

## SAES-422 Multistate Research Activity Accomplishments Report

Project No. and Title: NRSP-3, The National Atmospheric Deposition Program – A Long-Term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition

Period Covered: 10-2011 through 9-2012

Date of Report: Dec 11, 2012

Meeting Dates: October 1–5, 2012

### Participants

A list of meeting participants from our 2012 Fall Meeting and Scientific Symposium can be downloaded from our website (<http://nadp.isws.illinois.edu/conf/2012/>), along with all of the presentations, posters, and other materials. There were 139 registrants and attendees at this year's meeting.

### Meeting Minutes

All meeting minutes from our 2012 Spring Meeting (business meeting) and our 2012 Fall Meeting and Scientific Symposium (business, subcommittee meetings) are available on our website (<http://nadp.isws.illinois.edu/committees/minutes.aspx>). Several of the subcommittee minutes are delayed, but will be posted soon.

### Accomplishments

The NRSP-3 provides a framework for cooperation among State Agricultural Experiment Stations (SAES), the U.S. Department of Agriculture, and other cooperating governmental and nongovernmental organizations that support the National Atmospheric Deposition Program (NADP). The NADP provides quality-assured data and information on the exposure of managed and natural ecosystems and cultural resources to acidic compounds, nutrients, base cations, and mercury in precipitation and through dry deposition of several of these compounds. NADP data support informed decisions on air quality issues related to precipitation chemistry.

Specifically, researchers use NADP data to investigate the impacts of atmospheric deposition on the productivity of managed and natural ecosystems; the chemistry of estuarine, surface, and ground waters; and the biodiversity in forests, shrubs, grasslands, deserts, and alpine vegetation. These research activities address "environmental stewardship," one of the Experiment Station Section's research

challenges. Researchers also use NADP Mercury Deposition Network data to examine the role of atmospheric deposition in affecting the mercury content of fish, and to better understand the link between environmental and dietary mercury and human health. This fits with another research priority of “relationship of food to human health.”

The NADP operates three precipitation chemistry networks: the National Trends Network (NTN), the Atmospheric Integrated Research Monitoring Network (AIRMoN), and the Mercury Deposition Network (MDN).

The NTN provides the only long-term nationwide record of basic ion wet deposition in the United States. Sample analysis for these samples includes free acidity ( $H^+$  as pH), specific conductance, and concentration and deposition measurements for calcium, magnesium, sodium, potassium, sulfate, nitrate, chloride, bromide (new), and ammonium. We also measure orthophosphate ions ( $PO_4^{3-}$ , the inorganic form), but only for quality assurance as an indicator of sample contamination. At the end of September, 2012, 257 NTN stations were collecting one-week precipitation samples in 48 states, Puerto Rico, the Virgin Islands, Canada, and a new site in Argentina. Additionally, there are multiple quality assurance and test sites. Complementing the NTN is the seven-site AIRMoN. AIRMoN sites are essentially NTN sites operated on a daily basis (i.e., single precipitation events), with samples collected to support continued research of atmospheric transport and removal of air pollutants and development of computer simulations of these processes.

The 110-site MDN offers the only long-term and routine measurements of mercury in North American precipitation. Measurements of total mercury concentration and deposition (and optional methyl-mercury) are used to quantify mercury deposition to water bodies, some of which have fish and wildlife mercury consumption advisories. In 2008, every state and 10 Canadian provinces listed advisories warning people to limit fish consumption due to high mercury levels. Coastal advisories are also in place for Atlantic waters from Maine to Rhode Island, from North Carolina to Florida, for the entire U.S. Gulf Coast, and for coastal Hawaii and Alaska.

The NADP operates two newer gaseous atmospheric chemistry networks: the Atmospheric Mercury Network (AMNet) and the Ammonia Monitoring Network (AMoN), which is NADP's newest network. In each case, the network goal is to provide atmospheric concentrations of these particular gases, and then to estimate the rate of dry deposition (without precipitation) of the gas. In many cases, dry deposition of the gas could far exceed the wet deposition of the same compound.

