition Program

Total Deposition 2015





On the cover: Comparison of the 3-year averages of total nitrogen deposition for the periods 2000-2002 and 2013-2015. Significant reductions in nitrogen deposition have occurred over the past decade due to implementation of emission control programs for both the power and transportation sectors.

Suggested Acknowledgement and Citation:

Data users that present and/or publish research based on total deposition values derived from this multi-organization effort should acknowledge the Total Deposition (TDEP) Science Committee and the National Atmospheric Deposition Program (NADP). A suggested acknowledgement is:

"We acknowledge the Total Deposition (TDEP) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDEP data and maps available."

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Contents

About the total deposition maps
Composition of nitrogen deposition in the US for 2013-20157
Historical average total nitrogen deposition at CASTNET sites
Total annual precipitation in 2015
Percent deviation of 2015 precipitation values compared to the average of 2000-2015
Total nitrogen deposition in 20159
Percent deviation of 2015 nitrogen deposition values compared to the average of 2000-20159
Annual dry nitrogen deposition in 201510
Percent of total nitrogen deposition as dry deposition in 2015 10
Annual wet nitrogen deposition in 201511
Percent of total nitrogen deposition as wet deposition in 201511
Annual oxidized nitrogen deposition in 201512
Percentage of total nitrogen deposition as oxidized nitrogen in 201512
Annual reduced nitrogen deposition in 201513
Percentage of total nitrogen deposition as reduced nitrogen in 2015 13
Annual deposition of unmonitored nitrogen compounds in 201514
Percentage of total nitrogen deposition as unmonitored nitrogen compounds14
Annual gross ammonia deposition in 201515
Annual net ammonia deposition in 201515
Annual sulfur deposition in 201516
Percentage of total sulfur deposition as dry deposition in 201516
Annual nitrogen + sulfur deposition in 201517
Percentage of total equivalent deposition as nitrogen deposition in 201517
Annual base cation deposition in 201518
Percentage of total base cation deposition as dry deposition in 2015
Annual chloride deposition in 201519
Percentage of total chloride deposition as dry deposition in 2015

3

About the Total Deposition Maps

In October 2011, the National Atmospheric Deposition Program (NADP) Executive Committee formed the Total Deposition (TDEP) Science Committee. The mission of TDEP is to improve estimates of atmospheric deposition by advancing the science of measuring and modeling atmospheric wet, dry, and total deposition of species such as sulfur, nitrogen, and mercury by providing a forum for the exchange of information on current and emerging issues within a broad multi-organization context including atmospheric scientists, ecosystem scientists, resource managers, and policy makers.

For more information regarding TDEP, please visit the NADP-TDEP web page at

http://nadp.isws.illinois.edu/committees/tdep.

What is Total Deposition?

Total deposition estimates are derived from summing wet and dry deposition. Members of this multiorganization committee worked to develop a "hybrid approach" to mapping total deposition that combines measured and modeled values. One of the initial goals of TDEP was to provide estimates of total sulfur and nitrogen deposition across the U.S. for use in critical loads and other assessments, where loading results in the acidification and eutrophication of ecosystems. Measured values are given more weight at the monitoring locations, and modeled data are used to fill in spatial gaps and provide information on chemical species that are not measured by routine monitoring networks. One of the main advantages of this approach is that it will provide continuous spatial and temporal coverage of total deposition estimates in the U.S. (beginning in 2000), which until this point, have been unavailable.

Methodology

The original method was published in:

Schwede, D.B. and G.G. Lear, 2014. A novel hybrid approach for estimating total deposition in the United States, Atmospheric Environment, 92, 207-220. DOI:dx.doi.org/10.1016/j.atmosenv.2014.04.008.

Updates to the methodology have occurred since the publication of the manuscript and will continue to occur as the science evolves and new information is available. A Revision History and other important information are available at

ftp://ftp.epa.gov/castnet/tdep/Total Deposition Documentation current.pdf .

In brief, the method for making TDEP maps is as follows:

 Precipitation amounts (p. 8) are obtained by combining measured values of precipitation from NADP networks with precipitation estimates from the Parameter-elevation Regression on Independent Slopes Model (PRISM).

- Wet deposition values are the product of measured values of precipitation chemistry from NADP networks and the precipitation amount calculated above.
- Dry deposition values are obtained by combining measured air concentration data, principally from rural locations with Clean Air Status and Trends Network (CASTNET) sites (<u>https://www.epa.gov/</u> <u>castnet</u>), with modeled concentrations and deposition velocities from the Community Multiscale Air Quality (CMAQ) model. In general, modeled air concentrations are adjusted for bias where corresponding measurements are available. Modeled ammonia concentrations have not been adjusted for bias because the relationship between measured and modeled concentrations is not linear.
- Deposition values for unmeasured species (i.e., dry deposition of gaseous PAN, N₂O₅, NO, NO₂,
 HONO, and organic nitrates) are estimated from the CMAQ model (p. 14).
- Dry deposition values are combined with the wet deposition values to produce the final estimates of total deposition.
- Ammonia deposition is estimated using a bidirectional air-surface exchange model. For terrestrial surfaces, flux pathways include the soil, leaf stomata, and leaf cuticle. Gross ammonia deposition (p. 15) refers to the total amount of ammonia deposited to soil and vegetation within a model grid cell and is the amount used in calculating total nitrogen deposition.
- Net ammonia deposition is calculated by subtracting non-point source emissions, such as those from soils and leaf surfaces, from the gross deposition derived from the bidirectional model. Although point source emissions such as those from confined animal feeding operations and industrial sources are used in calculating air concentrations of ammonia and other air pollutants, they are not included in the net deposition amounts. Positive net deposition values indicate deposition to the landscape, whereas negative values indicate emission.
- S + N equivalent deposition (p. 17) is one measure of the combined acidifying effect of nitrogen and sulfur deposition on ecosystems and is a common metric in critical load determinations. This measure is calculated from the molar equivalents of sulfur and nitrogen deposition and assumes 1 equivalent/mole for nitrogen compounds and 2 equivalents/mole for sulfur compounds. The percentage of total S + N equivalent deposition as nitrogen describes the proportion of potential acidity that is due to nitrogen deposition.

