

em

The Magazine for Environmental Managers

July 2019

Improving Nitrogen Deposition Budgets in the United States





ACE 2020 GATEWAY TO INNOVATION

Air & Waste Management Association's 113th Annual Conference & Exhibition
June 29 – July 2, 2020 • San Francisco, CA

SAVE THE DATES

The Air & Waste Management Association (A&WMA) proudly invites you to San Francisco, CA, June 29 – July 2, 2020 for its 113th Annual Conference and Exhibition (ACE) with the theme "Gateway to Innovation".

Technical and political challenges often require innovative solutions. California is a global leader in environmental and energy technology and policy, making San Francisco the ideal place for scientists and practitioners from around the world to share ideas and develop solutions for current and future environmental issues.

San Francisco has a history of innovation. In the decades following the 1849 Gold Rush, San Francisco grew rapidly, hosted a world's fair, became a major military and shipbuilding center during World War II, and was the birthplace of the United Nations. The region became an important commercial and cultural center, as well as headquarters for many major corporations. The advent of the Digital Age in the 1980s sparked a new wave of innovation and rapid growth in semiconductor and computer manufacturing, software and internet services, and social media companies, all of which still thrive in the region today.

It is against this backdrop of innovation that environmental initiatives take place in the Bay Area throughout major industry, the private sector, government, and world-class universities. This environmental leadership will be the foundation of ACE 2020, embracing innovation and forward-looking vision to address the challenges posed by climate change, sustainability, and mitigation of environmental impacts while accommodating growth.

The return of the ACE to the City by the Bay after 36 years is an ideal opportunity for environmental professionals to learn the latest information and solutions to help advance our common goal of making the planet a better place for future generations.

Make your plans to be a part of the culmination of environmental innovation.

Visit www.awma.org/ACE2020.





Improving Nitrogen Deposition Budgets for Ecosystem Assessments in the United States

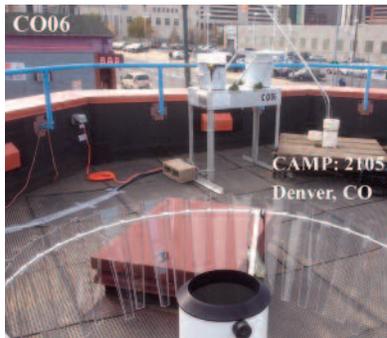
by John T. Walker

Accurate and complete budgets of reactive nitrogen deposition are needed for ecosystem risk assessments, including the development of critical loads for nutrients and acidity and review of the secondary National Ambient Air Quality Standards. In this month's *EM*, we summarize policy-relevant research needed to better understand emissions, air concentrations, and deposition of reactive nitrogen in the United States.



Evolution of Monitoring and Modeling of Reactive Nitrogen Deposition in the United States

by John T. Walker and Greg M. Beachley



Long-Term Trends in Reactive Nitrogen Deposition in the United States

by Greg M. Beachley, Chris M. Rogers, Tom F. Lavery, John T. Walker, and Melissa A. Puchalski



Need for Improved Monitoring of Spatial and Temporal Trends of Reduced Nitrogen

by Melissa A. Puchalski, John T. Walker, Gregory M. Beachley, Mark A. Zondlo, Katherine B. Benedict, Richard H. Grant, Bret A. Schichtel, Christopher M. Rogers, April B. Leytem, Joann Rice, Kristi Morris, James J. Schauer, and Rui Wang

Conference Highlights



Highlights from the Coordinating Research Council's 2019 Mobile Source Air Toxics Workshop

by Susan Collet, S. Kent Hoekman, Seungju Yoon, and Timothy J. Wallington



Highlights from the Coordinating Research Council's 29th Real-World Emissions Workshop

by Susan Collet, Dominic DiCicco, Scott Mason, Megan Beardsley, Naveen Berry, Tom Long, Tao Huai, Matthew Thornton, Radha Purushothaman, Shirish Shimpi, and Seungju Yoon

Departments

Message from the President: Advancing Our Understanding of Reactive Nitrogen Deposition

by Michele E. Gehring, P.E.

Back In Time: July 1999

A look back at this month 20 years ago in *EM* Magazine.

Reactive Nitrogen Deposition



Cover photo: Sonic anemometer above Duke Forest near Chapel Hill, NC. Photo courtesy of Ryan Daly, U.S. Environmental Protection Agency, Office of Research and Development.



Advancing Our Understanding of Reactive Nitrogen Deposition

by Michele E. Gehring, P.E. » president@awma.org

Wow! What an ACE! This year's program really brought together a great combination of technical programming and networking opportunities all with the incredible backdrop of Québec. It really was a tremendous week and I'd be remiss if I didn't take a moment to thank the A&WMA staff and volunteers who spent countless hours in bringing all of those elements together into one largely seamless package. The local host committee (LHC), led by Nicolas Turgeon and Jean-Luc Allard, created a hard act to follow and I sincerely thank each and everyone of you for your tireless efforts on integrating typical ACE content with new and exciting elements unique to Québec and the Canadian side of our border. I'm certain that the LHC team for San Francisco in 2020 will benefit from your hard work and that the conference next year, as well as in the years that follow, will be reshaped from your efforts.

To the members of our Technical Council who work hard to combine the many different papers, panels, and posters into a seamless, congruent program, I also want to thank you. It's hard work pulling the many different ideas together into an organized program and you take on this challenge year after year and that is greatly appreciated. And last, but certainly not least, to the A&WMA staff who spend the week putting out one fire after the next with the aptitude of a professional fire fighter and the stealth of a ninja, thank you! You are a small army that works very hard to pull together all the many pieces of this "Rube Goldberg machine" into a single system with one giant heartbeat and you do so with a professionalism and smile that keep us all going.

If you missed out on this year's conference, look for follow-up programming on our webinar platform. If you made it to ACE and saw or gave a presentation that you think we need to roll out into a webinar or webinar series, please let me or a member of the Board of Directors know. ACE isn't a singular event—it's a place where we can bring together the many different conversations we are having in the

Association, but certainly doesn't need to be the only place we have them.

Now onto the topic at hand! This month, *EM* focuses on the topic of reactive nitrogen deposition (RND), one that has significance on the global scale. Nitrogen, in the proper amounts, serves as a key nutrient to life. But, like many of the other problems we tackle in the environmental community, too much or too little can drive negative effects. Some of the major targets of RND include ecosystem biodiversity, soil acidity, and water quality. Researchers have been hard at work over the past decade to better understand the levels of RND that are occurring and to translate those levels into measures of effect. What are the threshold levels for different types of ecosystems, are there points of no return where an ecosystem will be irreversibly damaged, or how much time will it take for an ecosystem to respond to measured differences in deposition? All of these questions and many more are being tackled in laboratories and field research programs throughout the United States, Europe, and Asia. At ACE, we had the opportunity to hear about studies that are being conducted on the impacts of RND in our U.S. National Parks. And in this issue of *EM*, we continue that conversation and explore the topic in even more detail.

As I send you off to explore the pages of this month's issue, I encourage you to reach out and let me know what else you'd like to hear from the Association on this topic. Are there partners we should be reaching out to much like we did for the wildfires issue to provide a better breadth of coverage on the topic? Are there modeling programs we should be running tutorials and workshops on? Should we make sure our delegates at COP25 in Santiago are targeting sessions on this issue? If you have an expertise in this area or just want to learn more, please give me a call, shoot me an email, or track down one of our Board members. Expanding topics of interest to our members is always a priority! **em**



Clean Air Status and Trends Network (CASTNET, GTH161), National Atmospheric Deposition Program/National Trends Network (NTN, CO10), National Atmospheric Deposition Program/Ammonia Monitoring Network (AMoN, CO10) site in Gunnison County, CO.
Photo courtesy of U.S. Environmental Protection Agency, CASTNET.

Improving Nitrogen Deposition Budgets for Ecosystem Assessments in the United States

An overview of policy-relevant research needed to better understand emissions, air concentrations, and deposition of reactive nitrogen in the United States.

Accurate and complete budgets of reactive nitrogen (Nr) deposition are needed for ecosystem risk assessments, including the development of critical loads for nutrients and acidity and review of the secondary National Ambient Air Quality Standards. Members of the National Atmospheric Deposition Program Total Deposition Science Committee (NADP/TDep), along with collaborators from federal agencies and academia, recently completed a review of the state of the science of Nr deposition budgets in the United States. The report highlights that while much progress has been made in improving deposition budgets over the past decade, further improvements remain limited by important data and knowledge gaps. The report is categorized into specific areas of deposition research where these gaps are identified and briefly discussed in terms of their importance and, where applicable, potential research paths are identified.

In this issue of *EM*, we summarize several overarching examples of policy-relevant research needed to better understand emissions, air concentrations, and deposition of Nr, and to improve models and measurement-model fusion methods for estimating total and speciated Nr deposition for ecosystem assessments.

Evolution of Nr Monitoring and Modeling

The first article by Walker and Beachley summarizes advancements in both measurements and models needed to further improve nitrogen deposition budgets in the United States. Examples include the continued evolution of monitoring to characterize concentrations and deposition of reduced forms of nitrogen (NHx = ammonia (NH₃) and particulate ammonium (NH₄⁺)) and to better understand deposition in urban environments. An important advancement in chemical transport models is the estimation of land-use-specific deposition

for ecosystem assessments, which will help to reduce uncertainty in modeled dry deposition estimates.

Long-Term Trends in Nr Deposition

The next article by Beachley, et al. describes trends in emissions, air concentrations, and deposition of Nr species across the United States. Trends in deposition of oxidized nitrogen are reflective of downward trends in emissions since 2000. Patterns of NH₃ emissions and NHx deposition are less consistent. Though NH₃ emission inventories suggest a slight decrease since 2000, measured wet deposition of NH₄⁺ and modeled dry deposition of NH₃ have increased. Improved measurements, both for emissions and ambient concentrations, as well as the incorporation of satellite monitoring data, will help to reconcile differences in these trends.

Need for Improved Monitoring of Spatial and Temporal Trends

The importance of NHx to total Nr deposition budgets has increased over time as emissions of oxidized nitrogen have declined. The third article by Puchalski, et al. explores needs and opportunities for expanding ground-based monitoring to better understand spatial gradients and processes of NHx deposition over local-to-regional scales. Integration of ground- and satellite-based NH₃ measurements, as well as improved agricultural emissions inventories, will be important for better resolving NHx trends.

This month's feature articles briefly summarize several important research needs in Nr deposition science. For more detailed information on these and other topics, including a summary of current regulations relevant to Nr deposition, we encourage readers to refer to the above-mentioned report available at the NADP website at <http://nadp.slh.wisc.edu/committees/tdep/reports/nrDepWhitePaper.aspx>. **em**

John T. Walker, Ph.D., is a senior research chemist with the U.S. Environmental Protection Agency's Office of Research and Development, Air and Energy Management Division.

Disclaimer: The views expressed in this article are those of the author and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.



In Next Month's Issue...

NSR Reform 2.0

The U.S. Environmental Protection Agency's (EPA) New Source Review (NSR) program has been targeted for reform in the past, and additional changes are impending. Some NSR Reform programs were enacted in the early 2000s. The current round of "NSR Reform" seems focused on even broader changes to the program than previous reform efforts. The August issue will give multiple perspectives on the current NSR Reform efforts: from industry, environmental groups, to EPA, and states. How will these policies affect the permitting process, and what will be the aggregate effect on the environmental protection and economic priorities?



Clean Air Status and Trends Network (CASTNET, SPD111), National Atmospheric Deposition Program/National Trends Network (NTN, TN04), National Atmospheric Deposition Program/Ammonia Monitoring Network (AMoN, TN04) site in Claiborne County, TN.
Photo courtesy of U.S. Environmental Protection Agency, CASTNET.

Evolution of Monitoring and Modeling of Reactive Nitrogen Deposition in the United States

by John T. Walker and Greg M. Beachley

The authors consider three overarching examples where continued evolution of monitoring and modeling are needed to improve nitrogen deposition budgets.

Deposition of reactive nitrogen (Nr)—that is, all forms of nitrogen that are biologically, photochemically, or radiatively active—can contribute to eutrophication and acidification, changes in biodiversity, reduced resilience to climate variability, and other impacts in terrestrial and aquatic ecosystems.¹ Accurate and complete atmospheric deposition budgets of nutrients and acidity are fundamental to critical load frameworks, which are used by the U.S. Environmental Protection Agency (EPA) to quantitatively link deposition to negative effects on soils, water, vegetation, visibility, and other aspects of public welfare.

The critical load describes the amount of atmospheric deposition to an ecosystem below which harmful effects do not occur and has become an important component of the review of the secondary U.S. National Ambient Air Quality Standards (NAAQS).¹⁻⁴ Critical loads are also used by land management agencies to guide air pollution management for national parks, forests, and wilderness areas.^{5,6} An estimate of total Nr deposition is needed to determine if an ecosystem is receiving more or less Nr than the critical load (i.e., the exceedance). Nr deposition budgets used for critical loads assessments are developed from measurements, models, and combinations of the two.⁷

Members of the National Atmospheric Deposition Program Total Deposition Science Committee (NADP/TDep), along with collaborators from federal agencies and academia, recently completed a detailed report on the state of the science of Nr deposition budgets in the United States.⁸ The report highlights that while much progress has been made in improving deposition budgets over the past decade, further improvements remain limited by important data and knowledge gaps. Policy-relevant research needs identified in the report address monitoring, process-level measurements, modeling, and source apportionment. In this article, we summarize three overarching examples where continued evolution of monitoring and modeling are needed to inform changing trends in the atmospheric composition of Nr, better understand spatial patterns of deposition in urban environments, and improve the accuracy of modeled deposition estimates to account for specific land-types.

Sources, Patterns, and Processes of NH_x Deposition

Due to the decline in emissions of oxides of nitrogen (NO_x) under the U.S. Clean Air Act, reduced forms of atmospheric Nr (NH_x = ammonia (NH₃) + ammonium (NH₄⁺)) are becoming an increasingly important component of Nr deposition⁹ across the United States. However, development of a more complete understanding of the magnitude and spatial patterns of NH_x deposition is limited by the completeness and accuracy of NH₃ emission inventories, as well as monitoring and modeling of NH_x deposition. This is particularly

true of agricultural sources and regions, as confined animal feeding operations (CAFOs, 55%) and fertilized soils (25%) account for approximately 80% of NH₃ emissions in the United States.¹⁰ While increasing trends in NH₃ concentrations have been documented,^{11,12} linking these trends to changes in emissions is difficult due to limitations in inventories.^{13,14} Additionally, quantifying the dry component of NH_x deposition remains difficult due to uncertainties in modeling the bidirectional air–surface exchange of NH₃.¹⁵ While models are improving, there remains a paucity of flux measurement datasets by which to evaluate and improve air–surface exchange models for North American ecosystems.¹⁶

As further described in an accompanying article elsewhere in this issue, better characterization of the spatial variability of atmospheric NH₃ concentrations in agricultural areas is needed for evaluation and improvement of emission inventories, improvement of chemical transport models (CTMs) to more accurately simulate particulate matter formation and deposition, and treatment of NH₃ dry deposition in measurement-model fusion approaches.⁷ The NADP Ammonia Monitoring Network (AMoN), which began in 2007, is currently the only national monitoring effort for NH₃ in the United States (currently ~100 sites). However, most of the sites are located in the eastern United States, many in counties with relatively low NH₃ emissions. Broad geographical gaps in monitoring exist over areas of the West and Midwest, where agricultural NH₃ emissions are large, and many smaller hot-spot areas are also missed.