At the end of September 2012, 22 AMNet sites were collecting five-minute estimates of gaseous elemental mercury and two-hourly average concentrations of gaseous oxidized mercury and particulate bound mercury. The AMNet provides the only long-term region-wide record of basic atmospheric mercury concentrations in the United States.

The AMoN has 58 sites operating as of September 2012, where two-week averages of atmospheric ammonia gas are being collected with passive devices. This low-cost network is designed to provide long-running estimates of ammonia in the atmosphere. These data are particularly important to agriculture, since many sources of ammonia are agricultural in nature. Data from both gaseous networks support continued research of atmospheric transport and removal of air pollutants and development of computer simulations of these processes.

#### Short-term Outcomes and Outputs.

**Samples Collected.** NADP's principal objective and accomplishment/outcome is the collection and analysis of samples for precipitation chemistry. Briefly, the NADP processed a total of 13,251 samples from the NTN, including 246 quality assurance (QA) samples. The analyses included observations of 10 different analyte concentrations and precipitation volume, which allow for calculation of deposition flux for each analyte. These same data were collected daily (i.e., every day with measurable precipitation) from the AIRMoN network. For the year, AIRMoN collected and processed 1,128 precipitation samples, including 168 QA samples. The MDN collected and processed 4,309 weekly mercury-in-precipitation samples, including 3,582 QA samples. The AMoN collected and quality assured 2,937 ammonia samples, which included 1,390 QA samples. The AMNet collected, quality assured, and produced approximately 38,000 hourly and two-hourly averages.

**NADP Database.** Our second most important accomplishment/outcome is making data available to all for the support of continued research. Scientists, policymakers, educators, students, and others are encouraged to access data at no charge from the NADP website (<http://nadp.isws.illinois.edu>). This site offers online retrieval of individual data points, seasonal and annual averages, trend plots, concentration and deposition maps, reports, manuals, and other data and information about the program. As of today, 2011 calendar year data are complete and online, along with data through June of 2012. Data through September will be posted very soon. Website usage statistics provide evidence that our data are being used. During FY2012, website usage continued to grow. More than 40,000 registered users accessed our information, and have recorded over 27,800 data downloads from the site. The site annually receives well over than 1.25

million “hits.” We continually divide users into types, and for FY2012 about 40% were from federal and state agencies (somewhat higher than normal), 36% from universities, 16% from K-to-12 schools, and 8% from other individuals or organizations. The NADP website has registered users from more than 150 countries across the globe. These statistics demonstrate that NADP continues to be relevant to both the scientific and educational communities, and continues to attract new users.

**Map Summary.** As with every year, during FY12 the annual maps of atmospheric pollutant concentrations and depositions were developed. These maps are used widely and constitute one of the major products of the network. Individual maps are filed by network, year, and constituent, and can be downloaded in several formats, with other formats planned (see examples at <http://nadp.isws.illinois.edu/data/annualiso.aspx>). Individual maps are compiled into annual Map Summary reports, and the 2011 Map Summary is also available for download (<http://nadp.isws.illinois.edu/lib/dataReports.aspx>). We print 2,000 copies of the Annual Summary each year, and we have now completed the distribution of the 2010 Map Summary.

**Scientific Meeting (Fall 2011).** At the end of each federal year, a combined business and scientific meeting is held to showcase some of the latest deposition research that occurred during the year. During FY11, the meeting focused on “NADP at the Nexus: Cross System Connections” with a goal of determining new directions for the program (October 25 to 28, 2011 in Providence, Rhode Island). The meeting attracted 130 registered participants, and included six sessions, 30 oral presentations, and 24 posters. Individual talks discussed deposition estimates of other chemical species not currently sampled for, including organic nitrogen, metals, and bromine (new at the time). All presentations, posters, and meeting proceedings are available on the NADP website (<http://nadp.isws.illinois.edu/conf/2011/>).