Availability of Maps and Data

The hybrid maps are available for years 2000-2015 and for select 3-year averages for all components of total sulfur and nitrogen deposition. The most recent version is available as ESRI Grid[™] files and maps, which can be downloaded from the NADP website at http://nadp.isws.illinois.edu/tdepmaps. This data set will be updated each year as new data, both modeled and measured, become available and as the methodology evolves.

Use and Limitations

The TDEP maps have been used by the TDEP Science Committee to identify areas of research that are critical to advancing our understanding of accurately estimating total deposition. The maps are also being used by resource managers to assess ecosystem health. Critical load exceedances can be identified by combining maps of total deposition and critical loads. The TDEP maps provide the best available estimates of total deposition based on the most recent information; however, there are limitations, including, but not limited to the following:

- Interpolation techniques inherently minimize extreme values, so more variability would be expected if more spatially resolved observations were available for use.
- The use of monitoring data is limited to sites and times that meet network completion criteria to ensure that measurements are representative of actual conditions.
- Discontinuities in temporal and spatial trends at specific locations may occur where monitoring data are intermittent.
- The methodology used to develop the wet deposition grids differs from that used for the NADP network precipitation grids.
- Ammonia data from the NADP Ammonia Monitoring Network (AMoN) and SEARCH are only used for model evaluation and are not included in the development of the concentration surfaces because a method for combining a concentration measurement with a bidirectional flux has not yet been developed.
- There is likely an incomplete characterization of the wet and dry organic nitrogen components due to a lack of measurements resulting in an underestimate of total nitrogen deposition.
- Since the measurement sites used in the method are located primarily in rural areas, deposition in urban areas may not be well represented.
- Occult deposition is poorly understood and may not be accurately characterized in modeling.

The TDEP Science Committee is open to anyone that wants to participate and meets twice a year. Scientific contributions and collaboration towards this work are welcome. For more information, please contact the Chair or Co-Chair of the TDEP Science Committee (<u>http://nadp.isws.illinois.edu/committees/</u> tdep/contacts.aspx).


Composition of nitrogen deposition in the US for 2013-2015 (top), and historical average annual total nitrogen deposition at CASTNET sites (bottom).



Total annual precipitation in 2015 (top), and percent deviation of 2015 precipitation values compared to the annual average of 2000-2015 (bottom).



Total nitrogen deposition in 2015 (top), and percent deviation of 2015 nitrogen deposition values compared to the annual average of 2000-2015 (bottom).



Annual dry nitrogen deposition in 2015 (top), and percent of total nitrogen deposition as dry deposition in 2015 (bottom).



Annual wet nitrogen deposition in 2015 (top), and percent of total nitrogen deposition as wet deposition in 2015 (bottom).



Annual oxidized nitrogen deposition in 2015 (top), and percentage of total nitrogen deposition as oxidized nitrogen in 2015 (bottom).



Annual reduced nitrogen deposition in 2015 (top), and percentage of total nitrogen deposition as reduced nitrogen in 2015 (bottom).



Annual deposition of unmonitored nitrogen compounds in 2015 (top), and percentage of total nitrogen deposition as unmonitored nitrogen compounds (bottom).



Annual gross ammonia deposition in 2015 (top), and net ammonia deposition in 2015 (bottom).



Annual sulfur deposition in 2015 (top), and percentage of total sulfur deposition as dry deposition in 2015 (bottom).



Annual S + N equivalent deposition in 2015 (top), and the percentage of S + N equivalent deposition as nitrogen in 2015 (bottom).



Annual base cation $(Ca^{2+}, K^+, Mg^{2+}, Na^+)$ deposition in 2015 (top), and percentage of total base cation deposition as dry deposition in 2015 (bottom).



Annual chloride deposition in 2015 (top), and percentage of total chloride deposition as dry deposition in 2015 (bottom).

National Atmospheric Deposition Program

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Editor: Gary Lear; Review: Total Deposition Steering Committee, Tonnie Cummings, Claire O'Dea.

All NADP data and information, including color contour maps in this publication, are available from the NADP website: <u>http://nadp.isws.illinois.edu</u>. 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.

The NADP Program Office is located at the Illinois State Water Survey, a division of the Prairie Research Institute at the University of Illinois at Urbana-Champaign.



附錄 5、NITROGEN FROM THE ATMOSPHERE

NITROGEN FROM THE ATMOSPHERE



SUMMARY: NITROGEN FROM THE ATMOSPHERE

Nitrogen surrounds us.

Nitrogen (N) is required by all life on earth. N is also the most abundant gas in our atmosphere, existing primarily as N₂, a form of N that almost all plants and animals cannot use. It is therefore termed non-reactive nitrogen (N_n-r). Reactive forms of nitrogen (N_r), nitrogen that can be used by organisms, is a small fraction of what's naturally found in the atmosphere. However, humans learned in the early 1900s to change N₂ into reactive forms of N to create N-based fertilizers to increase plant growth. Humans also began to burn fossil fuels, changing N_{n-r} to N_r. This N_r is the N that is most important to us.

Reactive nitrogen causes a cascade of effects.