As shown in Figure 1, landscapes often contain a patchwork of agricultural sources and natural land use, creating high spatial and temporal variability in NH₃ concentrations and deposition that can be challenging for both monitoring and modeling. Expansion of AMoN monitoring in agricultural areas, informed by satellite measurements and emission inventories to identify the most valuable and representative new monitoring locations, would help to better characterize spatial and temporal patterns in agricultural regions at relatively low cost.

Urban Deposition Issues

The primary monitoring networks that support deposition assessments in the United States—NADP and Clean Air Status and Trends Network (CASTNET)—were originally designed in the 1970s and 1980s to track changes in acidic deposition resulting from NO_x and sulfur oxides (SO_x) emission reductions from electricity generating units. Monitoring sites were therefore intentionally located in primarily rural locations to be regionally representative. For this reason, urban areas are not well characterized by these networks and deposition in urban environments is instead extrapolated from measurements in non-urban locations (e.g., NADP wet deposition mapping protocol) or modeled (e.g., TDep dry deposition⁷).

However, both measurements and models show urban areas (Figure 1, lower right) as hot-spots for deposition of oxidized and reduced forms of Nr, owing to a high density of mobile source emissions. Numerous studies have documented gradients in Nr deposition from urban to rural areas in the United States (e.g., Los Angeles,¹⁷⁻¹⁹ New York,²⁰ Boston,^{21,22} Phoenix,²³ and Salt Lake City²⁴).

Expanded routine monitoring is needed to better understand the role of atmospheric Nr deposition in urban water quality and to better inform management of total maximum daily loads (TMDL) and other water quality issues downstream.²⁵ This would involve the expansion of networks such as NADP National Trends Network (NTN) in urban areas, which would benefit from coordination of deposition and water quality monitoring.²⁶ Air concentrations of oxidized Nr (NO_x, NO_y, NO₂) are already monitored in many urban areas (e.g., EPA Air Quality System <www.epa.gov/aqs>). Utilization of these datasets in measurement-model fusion techniques such as NADP TDep⁷ is needed. Existing monitoring could be complemented with urban sampling of NH₃ using low-cost passive sampling such as employed by AMoN²⁷ to better understand patterns of NH_x deposition.¹⁹ Improvements to deposition algorithms in CTMs will also be needed to more accurately represent Nr dry deposition in urban environments.

Land-Use-Specific Deposition Estimates

CTMs and measurement-model fusion techniques⁷ used for

North American deposition assessments provide estimates of deposition as averages over model grid cells. Grid cells may be on the order of 10 km × 10 km or larger in size and often contain multiple types of land use and land cover, each of which has different physical, biological, and biogeochemical characteristics that affect air–surface exchange. Through their influence on air–surface exchange, these characteristics can result in large differences in deposition among the ecosystems present in the cell. To estimate fluxes to the grid cell, models average sub-grid variability in land surface characteristics or the deposition velocities derived from the model, leading to often large differences between grid-average and ecosystem-specific fluxes. Calculation of a critical load exceedance for a specific ecosystem using a grid-average deposition estimate may therefore contain large uncertainty.

Differences may be particularly large for species that deposit rapidly, such as nitric acid (HNO₃), or that depend on biogeochemical characteristics of the vegetation and soil such as NH₃. Deposition of HNO₃ is limited primarily by turbulent transfer from the atmosphere to the receptor surface, the resistance to deposition being a strong function of the roughness and surface area of the vegetation. HNO₃ will therefore deposit more rapidly to a forest (Figure 1, bottom left) than a grass field. Recent studies show that deposition of HNO₃ to forests can differ substantially from the corresponding grid average value,^{28,29} highlighting the impact of sub-grid heterogeneity and model grid size on deposition estimates from CTMs.

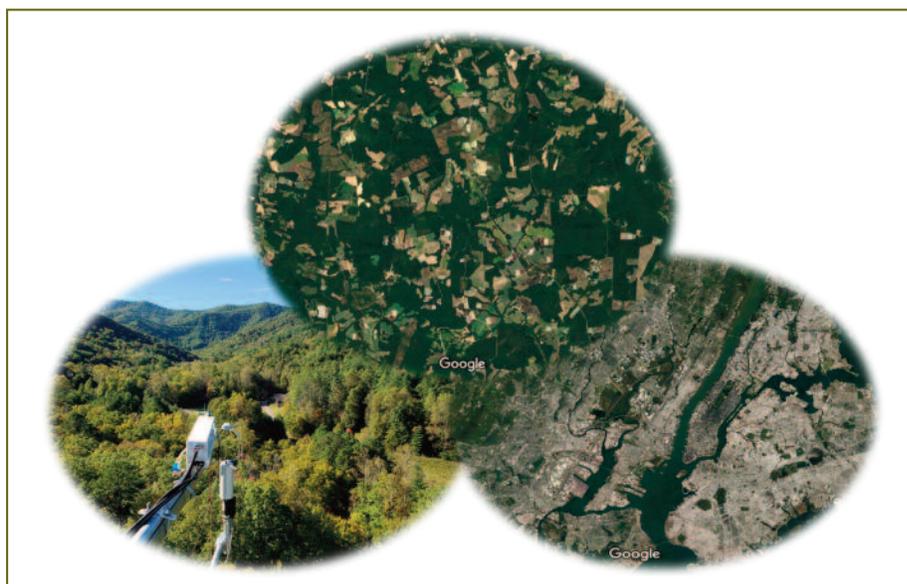


Figure 1. Examples of landscapes where improvements in monitoring and modeling of Nr deposition are needed: (1) mixed agricultural (light colored fields and CAFOs) and natural land use types (top center); (2) rural forest (bottom left); and (3) highly urbanized (bottom right).

Source: Images of agricultural and urban landscapes attributed to Google DigitalGlobe and TerraMetrics Map Data.

NH₃ is exchanged bidirectionally with the surface depending on the difference between the atmospheric concentration and the surface compensation point, which is a function of the nitrogen status and acidity of the exchange surface.¹⁵ While forests may be net sinks for atmospheric NH₃, crops are expected to be net sources due to higher nitrogen content of the soil and vegetation resulting from fertilization.³⁰ In model grid cells containing a mix of crops and natural land use types (Figure 1, top center), the grid-average flux may therefore be much different than the actual flux to the natural ecosystems. These studies highlight the need for CTMs and measurement-model fusion techniques to output land-use-specific fluxes for

critical load applications, an option that is becoming available in newer versions of CTMs.^{28,29,31}

These brief examples highlight aspects of monitoring and modeling that must continue to progress to reduce uncertainties in Nr deposition budgets used for policy

assessments in the United States. Additional detail on these and other topics can be found in the recent EPA report on the subject⁸ available at the National Atmospheric Deposition Program website at <http://nadp.slh.wisc.edu/committees/tdep/reports/nrDepWhitePaper.aspx>.^{em}

John T. Walker is with the U.S. Environmental Protection Agency's (EPA) Office of Research and Development in Durham, NC.

Greg M. Beachley is with EPA's Office of Air and Radiation in Washington, DC. E-mail: walker:johnt@epa.gov.

Disclaimer: The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency (EPA).

References

1. *Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria*; EPA/600/R-08/082F; U.S. Environmental Protection Agency, Research Triangle Park, NC, 2008.
2. Scheffe, R.D.; Lynch, J.A.; Reff, A.; Kelly, J.T.; Hubbell, B.; Greaver, T.L.; Smith, J.T., 2014. The Aquatic Acidification Index: A new regulatory metric linking atmospheric and biogeochemical models to assess potential aquatic ecosystem recovery; *Water Air Soil Pollut.* 2014, 225, 1838.
3. Rea, A.W.; Davis, C.; Evans, D.; Heninger, B.; Van Houtven, G. Using ecosystem services to inform decisions on U.S. Air Quality Standards; *Environ. Sci. Technol.* 2012, 46, 6481-6488.
4. *Integrated Review Plan for the Secondary National Ambient Air Quality Standards for Ecological Effects of Oxides of Nitrogen, Oxides of Sulfur and Particulate Matter*; EPA 452/R-17-002; National Center for Environmental Assessment and Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, 2017; <https://www3.epa.gov/ttn/naaqs/standards/no2so2sec/data/lrp-nox-sox-pm-eco.pdf>.
5. Blett, T.F.; Lynch, J.A.; Pardo, L.H.; Huber, C.; Haeuber, R.; Pouyat, R. FOCUS: A pilot study for national-scale critical loads development in the United States; *Environ. Sci. Pol.* 2014, 38, 225-236.
6. Pardo, L.H.; Fenn, M.; Goodale, C.L.; Geiser, L.H.; Driscoll, C.T.; Allen, E.; Baron, J.; Bobbink, R.; Bowman, W.D.; Clark, C.; Emmett, B.; Gilliam, F.S.; Greaver, T.; Hall, S.J.; Lilleskov, E.A.; Liu, L.; Lynch, J.; Nadelhoffer, K.; Perakis, S.; Robin-Abbott, M.J.; Stoddard, J.; Weathers, K.; Dennis, R.L. Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States; *Ecolog. Appl.* 2011, 21, 3049-3082.
7. Schwede, D.B.; Lear, G.G. A novel hybrid approach for estimating total deposition in the United States; *Atmos. Environ.* 2014, 92, 207-220.
8. Walker, J.T.; Beachley, G.M.; Amos, H.M.; Baron, J.S.; Bash, J.; Baumgardner, R.; Bell, M.D.; Benedict, K.B.; Chen, X.; Clow, D.W.; Cole, A.; Coughlin, J.G.; Cruz, K.; Daly, R.W.; Decina, S.M.; Elliott, E.M.; Fenn, M.E.; Ganzeveld, L.; Gebhart, K.; Isil, S.S.; Kerschner, B.M.; Larson, R.S.; Lavery, T.; Lear, G.G.; Macy, T.; Mast, M.A.; Mishoe, K.; Morris, K.H.; Padgett, P.E.; Pouyat, R.V.; Puchalski, M.; Pye, H.O.T.; Rea, A.W.; Rhodes, M.F.; Rogers, C.M.; Saylor, R.; Scheffe, R.; Schichtel, B.A.; Schwede, D.B.; Sextone, G.A.; Sive, B.C.; Templer, P.H.; Thompson, T.; Tong, D.; Wetherbee, G.A.; Whitlow, T.H.; Wu, Z.; Yu, Z.; Zhang, L. *Science needs for continued development of total nitrogen deposition budgets in the United States*; EPA 601/R-19/001; U.S. Environmental Protection Agency, Washington, DC, 2019; <http://nadp.slh.wisc.edu/committees/tdep/reports/nrDepWhitePaper.aspx>.
9. Li, Y.; Schichtel, B.A.; Walker, J.T.; Schwede, D.B.; Chen, X.; Lehmann, C.M.B.; Puchalski, M.A.; Gay, D.A.; Collett, J.L. Increasing importance of deposition of reduced nitrogen in the United States; *Proc. Nat. Acad. Sci. USA* 2016, 113, 5874-5879.
10. U.S. Environmental Protection Agency, 2014. See <https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data>.
11. Butler, T.; Vermeylen, F.; Lehmann, C.M.; Likens, G.E.; Puchalski, M. Increasing ammonia concentration trends in large regions of the USA derived from the NADP/AMoN network; *Atmos. Environ.* 2016, 146, 132-140.
12. Warner, J.X.; Dickerson, R.R.; Wei, Z.; Strow, L.L.; Wang, Y.; Liang, Q. Increased atmospheric ammonia over the world's major agricultural areas detected from space; *Geophys. Res. Letts.* 2017, 44.
13. Xing, J.; Pleim, J.; Mathur, R.; Pouliot, G.; Hogrefe, C.; Gan, C.-M.; Wei, C. Historical gaseous and primary aerosol emissions in the United States from 1990 to 2010; *Atmos. Chem. Phys.* 2013, 13, 7531-7549.
14. Zhang, Y.; Mathur, R.; Bash, J.O.; Hogrefe, C.; Xing, J.; Roselle, S.J. Long-term trends in total inorganic nitrogen and sulfur deposition in the US from 1990 to 2010; *Atmos. Chem. Phys.* 2018, 18, 9091-9106.
15. Flechard, C.R.; Massad, R.-S.; Loubet, B.; Personne, E.; Simpson, D.; Bash, J.O.; Cooter, E.J.; Nemitz, E.; Sutton, M.A. Advances in understanding, models and parameterizations of biosphere-atmosphere ammonia exchange; *Biogeosciences* 2013, 10, 5183-5225.
16. Zhang, L.; Wright, L.P.; Asman, W.A.H. Bi-directional air-surface exchange of atmospheric ammonia: A review of measurements and a development of a big-leaf model for applications in regional-scale air-quality models; *J. Geophys. Res. Atmos.* 2010, 115, D20310.
17. Padgett, P.E.; Allen, E.B.; Bytnerowicz, A.; Minich, R.A. Changes in soil inorganic nitrogen as related to atmospheric nitrogenous pollutants in southern California; *Atmos. Environ.* 1999, 33, 769-781.
18. Bytnerowicz, A.; Johnson, R.F.; Zhang, L.; Jenerette, G.D.; Fenn, M.E.; Schilling, S.L.; Gonzalez-Fernandez, I. An empirical inferential method of estimating nitrogen deposition to Mediterranean-type ecosystems: the San Bernardino Mountains case study; *Environ. Pollut.* 2015, 203, 69-88.
19. Fenn, M.E.; Bytnerowicz, A.; Schilling, S.L.; Vallano, D.M.; Zavaleta, E.S.; Weiss, S.B.; Morozumi, C.; Geiser, L.H.; Hanks, L. On-road emissions of ammonia: An underappreciated source of atmospheric nitrogen deposition; *Sci. Total Environ.* 2018, 625, 909-919.
20. Lovett, G.M.; Traynor, M.M.; Pouyat, R.V.; Carreiro, M.M.; Zhu, W.-X.; Baxter, J.W. Atmospheric deposition to oak forests along an urban-rural gradient; *Environ. Sci. Technol.* 2000, 34, 4294-4300.
21. Templer, P.H.; McCann, T.M. Effects of the hemlock woolly adelgid on nitrogen losses from urban and rural northern forest ecosystems; *Ecosystems* 2010, 13, 1215-1226.
22. Rao, P.; Hutryra, L.R.; Raciti, S.M.; Templer, P.H. Atmospheric nitrogen inputs and losses along an urbanization gradient from Boston to Harvard Forest, MA; *Biogeochemistry* 2014, 121, 229-245.
23. Lohse, K.A.; Hope, D.; Sponseller, R.; Allen, J.O.; Grimm, N.B. Atmospheric deposition of carbon and nutrients across an arid metropolitan area; *Sci. Total Environ.* 2008, 402, 95-105.
24. Hall, S.J.; Maurer, G.; Hoch, S.W.; Taylor, R.; Bowling, D.R. Impacts of anthropogenic emissions and cold air pools on urban to montane gradients of snow-pack ion concentrations in the Wasatch Mountains, Utah; *Atmos. Environ.* 2014, 98, 231-241.
25. Howarth, R.W. *Atmospheric deposition and nitrogen pollution in coastal marine ecosystems*, *Acid in the Environment*; Springer U.S., 2007; pp. 97-116.
26. Amos, H.M.; Miniati, C.F.; Lynch, J.; Compton, J.; Templer, P.H.; Sprague, L.A.; Shaw, D.; Burns, D.; Rea, A.; Whitall, D.; Myles, L.; Gay, D.; Nilles, M.; Walker, J.; Rose, A.K.; Bales, J.; Deacon, J.; Pouyat, R. What goes up must come down: Integrating air and water quality monitoring for nutrients; *Environ. Sci. Technol.* 2018, 52, 11441-11448.
27. Puchalski, M.A.; Rogers, C.M.; Baumgardner, R.; Mishoe, K.P.; Price, G.; Smith, M.J.; Watkins, N.; Lehmann, C.M. A statistical comparison of active and passive ammonia measurements collected at Clean Air Status and Trends Network (CASTNET) sites; *Environmental Sciences: Process & Impacts* 2015, 17, 358-369.
28. Schwede, D.; Simpson, D.; Tan, J.; Fu, J.; Dentener, F.; Du, E.; deVries, W. Spatial variation of modelled total, dry, and wet nitrogen deposition to forest at global scale; *Environ. Pollut.* 2018, 243, 1287-1301.
29. Paulot, F.; Malyshev, S.; Nguyen, T.; Crouse, J.D.; Shevliakova, E.; Horowitz, L.W. Representing sub-grid scale variations in nitrogen deposition associated with land use in a global Earth System Model: Implications for present and future nitrogen deposition fluxes over North America; *Atmos. Chem. Phys.* 2018, 18, 17963-17978.
30. Bash, J.O.; Cooter, E.J.; Dennis, R.L.; Walker, J.T.; Pleim, J.E. Evaluation of a regional air-quality model with bidirectional NH₃ exchange coupled to an agroecosystem model; *Biogeosciences* 2013, 10, 1635-1645.
31. Bash, J.O.; Schwede, D.; Campbell, P.; Spero, T.; Appel, W.; Pinder, R. Introducing the Surface Tiled Aerosol and Gaseous Exchange (STAGE) dry deposition option for CMAQ v5.3. Presented at the 2018 Community Modeling and Analysis System (CMAS) Conference, October 22-24, 2018, Chapel Hill, NC.