**Scientific Meeting (Fall 2012).** The latest scientific meeting was held in Portland, ME (October 1-5, 2012, “The NADP Cooperative: State, Local, and tribal Perspectives”). The goal of this meeting was to highlight the non-federal perspectives of the network and data use. The meeting had 139 registered participants, and included eight sessions, 41 oral presentations, and 18 posters. An agriculture/ammonia session discussed better emission inventories, confined animal emission rates, and using isotopes for ammonia deposition source attribution. All presentations, posters, and meeting proceedings are available on the NADP website (<http://nadp.isws.illinois.edu/conf/2012/>). Of specific note for this meeting was a session held on October 5<sup>th</sup> focusing on improving the estimates of total deposition (wet plus dry deposition). This session was very well

attended, and minutes should also be available online soon (<http://nadp.isws.illinois.edu/committees/tdep/minutes.aspx>).

These basic activities fulfilled the project objectives: (1) coordination of three networks; (2) quality assurance to ensure consistency; and (3) analytical, site support, and data validation services for the sites financed directly through this agreement.

Additional Operation Notes. The NADP continues to convert our precipitation gages to an all-digital network, originating with a Technical Committee decision in 2006 (<http://nadp.isws.illinois.edu/newissues/newgages/newequip.aspx>). Currently, the network is operating with approximately 85% new digital networks.

Further, an independent committee conducted an external review of the Mercury Analytical Laboratory during the summer of 2012. Reports of the review were provided at the Fall Meeting 2012, with a formal response and questions provided to the Executive Committee, with final reports forthcoming. Each laboratory and the Program Office (management) are independently reviewed every three years (one every year).

NADP's fifth network, the Ammonia Monitoring Network (AMoN) has agricultural scientists in mind. Ammonia is of great concern regarding agriculture and air pollution. AMoN currently operates 58 sites, and has approximately 10,500 observations of atmospheric ammonia. AMoN's cost-efficient passive measurements can be used to estimate ammonia dry deposition, a process which is being considered ([nadp.isws.illinois.edu/AMoN/](http://nadp.isws.illinois.edu/AMoN/)).

The Central Analytical Laboratory has begun to measure the concentration of bromide ion in all NADP samples as a routine analyte of the NTN and AIRMoN sites. Regular measurements will be released for the 2012 year. Bromide is important to agricultural users, given its fumigant usage.

During the 2012 calendar year, 166 journal articles and reports were generated using the NADP data. These are listed in the Publications section. This is again evidence that NADP is producing data that are both valuable and useful.

The USGS and NADP collaborated on tracking radionuclides wet deposition ( $^{131}\text{I}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ) from the Japanese nuclear incident resulting from the March 2011 earthquake and tsunami. Normal precipitation samples from the NTN, AIRMoN, and MDN were used during the project, and the resulting studies (Wetherbee et al., 2012) can be found on the NADP website. By using the existing infrastructure of the NADP's

networks in a new and important way, measurements were made that greatly added to the body of information on the impact of this accident on U.S. lands and population.

At the Spring 2011 Meeting, the NADP committees voted to modify the maps from an earlier discrete contour map style to a new continuous color gradient map. The new maps are now available going back to 1994, and the older-style maps are also still available through 2010. These maps provide much more information to the depositional community by adding precipitation adjustments for elevation and locations.

U.S. EPA scientists, with NADP, continued special studies to determine whether organic nitrogen deposition can be measured reliably and accurately. The results indicated that the measurements are reliable, and that organic N can be differentiated from the inorganic N in our samples. This will add much needed information to the understanding of N deposition patterns and sources.

A new litterfall mercury monitoring initiative will measure mercury and methyl mercury in forest litterfall (leaves, twigs, etc.). These dry deposition estimates will complement the MDN wet deposition mercury monitoring. Initiation of the trial began in September 2012. Analysis and field support will be provided through the USGS.

### Impacts

As a National Research Support Project, the NADP's most important impact is that our data are used in research, per our research support mission. From January through December 2012, we identified 166 journal articles and reports that used NADP data, maps, and procedures in their own research; for modeling applications, etc.; and for comparison to NADP results. These articles are included in our online database of NADP publications.