 N_r can enter ecosystems from the air or through fertilizer application to soils, having unintended effects. N_r cycles through many other forms that can move from the soil into water resources or to and from the atmosphere. For example, too much N_r in streams can cause overgrowth of algae that chokes out fish. Too much N_r in soils can damage non-crop plants, such as trees, and change soil chemistry. N_r that goes back to the air contributes to air pollution such as acid rain, ozone, and visibility problems. Nitrogen can then fall back to land and water in wet deposition (rain or snow), or as dry deposition of N_r particles and gases.

NADP measures Nr from the atmosphere.

The National Atmospheric Deposition Program (NADP) began measuring some forms of N_r in 1978. Ammonia (NH₃) and nitrogen oxides (NO_x) react in the atmosphere and can dissolve in precipitation, falling as rain or snow in the forms of ammonium (NH₄⁺) and nitrate (NO₃⁻). Measuring this wet atmospheric deposition is a relatively simple way to estimate how much of these N_r pollutants were emitted into the air and to gauge how much N_r is being added to different ecosystems. Nitrogen can also be deposited in dry form (as both gas and particles) but is more difficult to measure directly. NADP works closely with the Clean Air Status and Trends Network (CASTNET) to estimate N dry deposition.

Why is it important to measure Nr deposition? Man-made processes have doubled the global amount of Nr in the environment compared to pre-industrial times. The long record of data collected by NADP across the USA gives valuable information about how and where Nr deposition has changed. Continuing to measure Nr in deposition can help policymakers make good decisions about protecting the environment while meeting our energy and food needs. NADP gives land managers important data about agricultural inputs and outputs and emission products. Scientists can continue to use NADP data to monitor changes in ecosystems as a result of changes in Nr. All of us can consider what actions we might take to limit our contribution to Nr in the environment.

Chemical terms

 N_r = Reactive nitrogen Nn-r = Non-reactive nitrogen N₂ = Molecular nitrogen $NH_3 = Ammonia$ $NH_4^+ = Ammonium$ NH_x = Ammonia plus ammonium $NO_3^- = Nitrate$ NO = Nitric oxide $N_2O = Nitrous oxide$ $NO_2 = Nitrogen dioxide$ $NO_x = Nitrogen oxides$ $NO_{v} = NO_{x}$ and other combinations of nitrogen and oxygen (except N₂O) HNO₃ = Nitric acid HONO = Nitrous acid $O_3 = Ozone$





Illustration of the nitrogen cascade showing the sequential effects that a single atom of nitrogen in its various molecular forms can have in various reservoirs after it has been converted from nonreactive N₂ to a reactive form by energy and food production (orange arrows). Once created, the reactive nitrogen contributes to impacts until it is converted back to N₂, a process called denitrification. The small black circle indicates the potential for denitrification to occur within that reservoir. Source: adapted from Ciais et al., 2013 with permission from the GEO Yearbook 2003.

WHICH HUMAN ACTIVITIES CONTRIBUTE NITROGEN?

Fossil Fuel Combustion

Combustion creates high temperatures in which atmospheric N_2 is transformed to reactive NO_x . It's not surprising, then, that emissions from motor vehicles, electric utilities, and industrial processes are the largest sources of atmospheric NO_x in the United States. Human (anthropogenic) activities now account for more than 80% of USA NO_x emissions. According to the US National Emissions Inventory (NEI), anthropogenic NO_x emissions peaked around 1980 at 24.6 million metric tons and have declined, especially after 1995 when the 1990 Clean Air Act Amendments legislation took effect, to a low of 11.3 million metric tons by 2014. NO_x emissions expressed as units of N only were 7.5 million metric tons for 1980 and 3.4 million metric tons for 2014.

Atmospheric chemical reactions that occur when sunlight is present strongly link NO_x and other trace gases to the formation of O_3 . Depending on atmospheric conditions, these reactions can occur within several hundred meters of the original NO_x source or after the pollutants have been transported several hundred to thousands of kilometers downwind-perhaps crossing state or national borders. Ultimately, some NO_x is converted to HNO_3 vapor or particulate NO_3^- , both of which are efficiently removed from the atmosphere by deposition processes.

As a consequence, NO_3^- concentrations in precipitation tend to be highest where the air is most polluted with NO_x . These areas (e.g., the eastern USA) are likely to have high population densities, numerous motor vehicles (mobile sources), and many power plants or industrial boilers (stationary sources). A regional-scale study (Elliot et al., 2007) that analyzed stable nitrogen isotopes in NADP precipitation samples, shows a strong link between surrounding stationary NO_x emission sources and NO₃⁻ in precipitation for the Northeastern and Midwestern USA. According to emissions inventories, stationary source NO_x emissions at the time were smaller than vehicle emissions in these regions, suggesting that NO_x deposition end products from the transportation samples.

Agricultural Sources

Fertilizer use greatly augments the agriculture industry allowing for more production, but also increases the amount of N_r cycling into the environment. Fertilizer is often applied in reduced form (NH₃ & NH₄⁺) and can enter ecosystems directly via volatilization during application or because of runoff into waterways. Emissions of reduced, reactive nitrogen are also a by-product of livestock production usually entering the ecosystem via the handling of animal waste. Livestock production represents the largest source of NH₃ emissions.

Together, livestock production and fertilizer use are the primary sources of NH₃ emissions and account



USA 2014 NO_x emissions by source from National Emissions Inventory (NEI).

for over 80% of total NH_3 emissions in the United States. The National Emissions Inventory (http:// www3.epa.gov/ttn/chief/net/2011inventory.html) reports emissions of approximately 1 million metric tons of NH_3 from fertilizer application and 2 million metric tons of NH_3 from livestock production in the USA during 2011.