C006



CAMP: 2105 Broadway
Denver, CO

Urban wet deposition monitoring station, Denver, CO.
Photo courtesy of Gregory Wetherbee, U.S. Geological Survey.

Long-Term Trends in Reactive Nitrogen Deposition in the United States

by Greg M. Beachley, Chris M. Rogers, Tom F. Lavery, John T. Walker, and Melissa A. Puchalski

The authors identify several examples where improvements in monitoring, modeling, and emissions inventories are needed to better characterize the linkages between trends in emissions and changes in the atmospheric composition of reactive nitrogen.

Long-term monitoring of ambient air quality and deposition is necessary to characterize trends in human and ecosystem exposure and to gauge the effectiveness of air pollution control programs. Such datasets are rare because of the difficulty and capital required to consistently and accurately collect and analyze samples over time from a spatially adequate number of regionally representative sites. Most of the national air pollutant monitoring networks producing these datasets were established in the 1970s and 1980s and focused on the human health-based U.S. National Ambient Air Quality Standards (NAAQS) criteria pollutants (e.g., sulfur dioxide [SO₂], nitrogen dioxide [NO₂], ozone [O₃], and particulate matter < 2.5 μm [PM_{2.5}]) or reporting acid rain trends and visibility impairment.

Under Title IV of the U.S. Clean Air Act Amendments (CAAA), electric generating units (EGU) were required to make significant reductions in emissions of SO₂ and oxides of nitrogen (NO_x; i.e., nitric oxide [NO] and nitrogen dioxide [NO₂]). While NO_x has continued to be regulated under stationary and mobile emissions programs (e.g., NO_x Budget Trading Program), reduced nitrogen (NH_x; i.e., particulate ammonium [pNH₄] plus gaseous ammonia [NH₃]) remains unregulated despite its contributions to PM_{2.5} formation and total reactive nitrogen (Nr) deposition. Several long-term monitoring networks have measured components of Nr species for several decades (see Table 1).

While monitoring data are used to assess regional long-term trends in air concentrations¹ and wet deposition of some Nr species,² the NADP Total Deposition (TDep) measurement-model fusion method³ is widely used for assessing trends in total (wet + dry) Nr deposition in the United States. Briefly, the TDep method combines measured concentrations and wet deposition with modeled values where measurements are lacking (spatial gaps or unmeasured species).

In this article, we use measurements, TDep products, and emission inventories to discuss current trends in atmospheric

concentrations and deposition of Nr and their relationship to trends in emissions. This analysis identifies several examples where improvements in monitoring, modeling, and emissions inventories are needed to better characterize the linkages between trends in emissions and changes in the atmospheric composition of Nr.

Current Monitoring Trends in Emissions, Ambient Concentrations, and Deposition

Annual emissions of SO₂ and NO_x have decreased substantially (by 83% and 57%, respectively) from the period from 1990–1992 to 2014–2016 (see Figure 1). This is attributable to EGU controls (i.e., EGU emission reductions of 85% for SO₂ and 77% for NO_x),⁴ market-driven changes to cleaner fuels, and mobile source controls (i.e., mobile source reductions of 89% for SO₂ and 46% in NO_x).⁴

This decline is reflected in the long-term monitoring of ambient concentrations over the same period. The decreasing SO₂ concentration trend measured at eastern CASTNET sites (86%; see Figure 2 and summarized in Table 2) shows a linear relationship between EGU emissions and ambient concentrations (R²= 99%).⁵ Data that support linkages between emissions and environmental results provide accountability for regulators and the regulated community.

Deriving this type of relationship between emissions and concentrations is more convoluted for Nr species. Atmospheric processing converts the NO_x emitted by sources (reported by emissions monitors) to a diverse number of oxidized N compounds (NO_y), which monitoring networks either measure as total NO_y (by chemical conversion of all NO_y compounds to NO prior to detection) or as a fraction of NO_y (e.g., filter-based methods report out on total nitrate [the sum of nitric acid (HNO₃) and particulate nitrate (pNO₃)]). Also, NO_x emissions are more distributed across source types (e.g., 26% EGUs, 52% transportation, 22% other in 1990)⁴ (Figure 1). Large decreases in NO_x emissions during the period from 1990–1992 to 2014–2016 are reflected in a



Annual emissions of SO₂ and NO_x have decreased substantially from the period 1990 to 2016. This is attributable to EGU controls, market-driven changes to cleaner fuels, and mobile source controls.

marked decrease in ambient concentrations of total nitrate (48%) at CASTNET eastern reference sites (Figure 2), and in NO₂ satellite observations.⁶

For NH_x species, emission sources emit NH₃, which in the

atmosphere can readily convert to pNH₄ or remain as NH₃ depending on meteorological conditions and availability of acidic pollutants as precursors to pNH₄. Monitoring networks need to measure both forms to accurately represent NH_x. CASTNET ambient pNH₄ concentrations show a similar

Table 1. Existing U.S. monitoring networks that measure components of reactive nitrogen (Nr) in the atmosphere or precipitation (wet deposition). Data from these networks are used by state, local, and federal agencies; researchers; and industries to assess trends in atmospheric pollution and deposition.

Network	Nr Measurements	Measurement Interval	Website
Clean Air Status and Trends Network (CASTNET)	Ambient concentrations of pNH ₄ ⁺ , particulate nitrate (pNO ₃ ⁻), nitric acid (HNO ₃)	Weekly	https://epa.gov/castnet
National Atmospheric Deposition Program (NADP) National Trends Network (NTN)	Concentrations of NO ₃ ⁻ and NH ₄ ⁺ in precipitation; precipitation amounts	Weekly	http://nadp.slh.wisc.edu/NTN/
NADP's Atmospheric Integrated Research Monitoring Network (AIRMoN)	Concentrations of NO ₃ ⁻ and NH ₄ ⁺ in precipitation; precipitation amounts	Daily (event-based)	http://nadp.slh.wisc.edu/AIRMoN/
NADP's Ammonia Monitoring Network (AMoN)	Ambient concentrations of NH ₃	Bi-weekly	http://nadp.slh.wisc.edu/AMoN/
Chemical Speciation Network (CSN)	Ambient concentrations of pNO ₃ ⁻ , pNH ₄ ⁺	Daily (1:3 or 1:6 day)	https://www3.epa.gov/ttn/amtic/speciepg.html
Interagency Monitoring of Protected Visual Environments (IMPROVE)	Ambient concentrations of pNO ₃ ⁻ , particulate nitrite (pNO ₂)	Daily (1:3 day)	http://vista.cira.coloradostate.edu/improve
National Core (NCore) Multipollutant Network; State and Local Air Monitoring Stations (SLAMS); National Air Monitoring Stations (NAMS)	Concentrations of NO, total oxidized nitrogen (NO _y); PM speciation (CSN or IMPROVE)	Hourly	https://www3.epa.gov/ttn/amtic/ncore ; https://www3.epa.gov/airquality/montring.html
Photochemical Assessment Monitoring Stations (PAMS)	Concentrations of NO, NO _y , NO _x	Hourly	https://www3.epa.gov/ttn/amtic/pamsmain.html
Near-road NO ₂ Monitoring	Concentrations of NO ₂	Hourly	https://www3.epa.gov/ttnamti1/nearroad.html

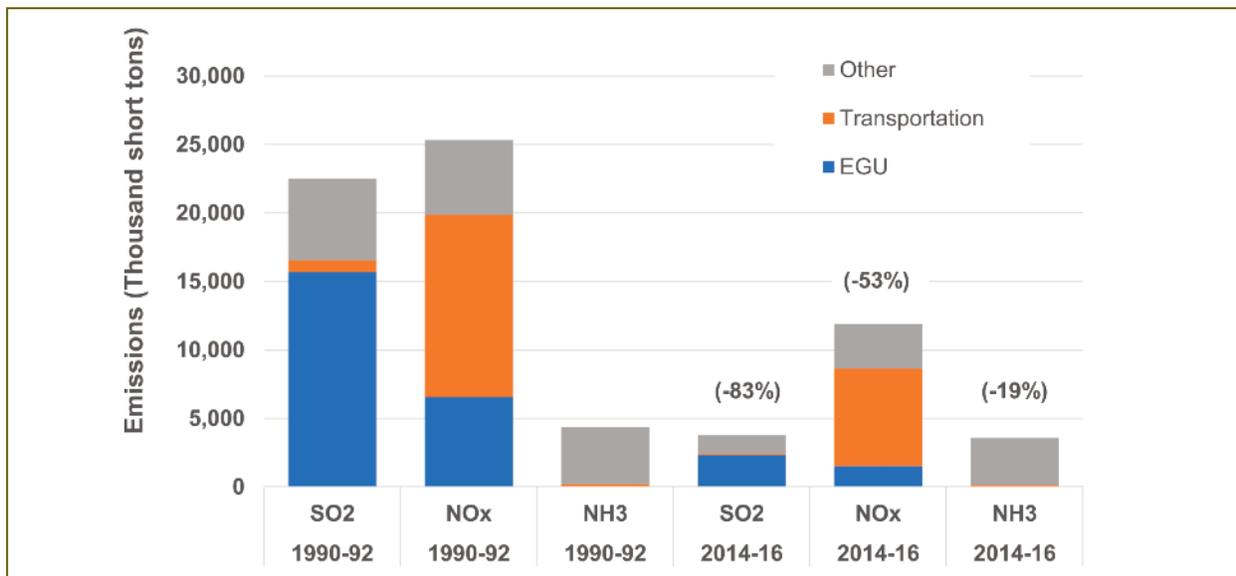


Figure 1. Three-year averaged annual emissions trends for SO₂, NO_x, and NH₃ by source category.⁴

Note: Source categories are grouped as regulated EGUs, transportation, and other, which includes everything from fuel combustion from non-EGU sources, industrial processes, and agricultural sources to events such as wildfires and prescribed burns. The percent decrease in overall emissions is noted above the 2014-16 bars.

decreasing trend (63%) as those reported for SO₂ and total nitrate (Figure 2), yet NH₂ emissions have decreased at a much slower rate (-19%) since 1990–1992.⁴ Measured annual ambient NH₃ concentrations at 21 NADP/AMoN sites with long-term sampling records increased 24% from 2008–2010 to 2014–2016 (see Figure 3). An increasing NH₂ trend (7 ± 2%) was also identified in a study on similar sites that accounted for variability in seasonality and regional location.⁸

Trends in total (wet + dry) deposition in the United States were derived from TDep results and should be reflective of those for emissions and ambient concentrations. Total Sulfur

(S) deposition decreased by 58% from 2000–2002 to 2014–2016 and total NO_y deposition decreased by 35% over the same period, showing significant but less dramatic trends than measured concentrations (see Figure 4; summarized in Table 2). However, total NH_x deposition increased by 30% over the same time period, and comprised a decrease in dry pNH₄ deposition (-17%) and increases in wet NH₄⁺ deposition (+24%) and dry NH₃ deposition (+54%), which contribute 2%, 30%, and 18% to the total Nr budget, respectively (Figure 4).

Ambient NH₃ can be entrained in precipitation, thus higher

Table 2. Summary of percent differences for oxidized sulfur, oxidized nitrogen, and reduced nitrogen in emissions, concentrations, and total deposition over different time periods of comparison. All percent differences are obtained from three-year averages at the beginning and end of the time period as indicated.