Here is a short summary of 11 articles and a listing of theses and dissertations that are of particular interest to the agricultural community.

- 1) Qi et al. (USDA-ARS scientists) developed a carbon-nitrogen cycle module for use in the Great Plains Framework for Agriculture Resource Management model (GPFARM-Range, simulations of forage growth and cow-calf production). This module predicts crop carbon and soil carbon and nitrogen over time. The model was verified against measurements in Wyoming. The model was developed to be used directly with NADP data; observations of ammonium and nitrate are N inputs to the module and system being evaluated.

- 2) Carlo and Norris evaluated the uptake of nitrogen directly by flower petals, showing experimentally that flower petals are very effective at capturing and absorbing atmospheric nitrogen deposited by wet deposition. Using simulated rain per the typical concentrations as measured by NADP, N was incorporated rapidly (in hours) and moved into ovaries and seeds (as shown by N isotopes). This N was very efficiently incorporated into the seeds (44%), as opposed to soil (<10%). A range of NADP-observed precipitation concentrations were used in their experiments.
- 3) Angradi et al. used a straightforward regression model, based upon land use and other sources, to predict the background concentrations of total nitrogen, phosphorus, and suspended solids in the midcontinent Great Rivers (Miss., Ohio, Mo.). These estimates can be used as basic water concentrations before anthropogenic and agricultural additions are made. The modelers used the 2001–2007 NADP nitrate and ammonium observations over the greater Midwest region as model input.
- 4) Han and Allen estimated the input of nitrogen to the Lake Michigan Basin from 1880 through 2000, showing six-fold increases until about 1980, and stable levels since that point. This increase corresponds to large increases in nitrogen fertilizers and atmospheric deposition. Nitrogen deposition was the dominant input early (66% of a modest amount), and is still a very significant input (48% currently). The authors used nitrate and ammonium NADP observations from about 40 sites and 25 years to make their estimates.
- 5) Ketterings et al. (including SAES and Extension scientists) conducted field trials of the application of sulfur-containing fertilizer to alfalfa crops. With application, alfalfa yields increased at several sites, but no increase in dairy output was noted. The authors conclude that soil monitoring of S is important for yield increases. NADP observations of S wet deposition from 12 NY sites were used to monitor the input of S to the systems.
- 6) Lawrence et al. (including USDA and SAES scientists) report early indications of soil recovery from reduced acidic deposition in Northeast forests. Their results suggest the beginnings of pH increases in soils, an ending of calcium loss, decreasing mobilization of aluminum into the B soil horizon, etc. The authors used NADP sulfate and pH observations from five NADP sites from 1985 through 2004.
- 7) Liao et al. developed a chemical transport model to track the movement of agricultural chemicals (nitrate in particular) into groundwater. The model was tested at 14 sites across the country with a variety of soil and cover crop types. The results show vertical profiles of a number of chemical species. Downward nitrate

migration was present at sites with low denitrification rates, and nitrate concentrations in groundwater are, in part, a function of nitrogen application rates. Infiltration rates were determined using several environmental tracers, including chloride. The chloride deposition rates for all sites were developed from long-term NADP Cl observations at each of the sites.