Precipitation readily removes NH₃ and NH₄⁺ from the air. Wet deposition of these compounds (along with atmospheric NO₃-) could be viewed as another source of fertilizer for agricultural crops. It can also be an unwanted input of fertilizer to sensitive ecosystems. The maps below show the inorganic nitrogen deposited in precipitation (i.e., $NO_3^- + NH_4^+$) in 1990 and 2014 in the USA. Wet inorganic nitrogen deposition is highest in the intensely cultivated upper Midwest. Parts of eight states from eastern Nebraska to western Ohio received 5 kg-N/ha (4.4 pounds/acre) or more of deposition annually. Sixty percent to 75% of the wet inorganic nitrogen deposited in this area is from NH4+ deposition, which peaks in this same area. Atmospheric NH₃ emissions also peak in this region.



USA NO_x and NH₃ emissions expressed as million metric tons or teragrams (10^{12} grams) of N. There have been significant declines in NO_x emissions, but very little change in NH₃ emissions since 1990.



Comparison of NH₄⁺ and NO₃⁻ content (as N) of precipitation in remote (Hawaii, Alaska, Puerto Rico) and more highly populated (eastern USA) areas of the USA. Based on NADP 2012 to 2014 annual volume-weighted mean concentrations (except Hawaii, which is based on 2002 to 2004; site closed in 2005).







Inorganic nitrogen (NO $_3^-$ and NH $_4^+$) wet deposition for 1990 and 2014.



Percentage of inorganic nitrogen from NH₄⁺ and NO₃⁻ as measured in precipitation samples for the Northeast, Southeast, and Midwest sectors of the USA from 1994 to 2014. These data are based on five long-term NADP sites in the Northeast (VT01, MA08, NY68, PA42, and MD13), Southeast (AL10, GA41, SC06, NC36, and KY22), and Midwest (IL11, IN20, IA23, MI26, and MN27).



NITROGEN AND AGRICULTURAL PRODUCTION

Over the past several decades, the crop and animal agriculture industries have become increasingly focused on the issue of nitrogen deposition. This focus is motivated by increasing the productivity and efficiency of farming practices, while increasing environmental sustainability.

Plant growth and crop yield are dependent on numerous factors including historical land use, crop type, soil type and condition, and availability of nutrients required for growth, especially nitrogen. Nitrogen availability in soils is influenced by the amount of N mineralized from previous crop residues, the amount of N released by organic matter, and the amount of N deposited from the atmosphere. Precipitation over the Midwest annually contributes 4 to 7 kilograms per hectare of inorganic N to the soil. This represents less than 5% of the inorganic N needs of corn and up to 15% of the N needs of wheat, depending on the target yield of the crop and on soil quality. Estimated wet and dry atmospheric N deposition for areas in the eastern United States could account for at least 10%



2014 NH₃ Emissions Sources (3.1 million metric tons N)

These reduced forms of nitrogen (NH₃ gas and NH₄⁺ as a particulate or dissolved in water) are becoming relatively more important in terms of emission levels and atmospheric deposition. NH₃ emissions have not substantially declined over the past two decades in comparison to NO_x emissions, which have declined significantly due to regulated controls on NO_x emissions. of the nitrogen needs of major, non-nitrogen-fixing crops. In order to meet crop needs, application of N-based fertilizers to crop systems is generally very large compared to these sources, and has proven very effective in increasing crop yields, but excess fertilizer can result in unnecessary costs and nitrogen losses leading to unintended environmental effects. Research has focused on development of technologies and management practices that can decrease emissions of NH₃ and control N runoff, and especially on innovations that provide economic incentives for the farmer.

The animal agriculture industry has evolved so that most livestock and poultry produced for food in the USA are raised in large, concentrated operations. On these farms, large numbers of hogs, cattle, turkeys, and chickens as well as their feed, feces, and urine are confined to a relatively small area. Animal houses and waste lagoons are large sources of NH₃. Application of manures to nearby cropland takes advantage of the nutrients contained in the manure for crop production, but is another source of N emission and potential runoff. Proper management of these significant sources can severely cut back on unintended N losses to air and water, and farmers develop animal waste management plans that are tailored to their operations. New measures are being investigated and implemented that focus on reducing water pollution and air emissions associated with animal agriculture.

Our knowledge base of N emissions from agricultural production has grown over the past 30 years and technologies have been developed that can limit those emissions. Because of the additional costs often associated with these measures, economic factors such as market demand can play a role in widespread adoption of some of these practices. Ongoing monitoring of N deposition by NADP offers a quantitative measure of the impact of changing management practices on regional deposition.

All of us benefit as science and technology continue to work together to optimize crop and animal production and safeguard terrestrial and aquatic ecosystems, as well as drinking water supplies.

WHAT EFFECTS ARE ASSOCIATED WITH NITROGEN DEPOSITION?

Depending on the chemical form and amount in the environment, nitrogen can serve as a nutrient, enhancing growth and productivity, or as a toxin, causing ecological damage or harming human health. Scientists often refer to N as a macronutrient because plants and animals require it in relatively large proportions compared to other essential nutrients such as iron or copper.

Nitrogen needs vary, depending on the ecosystem and the plant or animal species. Different life forms within the same ecosystem do not have the same N requirements. Many ecosystems and crops are limited by the availability of nitrogen. That's why the advent of synthetic fertilizers via the Haber-Bosch process early in the 20th century has been such a boon to agricultural productivity. That is also why atmospheric deposition of nitrogen in some ecosystems may stimulate unhealthy growth or cause growth of some plants at the expense of others.

Air quality and atmospheric deposition are closely linked. NO_x contributes to the formation of O_3 , a serious lung irritant. Many studies have shown that elevated O_3 levels also damage plant leaves and reduce crop yields. Near urban or industrial air pollution sources, high concentrations of particulate NH_4^+ and NO_3^- and NO_x gas can irritate human lung tissues and lower resistance to influenza or other respiratory infections.