Species	Time Period	Emissions	Concentrations	Total Deposition
SO ₂	1990–92 to 2014–16	-83	-86	-
	2000–02 to 2014–16	-76	-80	-58 [◊]
NO _y	1990–92 to 2014–16	-53 ^ζ	-48 [¥]	-
	2000–02 to 2014–16	-48 ^ζ	-48 [¥]	-35
NH _x	1990–92 to 2014–16	-19 [†]	-63 [‡]	-
	2000–02 to 2014–16	-15 [†]	-58 [‡]	30
	2008–10 to 2014–16	-17 [†]	-39 [‡] ; 24 [‡] ; 7 ± 2 ^δ	19

Notes:

◊ - reported as total S; ζ - reported as NO_x; ¥ - reported as total nitrate;

† - reported as NH₃; ‡ - reported as pNH₄⁺; δ - Ref.: Butler et al., 2016

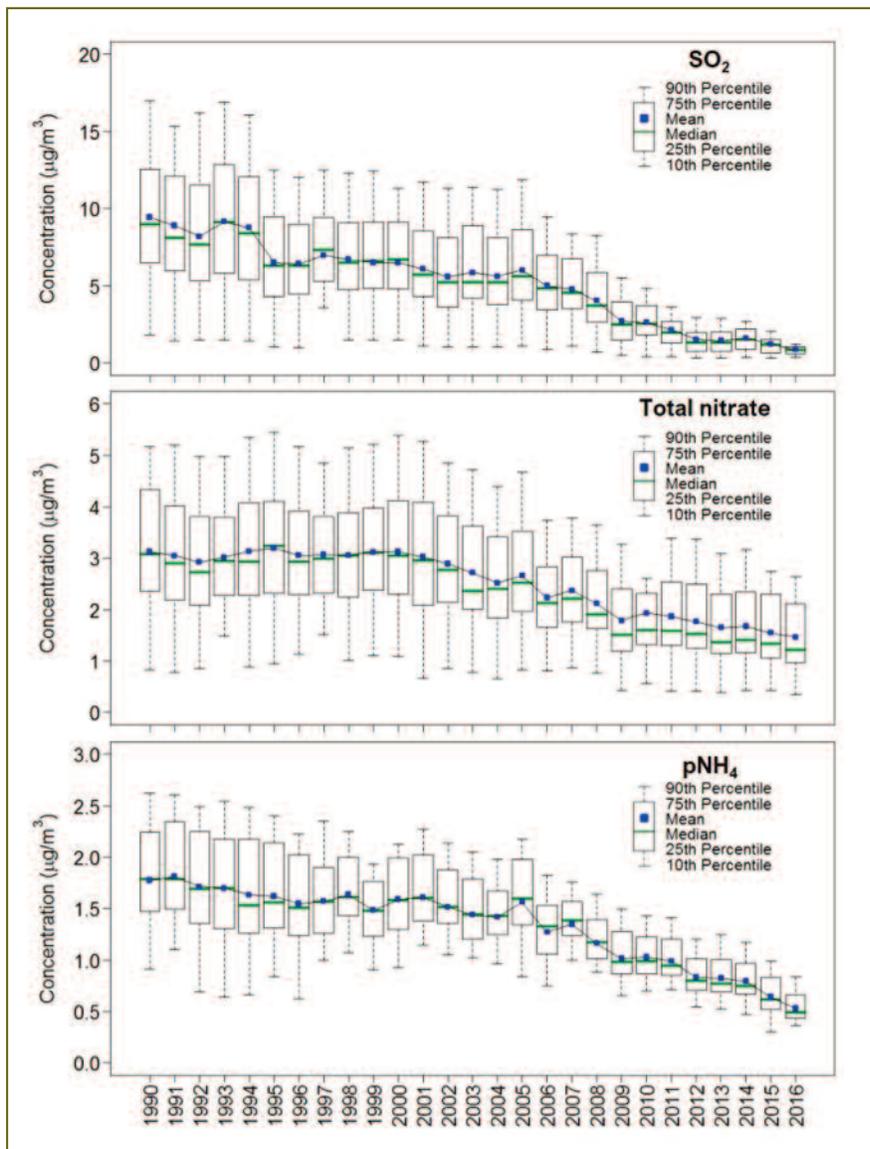


Figure 2. Trends in annual aggregate mean SO_2 (top), total nitrate (middle), and pNH_4 (bottom) concentrations from CASTNET eastern reference sites.⁷

Note: The CASTNET reference sites are split into eastern and western regions due to the spatial density of the measurement sites, concentration differences, a difference in filterpack collection flow rate, and different start dates of operation. Only eastern sites are discussed as they are in closer proximity to EGUs and more reflective of the trends.

NH_3 concentrations likely explain the observed increases in wet NH_4^+ deposition. The decreasing pNH_4 concentrations and the increasing NH_3 concentrations suggest that less of the NH_3 emissions are partitioning to the particle phase. This is supported by the concurrent decline in SO_2 and NO_y emissions and concentrations, which reduces the potential for acidic pollutants to react with gaseous NH_3 and convert to PM .⁸ Summing the concentration averages for pNH_4 and NH_3 over the period from 2008–2010 to 2014–2016 and calculating the difference provides a rough estimate of the

NH_x concentration trend (-4%), which is more proximate to the National Emissions Inventory (NEI) NH_3 emissions trend of -17% over this period, though still a substantial difference.

The TDep NO_y total deposition maps from 2000–2002 to 2014–2016 show that the reductions in NO_y deposition have been significant downwind of large EGU sources in the Eastern United States (see Figure 5). Urban areas are now easily identified as the major NO_y hotspots. The total NH_x deposition map shows increases in agricultural source regions (e.g., Midwest United States, eastern NC, southeastern PA) (Figure 5). The total Nr deposition predicted by the TDep method is now approximately half NO_y and half NH_x (Figure 4). This trend has also been observed in other studies.^{2,10}

Trends Analysis Limitations

The trends analyses in Nr emissions, concentrations, and deposition described in the previous section are not without limitations. Linking trends in emissions and atmospheric concentrations for Nr species is not as straightforward as for S , as there are more Nr species, more reactivity, and more sources to convolute these linkages. Emissions inventories for non-EGU sources are not robust and improvements are needed

for all Nr species. These sources have greater uncertainties, as they are more variable with time (e.g., agricultural and biogenic sources), are episodic (e.g., wildfires), and are typically calculated via mass-balance techniques.¹¹ Studies suggest current inventories for mobile emissions are overestimated for NO_x ¹²⁻¹⁴ and underestimated for NH_3 .^{15,16} Agricultural sources (e.g., livestock production, emissions from fertilized soils) account for 80% of U.S. NH_3 emissions^{4,17,18} and are poorly characterized by agricultural practice and activity data in emissions inventory development.¹⁹

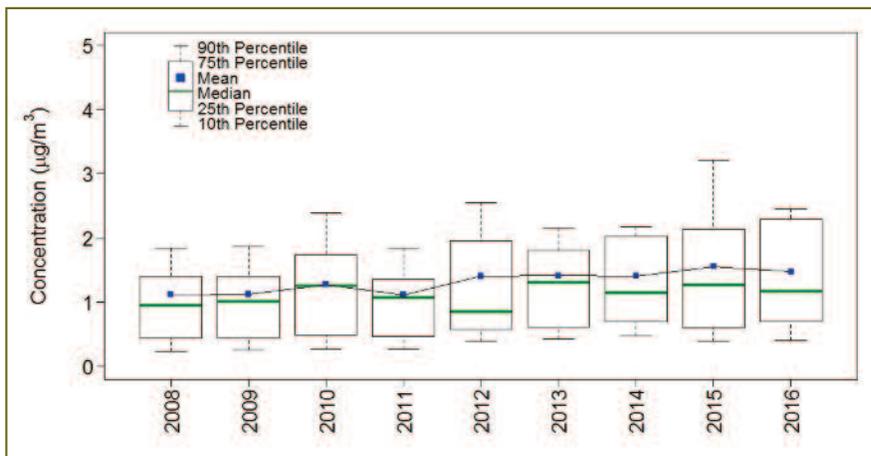


Figure 3. Trend in annual aggregate mean NH₃ concentrations from 21 NADP/AMoN sites.

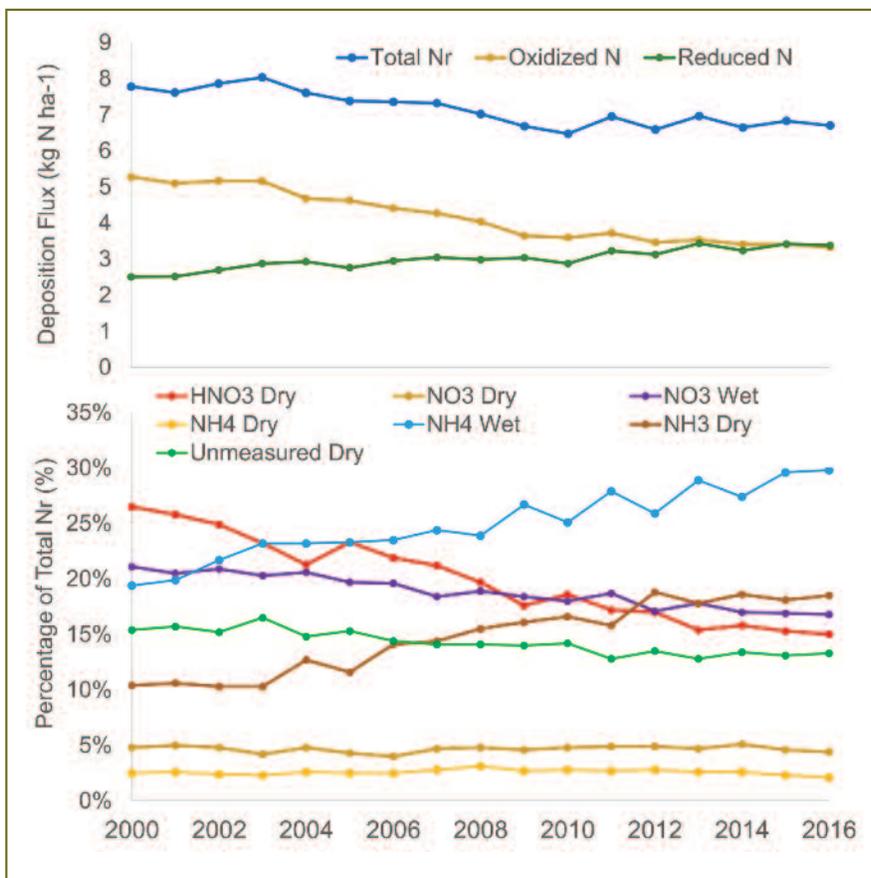


Figure 4. Trends in N_r deposition output by the TDep measurement-model fusion method.

Note: Top plot is the deposition flux of total N_r and its oxidized and reduced components (kg-N ha⁻¹). The lower plot is the percentage of total N_r deposition for each modeled species and its deposition pathway.

relationship with the modeled bi-directional deposition velocities. Also, existing network measurements for NO₂ (e.g., U.S. AQS), are also not currently utilized. Planned newer versions of the TDep method will address these limitations in the near future. Approximately 13% of the total N_r deposition budget is either not measured or not utilized by the TDep method (Figure 4). A fraction of this is organic nitrogen (ON), which is uncharacterized.

More Research Needed

Routine N_r monitoring could be expanded to include bulk sampling of ON in precipitation and PM to develop more complete N_r budgets. Additionally, low-cost passive samplers for NH₃ and NO₂ could be added to existing networks to help characterize gradients from urban and agricultural areas to rural, non-source impacted areas. This could be conducted in tandem with satellite assessments to identify new monitoring locations and to better understand measurement spatial representativeness. Further development of low-cost methods for directly measuring dry deposition, suitable for routine network operation, is also a high priority. Finally, there are constant improvements in the accuracy of chemical transport models (CTMs) used to develop long-term time series of concentrations and deposition. These new estimates need to be reconciled with older estimates, especially for trends assessment where consistency is essential.

Satellite measurements of tropospheric NO₂ and NH₃ concentrations can augment current monitoring and modeling strategies

for N_r and address some of these limitations. Satellite data products have been used to quantify regional and point-source scale emissions,^{20,21} including episodic emissions (e.g., wildfires)^{22,23} to improve emissions inventories.^{24,25} Also,

There are substantial limitations to the available N_r concentration measurements and how those measurements are used to assess total deposition. The TDep methodology does not utilize measured NH₃ concentrations because of a non-linear

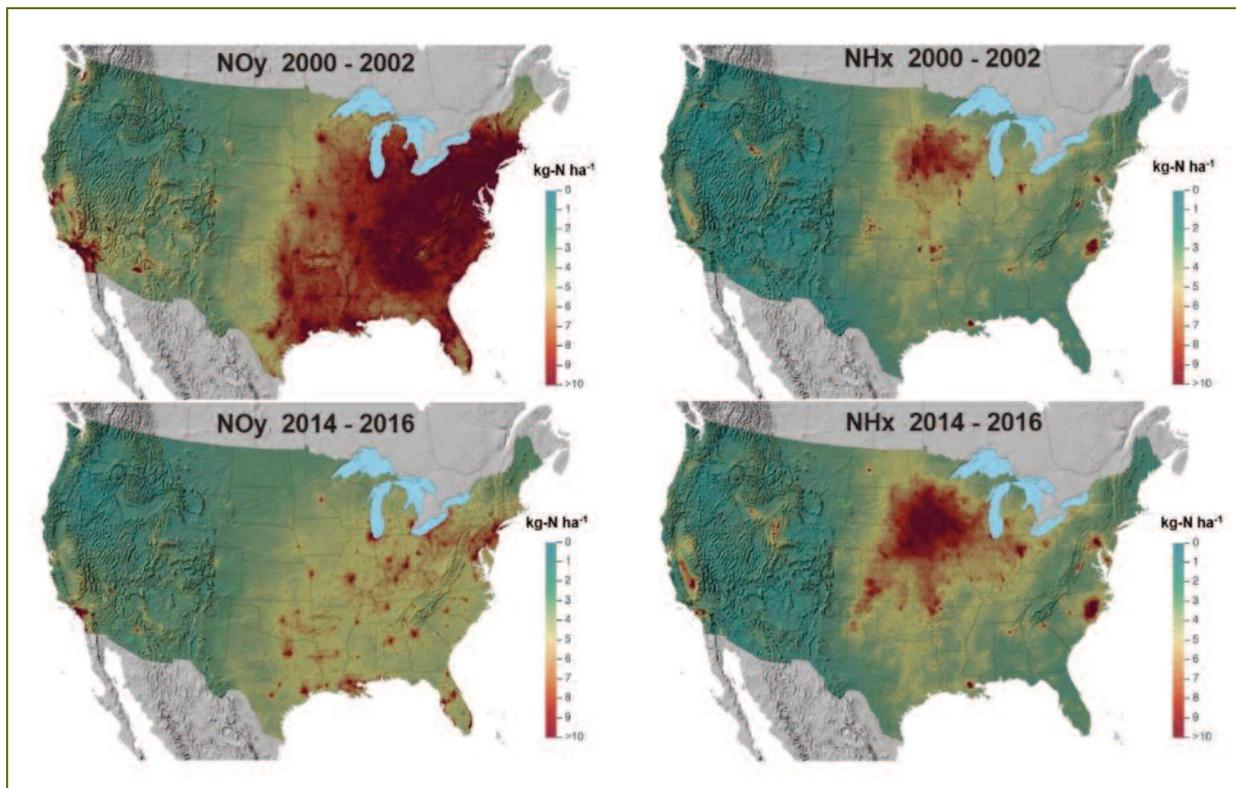


Figure 5. TDep method deposition maps of NO_y and NH_x from 2000–2002 to 2014–2016.⁹

satellite-derived long-term trends for concentrations of NO₂^{26,27} and NH₃²⁸⁻³⁰ support surface monitoring trend data and provide information on spatial variability³¹ not achievable with surface networks. Satellite data products have been used

in conjunction with measurements, CTMs, and deposition models to estimate trends in Nr deposition^{32,33} or to evaluate and improve the CTMs^{28,34-36} and thus improving modeled deposition estimates providing more accurate trends. **em**

Greg M. Beachley and **Melissa A. Puchalski** are with the U.S. Environmental Protection Agency's (EPA) Office of Air and Radiation in Washington, DC; **Chris M. Rogers** is with Wood Environment & Infrastructure Solutions Inc., Jacksonville, FL; **Tom F. Lavery** is an environmental consultant based in Cranston, RI; and **John T. Walker** is with EPA's Office of Research and Development in Durham, NC. E-mail: beachley.gregory@epa.gov.