- 8) Moore et al. (SAES and extension scientists) quantified the change in recharge rates in semiarid rangelands with brush management of the surface. The authors conclude that with removal of brush, modest but significant reductions in evapotranspiration and increases in groundwater recharge are realized. The researchers used nine Texas NADP sites and chloride observations as an environmental tracer to determine accurate recharge rates across the State of Texas.
- 9) Yager and McMahon compared the sources of groundwater nitrogen from an agricultural biosolids application project in Colorado. Prior to the addition of biosolids, the major N sources, animal manure, inorganic fertilizer, and atmospheric deposition, were all likely important sources. However, after the application, the biosolids were also a major N source, but the authors could not conclude that biosolids were more important than the animal manure. NADP N data were used to determine the atmospheric deposition source strength over time (back to 1983), and chloride values were used to determine infiltration rates.
- 10) Cai et al. evaluated soil chemistry in a high-elevation forest (TN) to compare trends in soil chemistry to the trends in chemical deposition as measured by NADP. With sulfate deposition decreasing, the soil was not decreasing in sulfate as expected, but still adsorbing sulfate (S sink). This was somewhat surprising, due to the long-term decreasing trend of sulfate (1980 to 2007) in the forest as measured by the NADP site very near the forest.
- 11) Fernandez et al. (SAES scientists) evaluated the response of corn to sulfur fertilizer addition, noting the serious reduction of sulfur deposition as measured by the NADP program. With field-scale plots, the researchers showed that surface soils had reached their full capacity to supply S to corn, and that sulfate migration from the subsoils or atmospheric deposition of S were required to meet the S needs. Some evidence for increased yield was evident with S application.
- 12) During this annual review of publications, we were able to identify four Master's theses and eight Doctoral dissertations that used NADP data and information. These are of particular importance, given the educational role that we were able to support with these students. Each reference is listed in the publications section.

## Publications

Include 166 publications used NADP data or resulted from NRSP-3 activities in 2012. A publicly available online database that lists citations using NADP data is accessible at: <http://nadp.isws.illinois.edu/lib/bibsearch.aspx>.

1. Air Resources Specialists, Inc., 2012. Oil and Gas Leasing in the Wyoming Range: Final Supplemental Environmental Impact Statement, Air Quality Analysis Technical Support Document for Bridger-Teton National Forest, 71 pp.
2. Alam, M. J., & Goodall, J. L., 2012. Toward disentangling the effect of hydrologic and nitrogen source changes from 1992 to 2001 on incremental nitrogen yield in the contiguous United States. *Water Resources Research* 48(4): W04506.
3. Allen, D. J., Pickering, K. E., Pinder, R. W., Henderson, B. H., Appel, K. W., & Prados, A., 2012. Impact of lightning-NO on eastern United States photochemistry during the summer of 2006 as determined using the CMAQ model. *Atmospheric Chemistry & Physics* 12: 1737 - 1758.
4. Amos, H. M., Jacob, D. J., Holmes, C. D., Fisher, J. A., Wang, Q., Yantosca, R. M., et al., 2012. Gas-particle partitioning of atmospheric hg(II) and its effect on global mercury deposition. *Atmospheric Chemistry & Physics* 12(1): 591 - 603.
5. Angradi, T. R., Bolgrien, D. W., Starry, M. A., & Hill, B. H., 2012. Modeled summer background concentration of nutrients and suspended sediment in the mid-continent (USA) great rivers. *JAWRA Journal of the American Water Resources Association* 48(5): 1054 - 1070. doi: 10.1111/j.1752-1688.2012.00669.x.
6. Arnett, H. A., Saros, J. E., & Alisa Mast, M., 2012. A caveat regarding diatom-inferred nitrogen concentrations in oligotrophic lakes. *J Paleolimnology* 47: 277 - 291. doi:10.1007/s10933-011-9576-z.
7. Arundale, R., 2012. The higher productivity of the bioenergy feedstock *Miscanthus x giganteus* relative to *Panicum virgatum* is seen both into the long term and beyond Illinois. Doctoral dissertation, University of Illinois, 116 pp.
8. Bagui, S., Brown, J., Caffrey, J., & Bagui, S., 2012. Designing a relational database for tracking and analysis of atmospheric deposition of mercury and trace metals in the Pensacola (Florida) Bay Watershed. *International Journal of Sustainable Society* 4(3): 240 - 265.
9. Bain, D. J., Yesilonis, I. D., & Pouyat, R. V., 2012. Metal concentrations in urban riparian sediments along an urbanization gradient. *Biogeochemistry* 107(1-3): 67 - 79.
10. Baiser, B., Gotelli, N. J., Buckley, H. L., Miller, T. E., & Ellison, A. M., 2012. Geographic variation in network structure of a nearctic aquatic food web. *Global Ecology & Biogeography* 21(5): 579 - 591.