Visibility degradation and acidic deposition are also linked to nitrogen. Too many fine particles in the air create the unsightly haze that reduces visibility in many USA cities and even occasionally shrouds the beautiful vistas in national park and wilderness areas. These fine particles contain nitrogen compounds (NO_3^- , NH_4^+ , or both) and other pollutants (sulfate [SO_4^{2-}] and carbon compounds).





Stream acidification in Shenandoah National Park has had effects on some native species, such as this brook trout. Stream-water nitrogen often reaches a peak during the spring when snowmelt or rainstorms can flush NO₃⁻ from the soils. Photo courtesy of U.S. National Park Service.

SO42- is often more important than nitrogen compounds in degrading visibility, especially in the eastern United States. When sunlight is present, NO_x gas may also contribute to degradation of visibility. Although precipitation cleans the air, rain and snow can contain acidic NO3⁻ and SO4²⁻. Statues, monuments, and the exteriors of buildings are all subject to acid rain damage. Acidic precipitation also affects sensitive streams, lakes, and soils, which are easily altered by chemical inputs. Acidic precipitation can disturb the delicate balance in these sensitive ecosystems. The good news is that because of large reductions of NO_x and SO₂, NADP data show acid deposition in large parts of the United States has been significantly decreasing in the past three decades. The same is true in much of Europe.

Effects on Freshwaters and Forests

Freshwater streams, ponds, and lakes respond to the water and chemical inputs from rain storms and snowmelt. On occasions when the ground is frozen, some headwater streams carry a surge of NO3⁻, SO4²⁻, and acidity provided directly by rain or melting snow. This also occurs in urban environments where the ground is covered with hard surfaces such as concrete or asphalt. More typically, precipitation soaks into the ground adding NO3⁻ and NH4+ to the nitrogen cycle, which also involves soils, decaying plant and animal matter, microbes, and living plant roots. Many factors control the rate at which nitrogen enters and leaves this complex cycle, including soil type, temperature, microbial activity, and plant needs. Precipitation is just one source of the nitrogen in soils.

How a rain of fertilizer caused a reign of fire Nitrogen deposition is like fertilizer raining down out of the sky. Just as the fertilizer that people put on their lawns causes them to be lush and grow quickly, atmospheric deposition of excess nitrogen can cause invasive grasses biomass to increase exponentially in natural areas, where they don't belong. In Joshua Tree National Park, a desert area in southern California, nitrogen deposition has caused non-native grasses to increase so much that they can now carry fire across some parts of the landscape. Park managers are now preparing for increased fire in the park, and it is unknown what will happen next, as large, intense fires have never been observed there since the establishment of Joshua Tree National Monument in 1936.



Scientists have found that the cumulative effect of years of nitrogen deposition does increase the amount of nitrogen carried by streamflow from some watersheds. Rain storms and snowmelt can flush accumulated NO_3^- from soils into these streams. Nitrogen deposition, especially in combination with SO_4^{2-} , can contribute to episodic acidification of streams. Not all aquatic organisms have the same tolerance for these episodes, which can cause a decline in populations of acid-sensitive fish, amphibians, and invertebrates.

Nitrogen deposition to forest and alpine soils can affect plant populations and overall forest health. Decades of acidic NO_3^- and SO_4^{2-} deposition have depleted the supply of calcium (Ca²⁺) and mobilized aluminum (Al³⁺) in some forest soils. Ca²⁺ is essential for tree growth, but Al³⁺ interferes with the uptake of this nutrient by tree roots. Low soil Ca²⁺ has been linked to the dieback of sugar maples in some northeastern forests. Researchers have studied nitrogen-saturated, high-elevation spruce/fir forests in the Great Smoky Mountains National Park. They have found that as AI^{3+} in soil water increases, the Ca^{2+} in spruce trees decreases, possibly making trees more vulnerable to drought and insect infestations. Further, experiments have shown that adding nitrogen to alpine forest and grass communities alters the species mix. Those plants that can store and use the added nitrogen become more dominant, while those that cannot decline in number.

Effects on Estuarine Systems

The numerous estuaries (where fresh and salt water mix) along the USA coastline have great economic, aesthetic, and ecological value. Watershed landscape characteristics, land use (e.g., agriculture vs. forest), and atmospheric deposition all play a part in the delivery of nitrogen to estuaries and coastal systems. Nitrogen from many sources enters an estuary; only a portion is from atmospheric deposition (see section on Chesapeake Bay).

Soils, plants, and animals retain much of the nitrogen deposited in estuarine watersheds. Much of the remainder leaves these watersheds in runoff to streams and rivers. Some N_r is removed as N_2 gas (and sometimes as gaseous N_2O) by microbial denitrification processes within the watershed or the estuary itself. Subsurface water carrying nitrogen can also enter these waterways, which feed into estuaries.

Nitrogen has unique effects on individual estuaries. Along the East and Gulf Coasts, nitrogen provides a fertilizer effect and promotes algae blooms, causing coastal eutrophication. These microscopic waterborne plants cloud water and block sunlight, which can interfere with other estuarine plant and animal productivity, and affect water temperature and currents. For example, algae can inhibit growth of sea grasses that offer habitat for fish and shellfish.

Although living algae can degrade habitat, decaying algae can also have effects as they complete their life cycle, sink to the bottom, and decompose. Decomposition of algae and other dead matter removes oxygen from bottom waters and can lead to hypoxia, a low-oxygen condition. Hypoxia has negative impacts on populations of bottom dwellers such as crabs, oysters, mussels, and clams.