Disclaimer: The views expressed in this article are those of the author(s) and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

References

- Holland, D.M.; Prindpe, P.P.; Sickles II, J.E. Trends in atmospheric sulfur and nitrogen species in the eastern United States for 1989-1995; *Atmos. Environ.* 1998, 33 (1), 37-49.
- Du, E.; de Vries, W.; Galloway, J.N.; Hu, X.; Fang, J. Changes in wet nitrogen deposition in the United States between 1985 and 2012; *Environ. Res. Lett.* 2014, 9, 095004; doi:10.1088/1748-9326/9/9/095004.
- Schwede, D.B.; Lear, G.G. A Novel Hybrid Approach for Estimating Total Deposition in the United States; *Atmos. Environ.* 2014, 92, 207-220; doi: 10.1016/j.atmosenv.2014.04.008.
- National Emissions Inventory Version 2; U.S. Environmental Protection Agency, 2014. See <https://gispub.epa.gov/neireport/2014/> (accessed April 2019).
- Clean Air Status and Trends Network (CASTNET) 2015 Annual Report*. Prepared for the U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. By Wood Environment & Infrastructure Solutions Inc., Gainesville, FL; Contract No. EP-W-15-003.
- Kim, S.-W.; McKeen, H.S.A.; Frost, G.J.; Hsie, E.-Y.; Trainer, M.K.; Richter, A.; Burrows, J.P.; Peckham, S.E.; Grell, G.A. Satellite-observed U.S. power plant NO_x emission reductions and their impact on air quality; *Geophys. Res. Lett.* 2006, 33 (22), L22812.
- Clean Air Status and Trends Network (CASTNET) 2016 Annual Report*. Prepared for the U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. By Wood Environment & Infrastructure Solutions Inc., Gainesville, FL; Contract No. EP-W-15-003.
- Butler, T.; Vermeylen, F.; Lehmann, C.M.; Likens, G.E.; Puchalski, M. Increasing ammonia concentration trends in large regions of the U.S.A derived from the NADP/AMoN network; *Atmos. Environ.* 2016, 146, 132-140; <https://doi.org/10.1016/j.atmosenv.2016.06.033>.

References Continued

9. TDep 2016 Annual Report; National Atmospheric Deposition Program (NADP). See <http://nadp.slh.wisc.edu/committees/tdep/reports/> (accessed April 2019).
10. Li, Y.; Schichtel, B.A.; Walker, J.T.; Schwede, D.B.; Chen, X.; Lehmann, M.B.; Puchalski, M.A.; Gay, D.A.; Collett, J.L. Increasing Importance of Deposition of Reduced Nitrogen in the United States; *Proc. Nat. Acad. Sci. USA* 2016; www.pnas.org/lookup/suppl/doi:10.1073/pnas.1525736113/-/DCSupplemental.
11. AP-42: Compilation of Air Emissions Factors; U.S. Environmental Protection Agency, 2018. See <https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors> (accessed May 2018).
12. McDonald, B.C.; Dallmann, T.R.; Martin, E.W.; Harley, R.A. Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales; *J. Geophys. Res. Atmos.* 2012, *117*, D00V18; doi:10.1029/2012JD018304.
13. Anderson, D.C.; Loughner, C.P.; Diskin, G.; Weinheimer, A.; Carty, T.P.; Salawitch, R.J.; Worden, H.M.; Fried, A.; Mikoviny, T.; Wisthaler, A.; Dickerson, R.R. Measured and modeled CO and NOy in DISCOVER-AQ: An evaluation of emissions and chemistry over the eastern US; *Atmos. Environ.* 2014, *96*, 78-87.
14. McDonald, B.C.; McKeen, S.A.; Cui, Y.Y.; Ahmadov, R.; Kim, S.-W.; Frost, G.J.; Pollack, I.B.; Peischl, J.; Ryerson, T.B.; Holloway, J.S.; Graus, M.; Warneke, C.; Gilman, J.B.; de Gouw, J.A.; Kaiser, J.; Keutsch, F.N.; Hanisco, T.F.; Wolfe, G.M.; Trainer, M. Modeling Ozone in the Eastern U.S. using a Fuel-Based Mobile Source Emissions Inventory; *Environ. Sci. Technol.* 2018, *52*, 7360-7370.
15. Sun, K.; Tao, L.; Miller, D.J.; Pan, D.; Golston, L.M.; Zondlo, M.A.; Griffin, R.J.; Wallace, H.W.; Leong, Y.J.; Yang, M.M.; Zhang, Y.; Mauzerall, D.L.; Zhu, T. Vehicle emissions as an important urban ammonia source in the United States and China; *Environ. Sci. Technol.* 2017, *51*, 2472-2481.
16. Fenn, M.E.; Bytnerowicz, A.; Schilling, S.L.; Vallano, D.M.; Zavaleta, E.S.; Weiss, S.B.; Morozumi, C.; Geiser, L.H.; Hanks, L. On-road emissions of ammonia: An underappreciated source of atmospheric nitrogen deposition; *Sci. Total Environ.* 2018a, *625*, 909-919.
17. Aneja, V.P.; Schlesinger, W.H.; Erisman, J.W. Effects of agriculture upon the air quality and climate: Research, policy and regulations; *Environ. Sci. Technol.* 2009, *43*, 4234-4240.
18. Battye, W.; Aneja, V.P.; Roelle, P.A. Evaluation and improvement of ammonia emissions inventories; *Atmos. Environ.* 2003, *37*, 3873-3883.
19. McQuilling, A.; Adams, P. Extended Abstract: Modeling livestock Ammonia Emissions in the United States: from Farms to Emissions to Particulate Matter. Presented at the EPA 2015 International Emission Inventory Conference; <https://www.epa.gov/air-emissions-inventories/2015-international-emission-inventory-conference-air-quality-challenges>.
20. de Foy, B.; Lu, Z.; Streets, D.G.; Lamsal, L.N.; Duncan, B.N. Estimates of power plant NOx emissions and lifetimes from OMI NO2 satellite retrievals; *Atmos. Environ.* 2015, *116*, 1-11.
21. Lu, Z.; Streets, D.G.; de Foy, B.; Lamsal, L.N.; Duncan, B.N.; Xing, J. Emissions of nitrogen oxides from US urban areas: Estimation from Ozone Monitoring Instrument retrievals for 2005-2014; *Atmos. Chem. Phys.* 2015, *15*, 10367-10383; doi:10.5194/acp-15-10367-2015.
22. Whitburn, S.; Van Damme, M.; Kaiser, J.W.; van der Werf, G.R.; Turquety, S.; Hurtmans, D.; Clarisse, L.; Clerbaux, C.; Coheur, P.-F. Ammonia emissions in tropical biomass burning regions: Comparison between satellite-derived emissions and bottom-up fire inventories; *Atmos. Environ.* 2015, *121*, 42-54; <https://doi.org/10.1016/j.atmosenv.2015.03.015>.
23. Luo, M.; Shephard, M.W.; Cady-Pereira, K.E.; Henze, D.K.; Zhu, L.; Bash, J.O.; Pinder, R.W.; Capps, S.L.; Walker, J.T.; Jones, M.R. Satellite observations of tropospheric ammonia and comparisons to model simulations; *Atmos. Environ.* 2015, *106*, 262-277; <http://dx.doi.org/10.1016/j.atmosenv.2015.02.007>.
24. Lamsal, L.N.; Martin, R.V.; Padmanabhan, A.; van Donkelaar, A.; Zhang, Q.; Sioris, C.E.; Chance, K.; Kurosu, T.P.; Newchurch, M.J. Application of satellite observations for timely updates to global anthropogenic NOx emission inventories; *Geophys. Res. Lett.* 2011, *28*, L05810.
25. Tong, D.Q.; Lamsal, L.; Pan, L.; Ding, C.; Kim, H.; Lee, P.; Chai, T.; Pickering, K.E.; Stajner, I. Long-term NOx trends over large cities in the United States during the great recession: Comparison of satellite retrievals, ground observations, and emission inventories; *Atmos. Environ.* 2015, *107*, 70-84.
26. Nowlan, C.R.; Martin, R.V.; Philip, S.; Lamsal, L.N.; Krotkov, N.A.; Marais, E.A.; Wang, S.; Zhang, Q. Global dry deposition of nitrogen dioxide and sulfur dioxide inferred from space-based measurements; *Global Biogeochem. Cycles* 2014, *28*, 1025-1043; <https://doi.org/10.1002/2014GB004805>.
27. Lamsal, L.N.; Duncan, B.N.; Yoshida, Y.; Krotkov, N.A.; Pickering, K.A.; Streets, D.G.; Lu, Z. U.S. NO2 trends (2005-2013): EPA Air Quality System (AQS) data versus improved observations from the Ozone Monitoring Instrument (OMI); *Atmos. Environ.* 2015, *110*, 130-145; <https://doi.org/10.1016/j.atmosenv.2015.03.055>.
28. Schiferl, L.D.; Heald, C.L.; Van Damme, M.; Clarisse, L.; Clerbaux, C.; Coheur, P.; Nowak, J.B.; Neuman, J.A.; Herndon, S.C.; Roscioli, J.R.; Eilerman, S.J. Interannual Variability of Ammonia Concentrations over the United States: Sources and Implications; *Atmos. Chem. Phys.* 2016, *16*, 1230-12328; <https://doi.org/10.5194/acp-16-12305-2016>.
29. Shephard, M.W.; Cady-Pereira, K.E.; Luo, M.; Henze, D.K.; Pinder, R.W.; Walker, J.T.; Rinsland, C.P.; Bash, J.O.; Zhu, L.; Payne, V.H.; Clarisse, L. TES ammonia retrieval strategy and global observations of the spatial and seasonal variability of ammonia; *Atmos. Chem. Phys.* 2011, *11* (20), 10743e10763; <http://dx.doi.org/10.5194/acp-11-10743-2011>.
30. Warner, J.X.; Dickerson, R.R.; Wei, Z.; Strow, L.L.; Wang, Y.; Liang, Q. Increased atmospheric ammonia over the world's major agricultural areas detected from space; *Geophys. Res. Lett.* 2017, *44*; doi:10.1002/2016GL072305.
31. Pinder, R.W.; Walker, J.T.; Bash, J.O.; Cady-Pereira, K.E.; Henze, D.K.; Luo, M.; Osterman, G.B.; Shephard, M.W. Quantifying spatial and seasonal variability in atmospheric ammonia with in situ and space-based observations; *Geophys. Res. Lett.* 2011, *38* (4); <http://dx.doi.org/10.1029/2010GL046146>.
32. Geddes, J.A.; Martin, R.V. Global deposition of total reactive nitrogen oxides from 1996 to 2014 constrained with satellite observations of NO2 columns; *Atmos. Chem. Phys.* 2017, *17*, 10071-10091; <https://doi.org/10.5194/acp-17-10071-2017>.
33. Kharol, S.K.; Shephard, M.W.; McLinden, C.A.; Zhang, L.; Sioris, C.E.; O'Brien, J.M.; Vet, R.; Cady-Pereira, K.E.; Hare, E.; Siemons, J.; Krotkov, N.A. Dry Deposition of Reactive Nitrogen From Satellite Observations of Ammonia and Nitrogen Dioxide Over North America; *Geophys. Res. Lett.* 2018, *45*, 1157-1166; <https://doi.org/10.1002/2017GL075832>.
34. Lonsdale, C.R.; Hegarty, J.D.; Cady-Pereira, K.E.; Alvarado, M.J.; Henze, D.K.; Turner, M.D.; Capps, S.L.; Nowak, J.B.; Neuman, J.A.; Middlebrook, A.M.; Bahreini, R.; Murphy, J.G.; Markovic, M.Z.; VandenBoer, T.C.; Russell, L.M.; Scarino, A.J. Modeling the diurnal variability of agricultural ammonia in Bakersfield, California, during the CalNex campaign; *Atmos. Chem. Phys.* 2017, *17*, 2721-2739; <https://doi.org/10.5194/acp-17-2721-2017>.
35. Zhu, L.; Henze, D.K.; Cady-Pereira, K.E.; Shephard, M.W.; Luo, M.; Pinder, R.W.; Bash, J.O.; Jeong, G.-R. Constraining U.S. ammonia emissions using TES remote sensing observations and the GEOS-Chem adjoint model; *J. Geophys. Res. Atmos.* 2013, *118*, 3355-3368; doi:10.1002/jgrd.50166.
36. Whaley, C.H.; Makar, P.A.; Shephard, M.W.; Zhang, L.; Zhang, J.; Zheng, Q.; Akingunola, A.; Wentworth, G.W.; Murphy, J.G.; Kharol, S.K.; Cady-Pereira, K.E. Contributions of natural and anthropogenic sources to ambient ammonia in the Athabasca Oil Sands and north-western Canada; *Atmos. Chem. Phys.* 2018, *18*, 2011-2034; <https://doi.org/10.5194/acp-18-2011-2018>.



Clean Air Status and Trends Network (CASTNET) site in Beaufort, NC.
Photo courtesy of the U.S. Environmental Protection Agency (EPA).

Need for **Improved Monitoring** of Spatial and Temporal Trends of Reduced Nitrogen

by **Melissa A. Puchalski, John T. Walker, Gregory M. Beachley, Mark A. Zondlo, Katherine B. Benedict, Richard H. Grant, Bret A. Schichtel, Christopher M. Rogers, April B. Leytem, Joann Rice, Kristi Morris, James J. Schauer, and Rui Wang**

The authors discuss needed improvements in monitoring and characterization of reduced inorganic nitrogen.

U.S. regulations have been effective at reducing emissions of oxidized nitrogen (NO_x) and associated secondary pollutants (e.g., ozone, nitrate).^{1,2} NO_x (nitrogen oxide [NO] + nitrogen dioxide [NO₂]) reductions have resulted in decreasing trends and shifting spatial patterns in wet and dry nitrate deposition as measured by urban and rural monitoring networks.^{3,4} As NO_x emissions have decreased, the atmospheric reactive nitrogen (Nr) budget is shifting toward a greater contribution from reduced inorganic nitrogen forms (NH_x = ammonia gas [NH₃] + ammonium aerosol [NH₄⁺]).⁵ Unlike NO₂, NH₃ and NH₄⁺ are not regulated under the U.S. Clean Air Act; however, as a component of Nr deposition and contributor to particulate matter < 2.5 μm (PM_{2.5}), NH_x is considered in the current review of the NO_x/SO_x/PM secondary National Ambient Air Quality Standards (NAAQS).⁶ While the primary NAAQS protect human health, the secondary NAAQS protect public welfare, which includes visibility and ecosystem health.