11. Baker, K. R., & Bash, J. O., 2012. Regional scale photochemical model evaluation of total mercury wet deposition and speciated ambient mercury. *Atmospheric Environment* 49: 151 - 162.
12. Bash, J. O., Cooter, E. J., Dennis, R. L., Walker, J. T., & Pleim, J. E., 2012. Evaluation of a regional air-quality model with bi-directional NH<sub>3</sub> exchange coupled to an agro-ecosystem model. *Biogeosciences Discussions* 9(8): 11375 - 11401.
13. Beaulieu, K. M., Button, D. T., Scudder Eikenberry, B. C., Riva-Murray, K., Chasar, L. C., Bradley, P. M., and Burns, D. A., 2012. Mercury bioaccumulation studies in the National Water-Quality Assessment Program—Biological data from New York and South Carolina, 2005 - 2009: U.S. Geological Survey Data Series 705, 13 p., at <http://pubs.usgs.gov/ds/705/>.
14. Berkelhammer, M., Stott, L., Yoshimura, K., Johnson, K., & Sinha, A., 2012. Synoptic and mesoscale controls on the isotopic composition of precipitation in the western United States. *Climate Dynamics* 38: 433 - 454.
15. Bradley, P. M., Journey, C. A., Lowery, M. A., Brigham, M. E., Burns, D. A., Button, D. T., ... & Riva-Murray, K., 2012. Shallow groundwater mercury supply in a coastal plain stream. *Environmental Science & Technology* 46(14): 7503 - 7511.
16. Brooks, R. T., Eggert, S. L., Nislow, K. H., Kolka, R. K., Chen, C. Y., & Ward, D. M., 2012. Preliminary assessment of mercury accumulation in Massachusetts and Minnesota seasonal forest pools. *Wetlands* 32: 653 - 663.
17. Brown, T. C., & Froemke, P., 2012. Nationwide assessment of nonpoint source threats to water quality. *BioScience* 62(2): 136 - 146.
18. Brown, T. C., & Froemke, P., 2012. Improved measures of atmospheric deposition have a negligible effect on multivariate measures of risk of water-quality impairment: response from Brown and Froemke. *BioScience* 62(7): 621 - 622.
19. Bruder, S. R., 2012. Prediction of spatial-temporal distribution of algal metabolites in Eagle Creek Reservoir, Indianapolis, IN. Doctoral dissertation, Department of Earth Sciences, Indiana University, 142 pp.
20. Bruesewitz, D. A., Tank, J. L., & Hamilton, S. K., 2012. Incorporating spatial variation of nitrification and denitrification rates into whole-lake nitrogen dynamics. *J Geophysical Research*. 117: G00N07, doi:10.1029/2012JG002006.
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27. Castro, M. S., Moore, C., Sherwell, J., & Brooks, S. B., 2012. Dry deposition of gaseous oxidized mercury in western Maryland. *Science of the Total Environment* 417 - 418: 232 - 240.
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29. Chen, C. Y., Driscoll, C. T., & Kamman, N. C., 2012. Mercury hotspots in freshwater ecosystems. *Mercury in the Environment: Pattern and Process*, 143, 340 pp.
30. Chen, J., Hintelmann, H., Feng, X., & Dimock, B., 2012. Unusual fractionation of both odd and even mercury isotopes in precipitation from Peterborough, ON., Canada. *Geochimica et Cosmochimica Acta* 90: 33 - 46.
31. Clark, E., Schlenker, K., & Filardi, C., 2012. Wilderness character monitoring report hyalite porcupine buffalo horn wilderness study area. U.S. Forest Service, Region 1 Report, Gallatin National Forest, 109 pp.
32. Coleman Wasik, J. K., Mitchell, C. P., Engstrom, D. R., Swain, E. B., Monson, B. A., Balogh, S. J., ... & Almendinger, J. E., 2012. Methylmercury declines in a boreal peatland when experimental sulfate deposition decreases. *Environmental Science & Technology* 46(12): 6663 - 6671.
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