CRITICAL LOADS: HOW MUCH N DEPOSITION IS TOO MUCH?

The term critical load is used to describe the threshold of atmospheric deposition that causes harm to sensitive resources in an ecosystem. Critical loads are typically expressed in terms of kilograms per hectare per year (kg/ha/yr) of wet or total (wet + dry) deposition. Critical loads can be developed for a variety of ecosystem responses, including shifts in microscopic aquatic species, increases in invasive grass species, changes in soil chemistry affecting tree growth, and lake and stream acidification to levels that can no longer support fish. When critical loads are exceeded, the environmental effects can extend over great distances. For example, excess nitrogen can change soil and surface water chemistry, which in turn can cause eutrophication of downstream estuaries. The long-term, spatially extensive wet deposition data provided by NADP are instrumental in developing critical loads in the USA, thereby helping to quantify the impacts of

air pollution on ecosystems. NADP also provides a format for critical loads development through the CLAD (Critical Loads and Atmospheric Deposition) Science Committee (http://nadp.isws.illinois.edu/ committees/clad/).

Critical loads are being developed in the USA for nitrogen and sulfur compounds, which are emitted by vehicles, power plants, industry, agriculture, and other sources.

As nitrogen deposition increases, impacts to sensitive ecosystem components also increase. Because pollutants accumulate in soils and lakes over time, it can take decades to reverse ecosystem degradation once it occurs. Prevention of the accumulation of pollutants in an ecosystem prior to any observable degradation is preferable. Both the US National Park Service and Forest Service are developing nitrogen critical loads for protection of the landscapes under their jurisdiction.



Schematic graph of the impact of increasing nitrogen deposition on different ecosystem health indicators. Establishment of a critical load value can depend on that which regulators want to protect. In this example, a lower critical loading value (#1) is necessary to maintain present water chemistry. A higher critical loading value (#2) is necessary if the goal is to maintain alpine plant diversity. (From http://www.nature.nps.gov/air/Studies/criticalloads/)

HOW IS NITROGEN DEPOSITION MEASURED?

Nitrogen deposition occurs as both wet and dry deposition. The NADP National Trends Network (NTN) measures NO₃⁻ and NH₄⁺ in one-week rain and snow samples at over 250 regionally representative sites in 47 states plus Canada, the Virgin Islands, and Puerto Rico. NO₃⁻ and NH₄⁺ are measured in daily samples at another six sites in NADP's Atmospheric Integrated Research Monitoring Network (AIRMoN). These two NADP networks measure the wet deposition of inorganic nitrogen.

The amount of nitrogen deposited by precipitation can be calculated for locations without NTN or AIRMoN sites. One approach uses NADP rainfall, NO_3^- and NH_4^+ concentration data, and digital terrain maps. These maps make it possible to generate plots that account for terrain effects on wet deposition. Maps generated using this technique include important information for planners, policymakers, and the scientific community about the complex relationship between the atmosphere and the ecological health of the nation's estuarine systems. In order to further understand N in the atmosphere and its impacts on landscapes, NADP is also measuring gaseous NH₃. A relatively new NADP network, begun in 2007, is the Ammonia Monitoring Network (AMoN). Atmospheric NH₃ concentrations are measured over a two-week period with passive samplers. There are currently 97 sites in the network.

The US Environmental Protection Agency Clean Air Status and Trends Network (CASTNET) operates 94 sites that measure weekly atmospheric concentrations of gaseous HNO₃ and particulate NH_4^+ and NO_3^- (as well as other non-nitrogen species) at rural locations nationwide. These measurements are used in atmospheric deposition models to calculate estimates of dry deposition of gases and particles. The model uses meteorological measurements and information on land use, vegetation, and surface conditions, in addition to the atmospheric concentrations, to calculate dry deposition of N_r .



THE CHESAPEAKE BAY: A CASE STUDY

The Chesapeake Bay is the largest of 130 estuaries in the nation and is located in coastal Maryland and Virginia. Its watershed covers 64,000 square miles over six states and the District of Columbia. The population within the Chesapeake Bay watershed is approximately 17 million and growing.

One of the largest problems facing the environmental health of the Bay is an overabundance of nutrients, especially N. This often leads to increased algal production and organic matter, a process known as eutrophication. Nitrogen is introduced into the Chesapeake Bay as runoff or wastewater from agricultural operations, storm water drainage, sewage and industry, and deposition from the air. An estimated 40.3 million kg of N (approximately one-third of the Bay's total annual load) is from atmospheric deposition as calculated by the Chesapeake Bay Program.

Most nitrogen pollutants introduced into the ecosystem are quickly converted into NO_3^- . This NO_3^- typically accumulates in the Bay during winter and spring and promotes excessive algal growth as temperatures rise. By mid-summer the decay of algae and other dead matter leads to hypoxia in the bottom waters of the Bay.

The Chesapeake Bay Program seeks ways to reduce the amount of N entering the Bay, which include programs to encourage farming conservation practices to curb drainage and runoff of fertilizers and animal



Pie Chart of Nitrogen Pollution to the Chesapeake Bay highlighting responsible sectors and sources of nitrogen pollution accumulating in the Bay. Source: Chesapeake Bay Foundation waste. Typical methods include installing streamside buffers and fences, the use of conservation tillage, and planting cover crops. Between 2004 and 2013, three of nine sites have shown improving flow-adjusted trends in nitrogen concentrations. Five have not significantly changed, but only one of the nine sites has shown a degrading trend.

Researchers are using NADP data to compute the amount of N deposited by precipitation in Chesapeake Bay and its watershed. Scientists are using computer modeling to simulate the complex cycling of nitrogen through the terrestrial watershed. High-quality data from NADP measurements give cooperating scientists and policymakers the information they need to meet this goal.