Livestock waste and fertilized soils account for approximately 80% of NH₃ emissions in the United States.⁷ Automobiles (urban) and wildfires are also important sources of NH₃ and are likely underestimated in current inventories.^{4,8-10} In the atmosphere, NH₃ reacts with acidic pollutants to form particulates (e.g., ammonium sulfate [(NH₄)₂SO₄], ammonium bisulfate [(NH₄)HSO₄], ammonium nitrate [NH₄NO₃]), which contribute to PM_{2.5}, climate forcing, and poor visibility.¹¹ NH₃ and NH₄⁺ are also components of Nr deposition, which can cause soil acidification,¹² NO and nitrous oxide (N₂O) emissions from microbial activity in soils,^{13,14} reductions in vegetation species diversity,¹⁵ and eutrophication of aquatic ecosystems.¹⁶ Measuring and modeling NH₃ dry deposition is challenging due to the presence of a surface compensation point and subsequent bidirectional exchange with the atmosphere.^{17,18}

Ambient NH₄⁺ has been monitored for more than 30 years by existing networks, but less information exists for gaseous NH₃. Over the last decade, ground-based monitoring and remote sensing have shown NH₃ to be increasing in some regions of the United States,^{19,20} yet uncertainties in emission inventories and gaps in monitoring make linking long-term trends in NH₃ emissions with ambient NH_x difficult.²¹ Expanded monitoring of NH_x is needed to better characterize these linkages and provide data to evaluate and improve chemical transport models (CTMs) to more accurately predict PM formation, visibility impacts, and ecosystem exposure. Better understanding of spatial variability of NH₃ concentrations and bidirectional exchange is also needed to improve the representation of NH₃ in measurement-model fusion techniques for total deposition.²²

Current Monitoring of NH_x

Particulate NH₄⁺ has been measured by atmospheric

monitoring networks in the United States for more than 30 years. None of the existing networks measure total NH_x, but data can be combined to develop estimates of reduced atmospheric nitrogen. The key U.S. networks that measure components of NH_x include:

- The **Clean Air Status and Trends Network (CASTNET)** measures weekly concentrations of particulate NH₄⁺, as well as nitric acid (HNO₃), sulfur dioxide (SO₂), nitrate (NO₃⁻), and sulfate (SO₄²⁻), at 92 sites. CASTNET data have provided estimates of dry deposition used to assess spatial and long-term trends since 1990.
- **National Atmospheric Deposition Program's (NADP) Ammonia Monitoring Network (AMoN)** uses passive samplers to measure two-week integrated NH₃ concentrations. Established in 2007, the network includes 105 sites.
- The **Chemical Speciation Network (CSN) and Interagency Monitoring of Protected Visual Environments (IMPROVE)** networks collect speciated 24-hour PM_{2.5} samples on a one-in-three-day schedule. CSN samples are analyzed for NH₄⁺.²³ In IMPROVE, NH₄⁺ is derived from assumed compositions of the measured SO₄²⁻ and NO₃⁻.²⁴

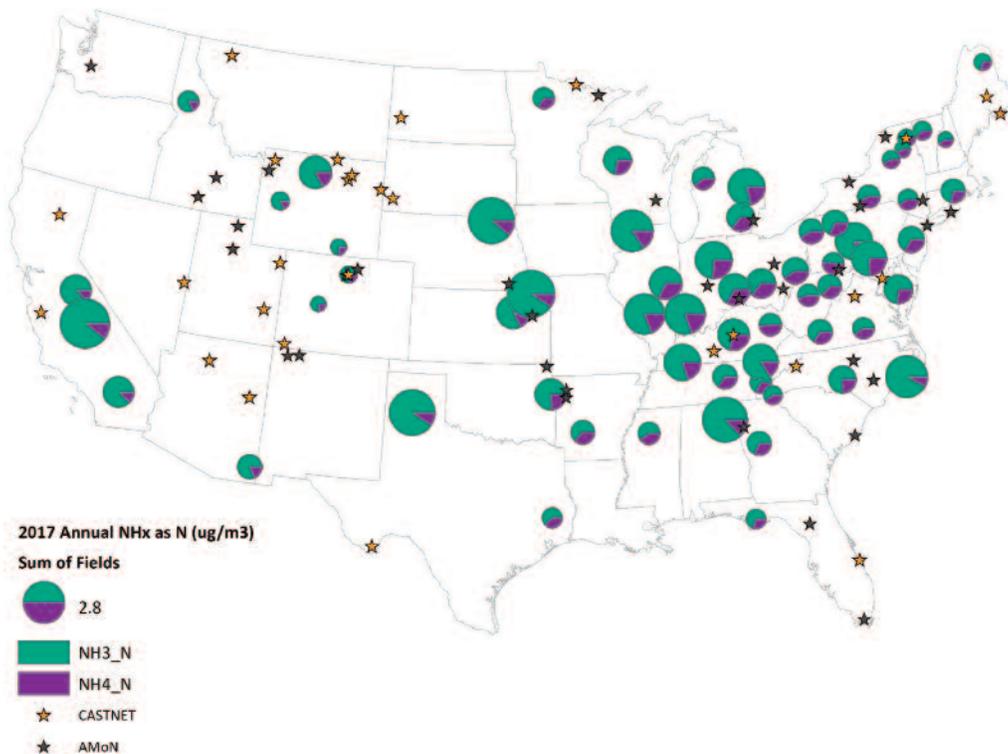
In the case of both CASTNET and CSN, NH₄⁺ concentrations are biased low due to losses of NH₄⁺ from dissociation of particulate nitrate from the Teflon and nylon filters, respectively.^{25,26} While the NH₄⁺ concentrations are comparable, IMPROVE and CSN use a PM_{2.5} cutpoint and CASTNET uses an open face filter pack.²⁷

The spatial distribution of ambient measurements of NH_x, calculated as the sum of NH₃ and NH₄⁺ at co-located AMoN/CASTNET sites, is presented in Figure 1a, showing a predominance of NH₃ at all locations. The majority of co-located AMoN/CASTNET sites are located in the eastern United States, many in counties with relatively low NH₃ emissions. Some hotspots are captured (i.e., eastern NC); however, large areas of agricultural NH₃ emissions across the Midwest and West are not well resolved by the existing networks, which can be seen by the discrepancy between Figure 1a and 1b. Outside of agricultural regions, monitoring is lacking in the Northwest, Gulf Coast region, and Florida.

Expansion of Routine Monitoring

Establishing additional co-located time-integrated NH₄⁺ and NH₃ sites would be a cost-effective way to better resolve broad spatial and temporal patterns of NH_x. Satellite measurements and NH₃ inventories are useful for identifying high-value locations for establishing new sites where monitoring is currently lacking. Figure 2 shows AMoN sites layered with the 2008–2016 average satellite NH₃ measurements,

(a)



(b)

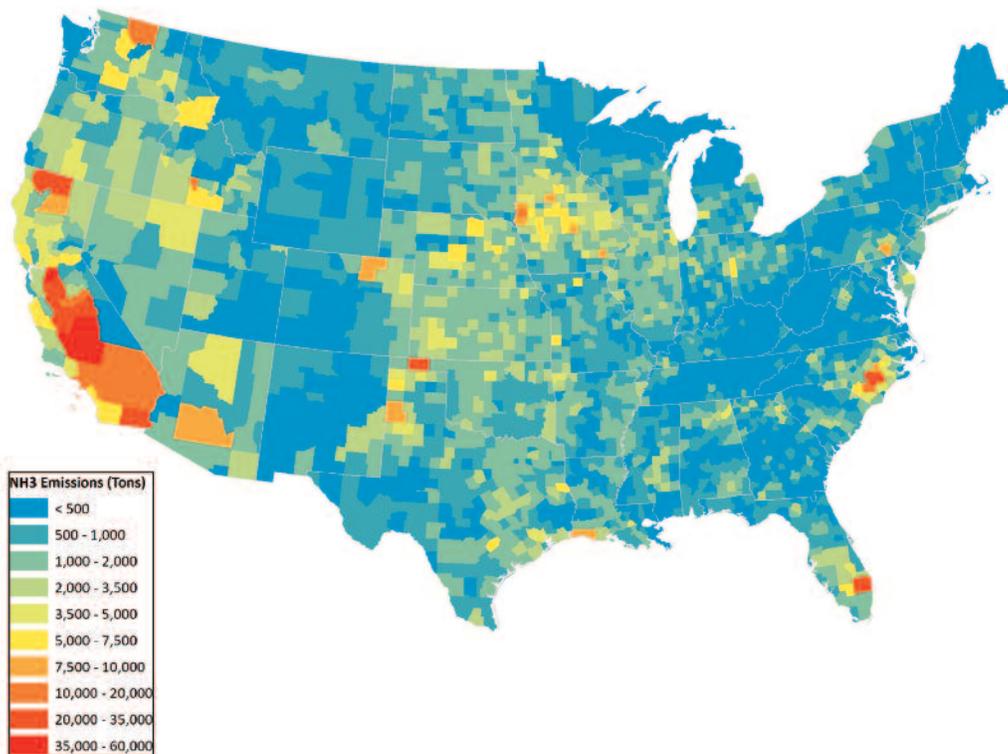


Figure 1. (a) Annual NHx measurements across the continental United States from CASTNET and AMoN in 2017; (b) map of 2014 NEI NH₃ emissions for all sectors.⁷

Note: (a) Pie charts represent total NHx as the sum of particulate NH₄⁺ (measured by CASTNET) and NH₃ (measured by AMoN). The size of the circle is representative of the total NHx concentration. Site locations that are not co-located are represented by a star.

highlighting monitoring gaps in high emission regions and difficulties in selecting representative sites. For example, the highest AMoN NH_3 concentration (2016–2018 average $16.8 \mu\text{g}/\text{m}^3$) is measured at UT01 (Cache Valley) located adjacent to a feedlot. This site is representative of the Cache Valley, but not representative of the northern UT region. The highest ground-level concentrations may not be well represented in the satellite observations due to a lack of vertical mixing, which illustrates the synergies between satellite and ground-based measurements.

Characterization of patterns across smaller source regions and land-use types is also needed. As an example, a regional passive NH_3 monitoring network has been conducted during the warmest months since 2010 in Colorado.^{31,32} This network provides data on NH_3 gradients across an agricultural–rural–suburban–urban region with concentrations ranging from less than $5 \mu\text{g m}^{-3}$ in rural–suburban locations to $42 \mu\text{g m}^{-3}$ near large feedlots,³¹ highlighting some of the gaps in existing national networks where the spatial gradients are not well represented.

CSN and IMPROVE offer additional opportunity for expanded rural and urban monitoring. Capturing the daily integrated NH_x concentrations with speciated $\text{PM}_{2.5}$

measurements would be beneficial for model evaluation and source apportionment. Acid-impregnated filters deployed in a pilot IMPROVE study in the West and Midwest showed good recovery of NH_x .³³ However, recent testing of acid-impregnated filters in CSN and IMPROVE deployed in the Southeast exhibited a negative bias in CSN as compared to the reference method; therefore, additional testing in humid environments is needed. If biases in the technique can be adequately understood, deployment of the acid-impregnated filters at existing sites could provide additional integrated NH_x concentrations in urban and rural environments at more than 300 sites for a relatively low cost.

High Time Resolution Measurements

Modeling the diurnal NH_3 concentration profile in CTMs is important to properly simulate PM formation and atmospheric deposition processes, but is difficult due to uncertainties in emission inventories, boundary layer dynamics, local dispersion, and bi-directional fluxes.^{17,34,35} Figure 3 summarizes diurnal NH_3 concentration profiles in several locations, highlighting the need for high-time resolution measurements in different environments. Profiles in agricultural areas (e.g., crops and concentrated animal feeding operations regions) can differ substantially from profiles measured in forested, coastal, and suburban locations. Patterns similar to the examples in Figure

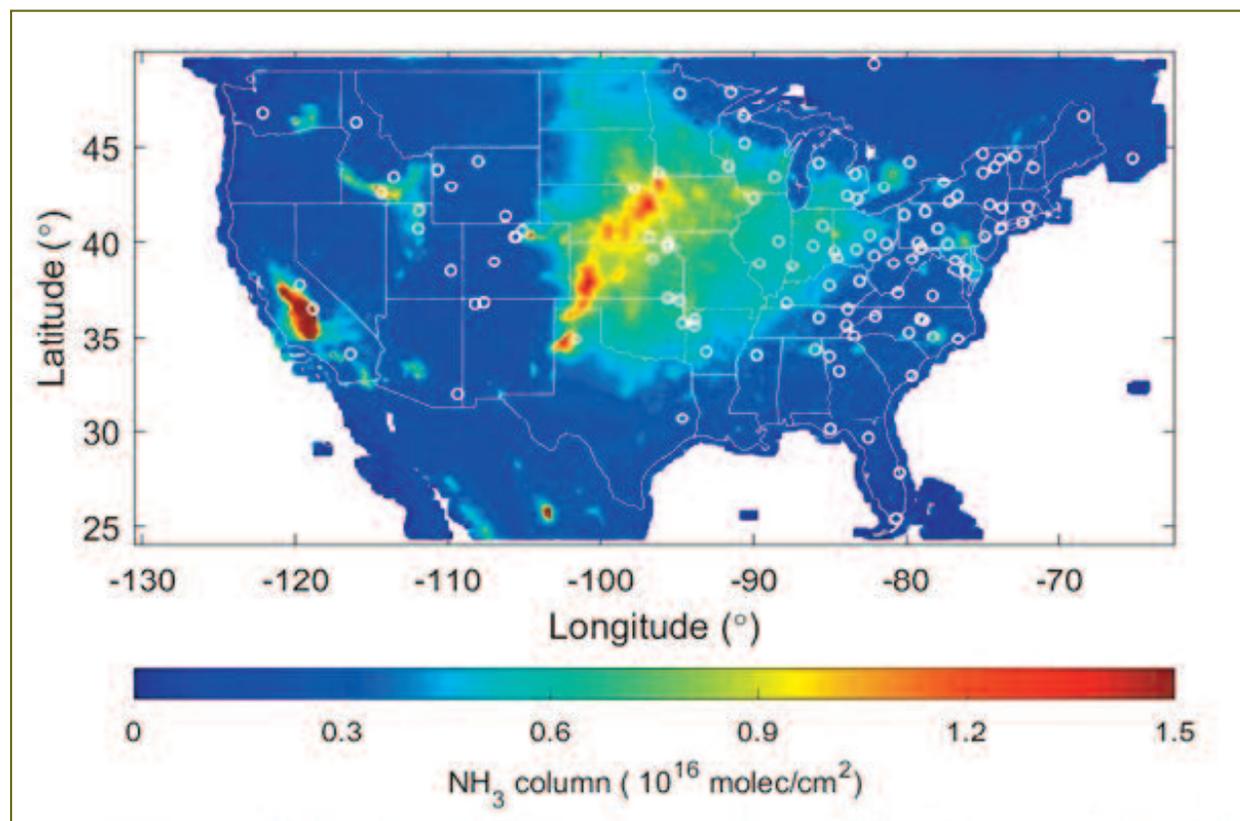


Figure 2. Average (2008–2016) satellite NH_3 measurements from the Infrared Atmospheric Sounding Instruments (IASI v2.2R) using an oversampling algorithm for high-spatial resolution.^{28–30}

Note: AMoN sites are noted by open circles.