Aerial view of algal blooms in the Elizabeth, Lafayette, and James Rivers, VA. N in the water is causing the explosive growth of algae, which later die, depleting the water of oxygen and leading to hypoxic zones. Source: Chesapeake Bay Foundation.



Trends in Total Nitrogen Concentration between 2004 and 2013 in the Chesapeake Bay Watershed. Although most sites have not seen significant changes, three have had improving trends, and one has had a degraded trend. Source: U.S. Geological Survey and Chesapeake Bay Program.

MEASURING TOTAL DEPOSITION

NADP has also attempted to better understand total wet and dry nitrogen deposition through the Total Deposition (TDEP) Science Committee (http:// nadp.isws.illinois.edu/committees/tdep/). Using a "hybrid" approach of combining measured data (e.g., precipitation NO3⁻ and NH4⁺, dry deposition of particulate NH4⁺ and NO3⁻, and gaseous NH3) with modeled deposition data of other known, but not measured, nitrogen species (e.g., wet and dry organic N, HONO, NO₂, etc.), estimates of total N deposition are obtained. The average annual total deposition for 2000 to 2002 and for 2013 to 2015 are shown below. These maps show dramatic improvements in decreasing total nitrogen deposition over large areas of the USA, a result of decreased emissions due to federal and state regulations during this period.

Such work aids another NADP science committee, the Critical Loads and Atmospheric Deposition (CLAD) Committee (http://nadp.isws.illinois.edu/ committees/clad/) in evaluating whether sensitive areas are experiencing too much N deposition.



Whooooooo cares about lichens?

Some types of lichens are very sensitive to air pollution, and have disappeared from forests in the Pacific NW in areas where air pollution has increased just a small amount. Many of these same lichen species serve as critical food and nesting material for mammals and birds. For example, the northern flying squirrel relies exclusively on forage lichens as a winter time food source. In turn, the flying squirrel is almost the exclusive food source of spotted owl. The spotted owl is an endangered species and its recovery plan has been controversial, because of the associated estimated \$3.6 billion in economic losses from logging and related industries that must be reduced for better habitat protection. Despite that investment, owl populations are continuing to decline because of many factors. Air pollution may be one of these factors, as decreases in sensitive lichen species and flying squirrels have also been documented. So when excess air pollution causes declines in sensitive lichen species, the whole food chain may be impacted, all the way up to the endangered spotted owl!





Total annual N deposition estimates for the continental USA for the average of 2000 to 2002 and the average for 2013 to 2015. These values are based on a "hybrid" approach of combining measured and, where measured values are not available, modeled nitrogen species data, and then summing all nitrogen species. More details are provided in http://nadp.isws.illinois.edu/committees/tdep/.

ABOUT THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

Evaluating nitrogen deposition, as well as deposition of other chemical species from the atmosphere, is a major role of the National Atmospheric Deposition Program (NADP)-a partnership of State Agricultural Experiment Stations, federal, state, and local government agencies, universities, public institutions, Native American organizations, and industries. Continued commitments by these organizations make it possible for NADP to provide the only long-term record of precipitation chemistry in the United States. This information is used by scientists, policymakers, and the public in addressing the health, environmental, and agricultural issues facing the nation, including policy decisions related to the Clean Air Act amendments. NADP was initiated in 1977 to address the problem of atmospheric deposition and its effects on agricultural crops, forests, rangelands, surface waters, and other natural resources. NADP coordinates over 250 sites in the National Trends Network, which collects weekly precipitation samples for chemical analysis. Samples are analyzed at the program's Central Analytical Laboratory in Champaign, Illinois, to determine the amounts of certain chemicals, including NO3⁻ and NH4+.

Two additional networks joined NADP in the 1990s: the Atmospheric Integrated Research Monitoring Network (AIRMoN) in 1992 (which includes a data record for some sites starting in 1976) and the Mercury Deposition Network (MDN) in 1996. The AIRMoN wet deposition program, presently consisting of six sites, evaluates the effect of emission changes on precipitation chemistry, combining measurements with atmospheric models. MDN is investigating the importance of atmospheric deposition as a source of mercury in terrestrial ecosystems, lakes, and streams, and includes 110 sites.

Further expansion of NADP after 2000 includes the start of the Atmospheric Mercury Network (AMNet) and the Ammonia Monitoring Network (AMoN). AMNet began in 2009 to measure atmospheric concentrations of gaseous oxidized, particulate-bound, and elemental mercury using consistent method-ologies. There are currently 24 sites. Additionally, estimates related to mercury deposition in forested landscapes are being complimented by the NADP Litterfall Mercury Monitoring Initiative. AMoN began operation in 2007 and currently operates 98 sites, making integrated bi-weekly measurements of atmospheric NH₃ concentrations using passive samplers.

A number of federal agencies support NADP, including the US Department of Agriculture (National Institute of Food and Agriculture and Forest Service); US Department of Commerce (National Oceanic and Atmospheric Administration); US Department of Interior (Bureau of Land Management, National Park Service, US Fish & Wildlife Service, and US Geological Survey); and US Environmental Protection Agency.

Additional support comes from various other federal agencies, State Agricultural Experiment Stations, state and local government agencies, universities, tribal organizations, and public and private research organizations.