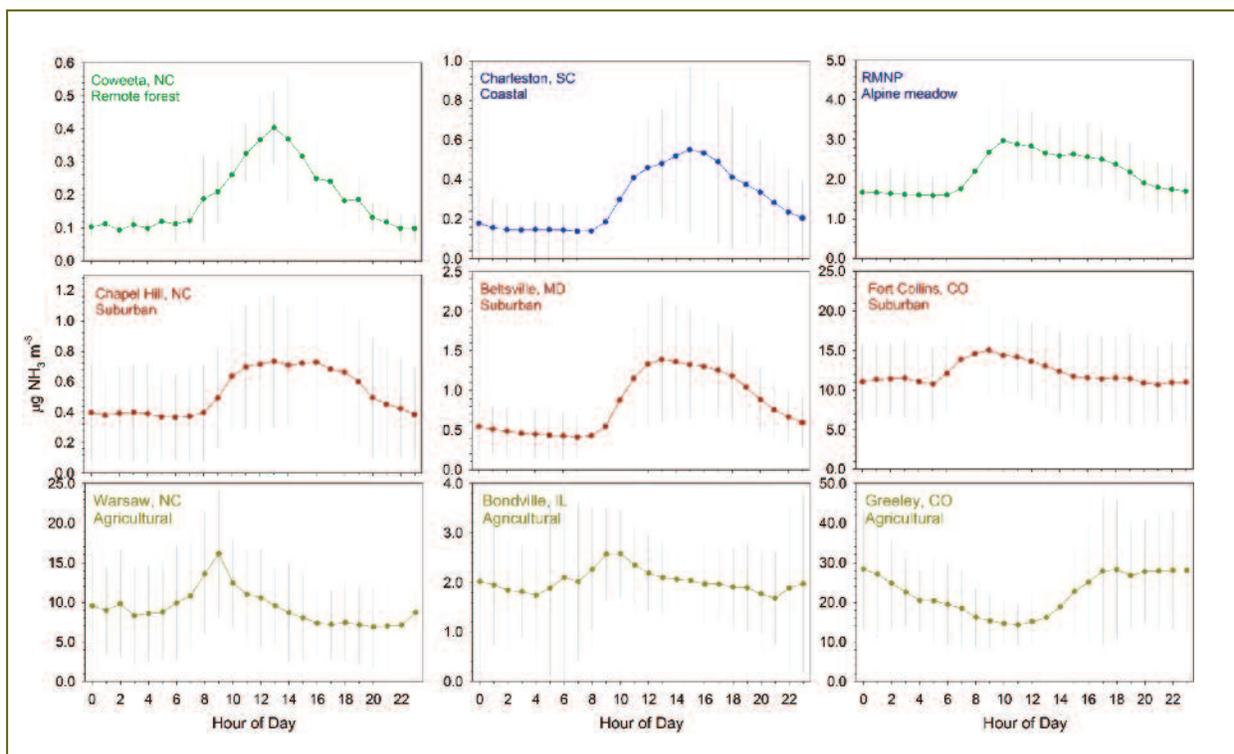


Figure 3. Diurnal concentration profiles of NH_3 at suburban, forested, coastal, and agricultural sites during summer months.

Note: Concentrations were measured using high temperature conversion/chemiluminescence (Warsaw, NC),¹⁸ the Monitor for Aerosols and Gases (MARGA, Coweeta, NC; Chapel Hill, NC; Charleston, SC; Bondville, IL; Beltsville, MD),^{39,40} Picarro (NH_3) analyzer (Rocky Mountain National Park [RMNP]); or a Particle Measuring System (Air Sentry II, 129 Fort Collins, CO; Greeley, CO).⁴¹ Data represent mean hourly concentration \pm 1 standard deviation.

3 have been observed at other locations in the United States.³⁶⁻³⁸

The diurnal concentration patterns in Figure 3 may not correlate directly to NH_3 emission rates, but rather reflect the net result of emissions, deposition, and atmospheric processes. Time-resolved monitoring of air concentrations is not a substitute for direct emission measurements, which are also needed to improve current inventories.

Methods for continuous NH_3 measurements include cavity ring-down, ion mobility, and quantum cascade laser spectroscopy, high temperature conversion with nitric oxide chemiluminescence, online wet denuder/conductivity techniques, chemical ionization mass spectrometry, and others.⁴² As an option for total NH_x , CASTNET designed an enhanced chemiluminescence $\text{NO}/\text{NO}_y/\text{total N}_r$ analyzer (nitrotrain). Hourly concentrations of NH_x are reported by subtracting NO_y from total N_r . The nitrotrain is currently deployed at Duke Forest, NC, in a routine-network mode. Deployment in other networks (e.g., NCore Network) could utilize existing infrastructure to measure hourly NH_x concentrations at 80+ urban and rural monitoring sites. Adsorption onto inlet and tubing surfaces, as well as particle filtration,⁴² continue to present

significant challenges for deployment of continuous NH_3 methods in a routine monitoring framework.

Conclusions

Improved characterization of NH_x will support the development of effective environmental regulations, guide the development of best management practices for emissions, and improve CTMs. A combination of time-integrated sampling and high-time resolution measurements are needed to better characterize spatial gradients, long-term trends and atmospheric processes. Ideally, any expansion of NADP's AMoN would be accompanied by NH_4^+ measurements, trace acidic pollutants, and meteorology to characterize gas-particle interactions and improve models used to assess $\text{PM}_{2.5}$ reduction strategies. Selecting new site locations should be informed by remote sensing and emission inventory data. Expanding NH_x monitoring presents an opportunity for greater engagement of agricultural, ecological, and atmospheric communities in the assessment of NH_x and for cooperation between federal, state, or local agencies, universities, tribes, or other private organizations.

Improvements in emission inventories are also urgently needed, particularly for agriculture. In addition to the emission

factors and emission models themselves, improvements in the activity data underlying the inventory are needed. For example, information on number of animals, facility characteristics and manure management, locations of emission sources, and timing and amount of fertilizer application are often lacking or inaccurate. A targeted approach to low-cost, time-integrated

NH_x measurements and high resolution, multi-pollutant intensive field studies is critical for the refinement of NH₃ emission inventories, improved model performance and their application to developing meaningful air quality management strategies. **em**

Melissa A. Puchalski and **Greg M. Beachley** are with the U.S. Environmental Protection Agency's (EPA) Office of Air and Radiation in Washington, DC; **John T. Walker** is with EPA's Office of Research and Development in Durham, NC; **Mark A. Zondlo** and **Rui Wang** are with the Department of Civil and Environmental Engineering at Princeton University, Princeton, NJ; **Katherine B. Benedict** is with the Department of Atmospheric Science at Colorado State University, Fort Collins, CO; **Richard H. Grant** is with the Department of Agronomy at Purdue University, West Lafayette, IN; **Bret A. Schichtel** is with the U.S. National Park Service, Cooperative Institute for Research in the Atmosphere at Colorado State University, Fort Collins, CO; **Christopher M. Rogers** is with Wood Environment & Infrastructure Solutions Inc. in Newberry, FL; **April B. Leytem** is with the U.S. Department of Agriculture, Agricultural Research Service in Kimberly, ID; **Joann Rice** is with EPA's Office of Air Quality Planning and Standards in Durham, NC; **Kristi Morris** is with the U.S. National Park Service, Air Resources Division in Lakewood, CO; and **James J. Schauer** is with the Wisconsin State Laboratory of Hygiene at the University of Wisconsin-Madison, Madison, WI. E-mail: puchalski.melissa@epa.gov.

Disclaimer: The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency (EPA).

Acknowledgment: The authors acknowledge Xi Chen (EPA) for processing of MARGA data for Coweeta and Chapel Hill, NC. They also thank Wyatt Sherlock and Sybil Anderson (Illinois State Water Survey) for sampling and processing the MARGA results from Bondville, IL.

References

1. Hand, J.L.; Schichtel, B.A.; Malm, W.C.; Pitchford, M.L. Particulate sulfate ion concentration and SO₂ emission trends in the United States from the early 1990s through 2010; *Atmos. Chem. Phys.* 2012, *12*, 10353-10365.
2. Russell, A.R.; Valin, L.C.; Cohen, R.C. Trends in OMI NO₂ observations over the United States: Effects of emission control technology and the economic recession; *Atmos. Chem. Phys.* 2012, *12*, 12197-12209.
3. Du, E.; de Vries, W.; Galloway, J.N.; Hu, X.; Fang, J. Changes in wet nitrogen deposition in the United States between 1985 and 2012; *Environ. Res. Lett.* 2014, *9*.
4. Fenn, M.E.; Bytnerowicz, A.; Schilling, S.L.; Vallano, D.M.; Zavaleta, E.S.; Weiss, S.B.; Morozumi, C.; Geiser, L.H.; Hanks, K. On-road emissions of ammonia: An underappreciated source of atmospheric nitrogen deposition; *Sci. Total Environ.* 2018, *625*, 909-919.
5. Li, Y.; Schichtel, B.A.; Walker, J.T.; Schwede, D.B.; Chen, X.; Lehmann, C.M.; Puchalski, M.A.; Gay, D.A.; Collett, Jr., J.L. Increasing importance of deposition of reduced nitrogen in the United States; *Proc. Natl. Acad. Sci.* 2016, *113*, 5876-5879.
6. U.S. Environmental Protection Agency. (2017). *Integrated Review Plan for the Secondary National Ambient Air Quality Standards for Ecological Effects of Oxides of Nitrogen, Oxides of Sulfur and Particulate Matter*; EPA 452/R-17-002; National Center for Environmental Assessment and Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 2017; available: <https://www3.epa.gov/ttn/naaqs/standards/no2so2sec/data/irp-nox-sox-pm-eco.pdf>.
7. U.S. Environmental Protection Agency. (2014). Data from the 2014 National Emissions Inventory, Version 2. See <https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data> (accessed 2019).
8. Benedict, K.B.; Prenni, A.J.; Carrico, C.M.; Sullivan, A.P.; Schichtel, B.A.; Collett Jr., J.L. Enhanced concentrations of reactive nitrogen species in wildfire smoke; *Atmos. Environ.* 2017, *148*, 8-15.
9. Sun, K.; Tao, L.; Miller, D.J.; Pan, D.; Golston, L.M.; Zondlo, M.A.; Griffin, R.J.; Wallace, H.W.; Leong, Y.J.; Yang, M.M.; Zhang, Y.; Mauzerall, D.L.; Zhu, T. Vehicle emissions as an important urban ammonia source in the United States and China; *Environ. Sci. Technol.* 2017, *51* (4), 2472-2481.
10. Prenni, A.; Levin, E.; Benedict, K.; Sullivan, A.; Schurman, M.; Gebhart, K.; Day, D.E.; Carrico, C.M.; Malm, W.C.; Schichtel, B.A.; Collett Jr., J.L.; Kreidenweis, S. Gas-phase reactive nitrogen near Grand Teton National Park: Impacts of transport, anthropogenic emissions, and biomass burning; *Atmos. Environ.* 2014, *89*, 749-756.
11. Wang, X.; Ding, X.; Fu, X.; He, Q.; Wang, S.; Bernard, F.; Zhao, X.; Wu, D. Aerosol scattering coefficients and major chemical compositions of fine particles observed at a rural site in the central Pearl River Delta, South China; *J. Environ. Sci.* 2012, *24* (1), 72-77.
12. Galloway, J.N.; Aber, J.D.; Erisman, J.W.; Seitzinger, S.P.; Howarth, S.P.; Cowling, E.B.; Cosby, B.J. The nitrogen cascade; *Bioscience* 2003, *53* (4), 341-356.
13. Galbally, I.E.; Roy, C.R. Loss of fixed nitrogen from soils by nitric oxide exhalation; *Nature* 1978, *275*, 734-735.
14. Matson, P. NO_x emission from soils and its consequences for the atmosphere and biosphere: critical gaps and research directions for the future; *Nutrient Cycling in Agroecosystems* 1997, *48* (1-2), 1-6.
15. Sheppard, L.J.; Leith, I.D.; Mizunuma, T.; Cape, J.N.; Crossley, A.; Leeson, S.; Sutton, M.A.; van Dijk, N.; Fowler, D. Dry deposition of ammonia gas drives species change faster than wet deposition of ammonium ions: evidence from a long-term field manipulation; *Global Change Biology* 2011, *17* (12), 3589-3607.
16. Camargo, J.A.; Alonso, A. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment; *Environment International* 2006, *32* (6), 831-849.
17. Bash, J.O.; Cooter, E.J.; Dennis, R.L.; Walker, J.T.; Pleim, J.E. Evaluation of a regional air-quality model with bidirectional NH₃ exchange coupled to an agroecosystem model; *Biogeosciences* 2013, *10*, 1635-1645.
18. Walker, J.T.; Robarge, W.P.; Wu, Y.; Meyers, T.P. Measurement of bi-directional ammonia fluxes over soybean using the modified Bowen-ratio technique; *Agric. & Forest Meteorol.* 2006, *138* (1-4), 54-68.
19. Butler, T.; Vermeylen, F.; Lehmann, C.M.; Likens, G.E.; Puchalski, M. Increasing ammonia concentration trends in large regions of the USA derived from the NADP/AMoN network; *Atmos. Environ.* 2016, *146*, 132-140.
20. Warner, J.X.; Dickerson, R.R.; Wei, Z.; Strow, L.L.; Wang, Y.; Liang, Q. Increased atmospheric ammonia over the world's major agricultural areas detected from space; *Geophys. Res. Lett.* 2017, *44* (6), 2875-2884.
21. Zhang, Y.; Mathur, R.; Bash, J.O.; Hogrefe, C.; Xing, J.; Roselle, S.J. Long-term trends in total inorganic nitrogen and sulfur deposition in the U.S. from 1990 to 2010; *Atmos. Chem. Phys.* 2018, *18* (12), 9091-9106.
22. Schwede, D.B.; Lear, G.G. A novel hybrid approach to estimating total deposition in the United States; *Atmos. Environ.* 2014, *92*, 207-220.