How acidification ruined Christmas (trees) and Easter (bunnies)

Balsam fir are an important tree species in cold high elevation areas of the eastern US. They represent a \$17,000,000 business in Christmas trees and aromatic oils in the U.S. They also serve as valuable habitat for small mammals and birds. However balsam fir trees are vulnerable to acid rain, because chemical changes in the soils deplete essential nutrients which many types

of tree species need to thrive. Acidification of soils in the eastern US has decreased the growth of balsam fir and made them susceptible to damage by ice storms, insects and disease. In the Southern Appalachians only small relic populations of these tree species remain. Snowshoe hare population declines (through decreased reproduction and increased predation) in the Appalachians have been associated with decreases in balsam fir tree health because hares require dense forests which they use for both





food and shelter. Acidification of forest soils in the eastern US has consequences throughout these ecosystems, impacting both the economic benefits of forest products, such as Christmas trees, and the societal desire to protect locally endangered species, such as the snowshoe hare.

GLOSSARY OF TERMS

Ammonia/Ammonium (NH₃/NH₄+)

Compounds of nitrogen and hydrogen that readily dissolve in water. In oxygen-rich water, NH_4^+ is microbially transformed to NO_3^- and in oxygen-poor water to molecular nitrogen. NH_4^+ and nitrate comprise most of the inorganic nitrogen in precipitation.

Atmospheric Deposition

The process whereby airborne particles and gases are deposited on the earth's surface by wet deposition (precipitation) or by dry deposition (processes such as settling, impaction, and adsorption).

Critical Load

The threshold of air pollution deposition that causes harm to sensitive resources in an ecosystem.

Denitrification

The microbial process of converting NO_3^- through a series of intermediate steps to N_2 gas, which occurs under very low oxygen conditions, such as in lake sediments.

Dry Deposition

Atmospheric deposition that occurs when particles settle to a surface, collide with and attach to a surface, or when gases stick to a surface (adsorption) or are absorbed.

Estuary

An arm of the sea at the mouth of a stream or river where freshwater and salt water meet.

Eutrophication

A process in which nutrients degrade water quality due to excessive growth of microscopic plants and animals. As this matter dies and decays, it sometimes removes so much dissolved oxygen from the water that fish and other organisms cannot survive.

Haber-Bosch process

Industrial process to convert inert, atmospheric N_2 into NH_3 using high pressures and temperatures and an iron catalyst.

Hypoxia

A low-oxygen condition whereby decaying microscopic plants and animals in estuarine waters remove oxygen to a level below which most aquatic animals can survive. Although fish and shrimp can migrate from hypoxic zones, less mobile bottom dwellers cannot.

Molecular nitrogen (N₂)

An extremely stable gas, comprises 78% of the atmosphere. Converting this gas to other chemical

compounds requires lots of energy. Also referred to as Nonreactive Nitrogen (Nn-r).

Nitrate (NO3-)

A compound of nitrogen and oxygen that is highly soluble in water. Nitrate is stable over a wide range of environmental conditions and is readily transported in surface water and groundwater.

Non-reactive Nitrogen (Nn-r)

A nitrogen compound that is not ecologically or biologically active.

Reactive Nitrogen (N_r)

Nitrogen compounds that are ecologically and biologically active. N_r can be in a reduced form as in ammonia (NH₃), ammonium (NH₄⁺), and organic compounds such as urea, amines, proteins, and nucleic acids. Nr can also be oxidized as in nitric acid (HNO₃), nitrous acid (HONO), nitrous oxide (N₂O), nitrogen dioxide (NO₂), nitric oxide (NO₂), and nitrate (NO₃⁻).

Total Deposition

The amount of a chemical compound that is deposited to earth's surface via wet and dry deposition processes.

Watershed

A land surface from which water drains to a lake, stream, river, estuary, or bay.

Wet Deposition

Atmospheric deposition that occurs when rain, snow, or fog carry gases, particles and dissolved materials to the earth's surface.



RESOURCES

Data products are available from the National Atmospheric Deposition Program (NADP) free of charge. The easiest way to obtain data is by visiting our Internet site at http://nadp.isws.illinois.edu.

NADP products include:

- Weekly (NTN) and daily (AIRMoN) precipitation
- ¹ chemistry data (e.g., ammonium (NH₄⁺) and nitrate (NO₃⁻, among many other elements);
- Monthly, seasonal, and annual precipitation-weighted mean concentrations (NTN);
- Annual and seasonal deposition totals;
- Total nitrogen deposition data and maps (TDEP);
- Daily precipitation totals;
- Color isopleth maps of precipitation concentrations and wet deposition;
- Mercury precipitation concentration and wet deposition data (MDN);
- Mercury air concentration data (AMNet);
- NH₃ air concentration data (AMoN);
- Site photos and information; and
- Quality assurance data and other information.

For further information, contact: NADP Program Office Illinois State Water Survey 2204 Griffith Drive Champaign, Illinois 61820 E-mail: nadp@isws.illinois.edu

Other Website Resources

Chesapeake Bay Program: www.chesapeakebay.net

Chesapeake Bay Foundation: www.cbf.org

National Atmospheric Deposition Program: nadp. isws.illinois.edu

National Oceanic and Atmospheric Administration AIRMoN Dry Deposition Program: http://www.atdd. noaa.gov/

National Park Service Air Resources Division: https:// www.nps.gov/orgs/1971/index.htm

US Environmental Protection Agency Clean Air Status and Trends Network: www.epa.gov/castnet

US Environmental Protection Agency National Emissions Inventory http://www3.epa.gov/ttn/chief/ net/2011inventory.html

National Estuary Program: www.epa.gov/nep

Office of Air & Radiation: www.epa.gov/oar

US Geological Survey Acid Rain, Atmospheric Deposition, and Precipitation Chemistry: https://bqs. usgs.gov/acidrain/

US Forest Service Critical Loads: http://srs.fs.usda.gov/ airqualityportal/critical_loads/cls_background.php

National Park Service Critical Loads: http://www. nature.nps.gov/air/Studies/criticalLoads/index.cfm

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