References Continued

23. Solomon, P.A.; Crumpler, D.; Flanagan, J.B.; Jayanty, R.M.; Rickman, E.E.; McDade, C.E. U.S. National PM_{2.5} Chemical Speciation Monitoring Networks—CSN and IMPROVE: Description of networks; *J. Air & Waste Manage. Assoc.* 2014, *64* (12), 1410-1438.
24. Malm, W.C.; Sisler, J.F.; Huffman, D.; Eldred, R.A.; Cahill, T.A. Spatial and seasonal trends in particle concentration and optical extinction in the United States; *J. Geophys. Res. Atmos.* 1994, *99* (D1), 1347-1370.
25. Yu, X.; Lee, T.; Ayres, B.; Kreidenweis, S.M.; Collett Jr., J.L.; Malm, W. Particulate nitrate measurement using nylon filters; *J. Air & Waste Manage. Assoc.* 2005, *55* (8), 1100-1110.
26. Yu, X.-Y.; Lee, T.; Ayres, B.; Kreidenweis, S.M.; Malm, W.; Collett Jr., J.L. Loss of fine particle ammonium from denuded nylon filters; *Atmos. Environ.* 2006, *40* (25), 4797-4807.
27. Lavery, T.F.; Rogers, C.M.; Baumgardner, R.; Mishoe, K.P. Intercomparison of Clean Air Status and Trends Network Nitrate and Nitric Acid Measurements with Data from Other Monitoring Programs; *J. Air & Waste Manage. Assoc.* 2009, *59* (2), 214-226.
28. van Damme, M.; Clarisse, L.; Whitburn, S.; Hadji-Lazaro, J.; Hurtmans, D.; Clerbaux, C.; Coheur, P.-F. Industrial and agricultural ammonia point sources exposed; *Nature* 2018, *564*, 99-103.
29. van Damme, M.; Whitburn, S.; Clarisse, L.; Clerbaux, C.; Hurtmans, D.; Coheur, P.-F. Version 2 of the IASI NH₃ neural network retrieval algorithm: Near-real-time and reanalysed datasets; *Atmos. Meas. Tech.* 2017, *10* (12), 4905-4914.
30. Sun, K.; Zhu, L.; Cady-Pereira, K.; Miller, C.C.; Chance, K.; Clarisse, L.; Coheur, P.-F.; Abad, G.G.; Huang, G.; Liu, X.; van Damme M.; Yang, K.; Zondlo, M. A physics-based approach to oversample multi-satellite, multispecies observations to a common grid; *Atmos. Meas. Tech.* 2018, *11*, 6679-6701.
31. Li, Y.; Thompson, T.M.; van Damme, M.; Chen, X.; Benedict, K.B.; Shao, Y.; Day, D.; Boris, A.; Sullivan, A.P.; Ham, J.; Whitburn, S.; Clarisse, L.; Coheur, P.-F.; Collett Jr., J.L. Temporal and spatial variability of ammonia in urban and agricultural regions of northern Colorado, United States; *Atmos. Chem. Phys.* 2017, *17*, 6197-6213.
32. Day, D.E.; Chen, X.; Gebhart, K.A.; Carrico, C.M.; Schwandner, F.M.; Bendict, K.B.; Schichtel, B.A.; Collett Jr., J.L. Spatial and temporal variability of ammonia and other inorganic aerosol species; *Atmos. Environ.* 2012, *61*, 490-498.
33. Chen, X.; Day, D.; Schichtel, B.; Malm, W.; Matzoll, A.K.; Mojica, J.; McDade, C.E.; Hardison, E.E.; Hardison, D.L.; Walters, S.; van de Water M.; Collett, Jr., J.L. Seasonal ambient ammonia and ammonium concentrations in a pilot IMPROVE NH_x monitoring network in the western United States; *Atmos. Environ.* 2014, *91*, 118-126.
34. Zhang, Y.; Wen, X.-Y.; Jang, C.J. Simulating chemistry-aerosol-cloud-radiation-climate feedbacks over the continental U.S. using the online-coupled Weather Research Forecasting Model with chemistry (WRF/Chem); *Atmos. Environ.* 2010, *44*, 3568-3582.
35. Werner, M.; Kryza, M.; Geels, C.; Ellermann, T.; Skjoth, A. Spatial, temporal and vertical distribution of ammonia concentrations over Europe: Comparing a static and dynamic approach with WRF-Chem; *Atmos. Chem. Phys. Discussions* 2015, *15*, 22935-22973.
36. Hansen, K.; Pryor, S.C.; Boegh, E.; Hornsby, K.E.; Jensen, B.; Sørensen, L.L. Background concentrations and fluxes of atmospheric ammonia over a deciduous forest; *Atmos. & For. Meteorol.* 2015, *214-215*, 380-392.
37. Langford, A.O.; Fehsenfeld, F.C.; Zachariassen, J.; Schimel, D.S. Gaseous ammonia fluxes and background concentrations in terrestrial ecosystems of the United States; *Global Biogeochem. Cycles* 1992, *6* (4), 459-482.
38. Saylor, R.D.; Edgerton, E.S.; Hartsell, B.E.; Baumann, K.; Hansen, D.A. Continuous gaseous and total ammonia measurements from the southeastern aerosol research and characterization (SEARCH) study; *Atmos. Environ.* 2010, *44* (38), 4994-5004.
39. Walker, J.T. (2018) Monitor for AeRosols and Gases. Unpublished raw data.
40. Beachley, G.M. (2017) Monitor for AeRosols and Gases. Unpublished raw data.
41. Benedict, K.B. (2017) Rocky Mountain National Park Nitrogen Study. Unpublished raw data.
42. von Bobrutzki, K.; Braban, C.F.; Famulari, D.; Jones, S.K.; Blackwell, T.; Smith, T.L.; Blom, M.; Coe, H.; Gallagher, M.; Ghalaieny, M.; McGillen, M.R.; Percival, C.J.; Whitehead, J.D.; Ellis, R.; Murphy, J.; Mohaschi, A.; Pogany, A.; Junninen, H.; Rantanen, S.; Sutton, M.A.; Nemitz, E. Field inter-comparison of eleven atmospheric ammonia measurement techniques; *Atmos. Meas. Tech.* 2010, *3*, 91-112.



Benefits that can make a difference for your career, your company, and the environment, including:

- Access to the latest technical information through *EM Magazine* and the *Journal*
- Discounts at ACE, our focused Specialty Conferences, Workshops, and Webinars
- Networking opportunities with leaders in the industry
- The chance to get involved, get noticed, and get ahead!

LEARN MORE DO MORE BE MORE

... through membership in the
Air & Waste Management Association

New Members—Join now so you can take advantage of member prices for multiple fall conferences and webinars. Savings of \$50 to \$150 per event can easily defray the cost of an individual membership!

Already a member? Help A&WMA grow and encourage others to join and write your name in the “recommended by” line on the online application.

Make your commitment to your career and the industry today and start taking advantage of all that A&WMA has to offer!

Find the complete Member Benefits Guide, the Top 10 Reasons, and join online now at www.awma.org/join.



Highlights from the Coordinating Research Council's **2019 Mobile Source Air Toxics Workshop**

by Susan Collet, S. Kent Hoekman, Seungju Yoon, and Timothy J. Wallington

The 2019 Coordinating Research Council's (CRC) Mobile Source Air Toxics (MSAT) Workshop was held February 4–6 at the California Environmental Protection Agency (CalEPA) Headquarters in Sacramento, CA. This was the ninth in a biennial series of CRC MSAT Workshops, which began in 2002. The purpose of the workshop was to bring together interested parties to review the status and current knowledge regarding mobile source air toxics. The 2019 workshop highlighted the ongoing trend of decreasing emissions and improving air quality in the United States. Despite the significant progress made, further reductions in MSAT emissions and improvement in air quality are needed. One plenary and five technical sessions covered regulatory needs, measurement and modeling of vehicle emissions, air quality and exposure measurements, air quality and exposure modeling, and accountability. The workshop featured 32 oral presentations and six posters with 120 participants. The agenda, final report, and presentations are available on the CRC website at www.crcao.org. Highlights from the sessions follow.

Strategies to reduce mobile source criteria, toxic, and greenhouse gas (GHG) emissions include: electrification of mobility; wider availability of micro-mobility (scooters, bikes), micro-transit, ride-hailing, and car sharing; and better linkages between mass transit and private services. To promote these strategies, more incentives for pooling and disincentives for single-passenger/single-occupant travel may be needed. The strategies could increase pooling, which may increase person miles traveled (PMT), but decrease vehicle miles traveled (VMT).

Figure 1 shows trends of ambient benzene concentrations measured in U.S. cities from 2003 to 2016. As illustrated in Figure 2 (left panel), reductions of MSAT emissions in California between 1990 and 2012 have lowered estimated cancer risks by 76–90%. Yet, unacceptable risk remains. This is particularly true in environmental justice areas where levels of pollution typically exceed those in surrounding areas (see Figure 2, right panel). In response to Assembly Bill 617 the California Air Resources Board (CARB) has established the Community Air Protection Program to reduce exposures in communities most affected by air pollution by increased monitoring at the local scale. On a national level, the latest update of the U.S. National Emissions Inventory (NEI) in 2018 provided detailed estimates of air emissions for criteria air pollutants and hazardous air pollutants for the period 2014–2017.

Regulatory Needs

It seems likely that emissions of mobile source toxics and criteria air pollutants will remain an issue for the foreseeable future. The mobile source contribution is particularly pronounced in local hotspots such as railyards, ports, and near major road intersections. Areas of future research focus include secondary organic aerosol (SOA) and brake and tire wear. In California, CARB and local air districts have launched a community air protection program and are jointly developing new approaches combining finer-scale air quality data collection and community emissions inventories to support local strategy development. Fragmented and sometimes overlapping authority provides challenges for regulating mobile sources: international authority for aircraft and ships; federal authority for motor vehicles, off-road equipment, and locomotives; and state (CARB) authority for California new engines and fuels. Local air quality management districts have limited authority for in-use fleets serving governments and some large facilities (e.g., warehouses).

Measurements and Modeling of Vehicle MSAT Emissions

On-road vehicle emissions were measured and modeled. Cold temperatures were found to substantially increase volatile and semi-volatile organic carbon (VOC, SVOC) emissions in gasoline direct injection (GDI) vehicles. The U.S. Environmental Protection Agency (EPA) is developing

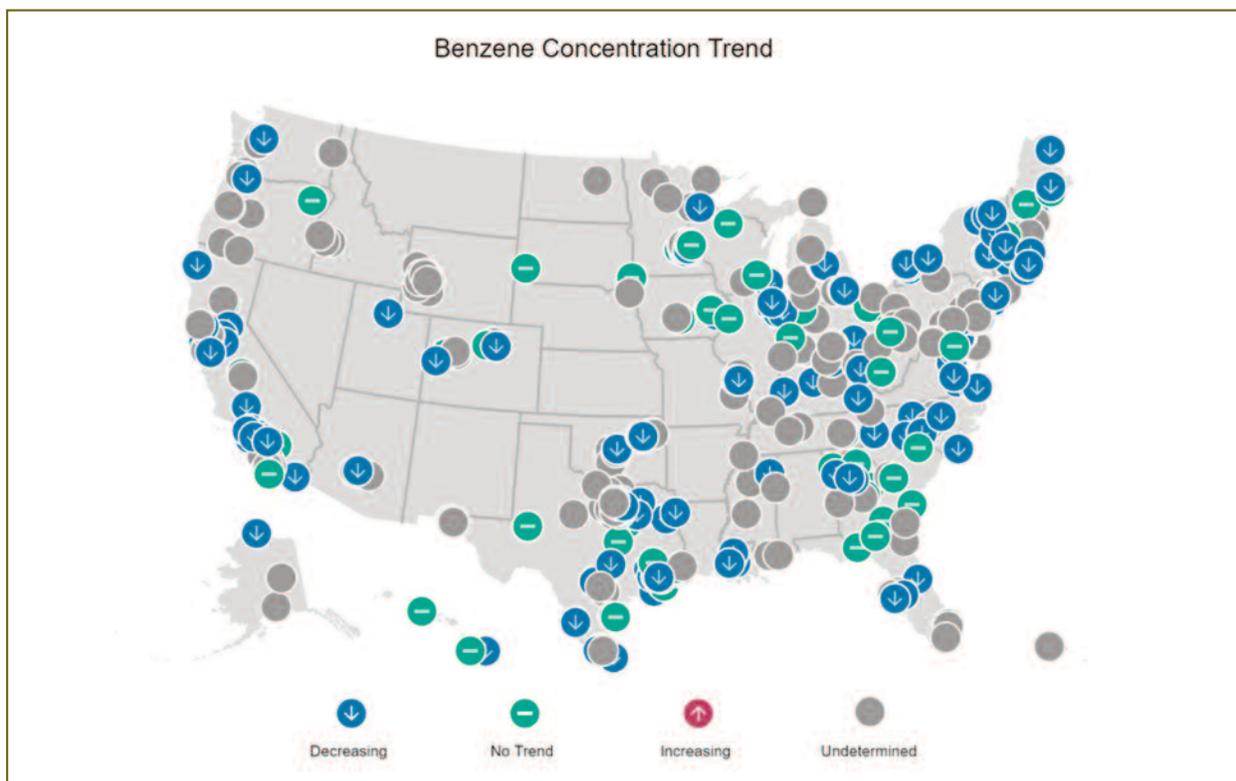


Figure 1. U.S. ambient benzene concentrations, 2003–2016.

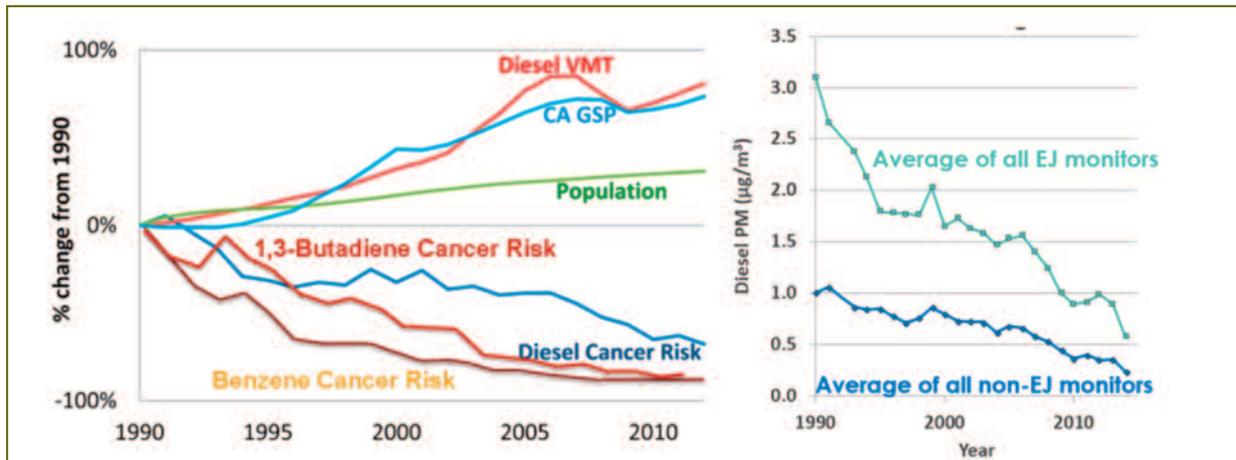


Figure 2. California MSAT emissions 1990–2012 (left panel); pollution levels in environmental justice areas (right panel).

volatility-based emission profiles for use in air quality models. Emissions from current technology GDI vehicles showed higher potential SOA formation with higher aromatic fuel content and an ethanol reinforcing effect was found for fuels with a high particulate matter index (PMI).

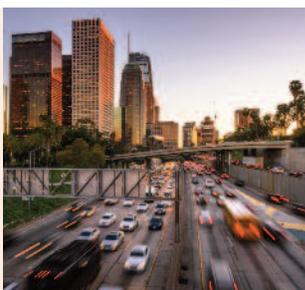
Emissions from port fuel injected (PFI) vehicles using E10 fuel decreased with increasing ambient temperature. The phenomenon was more pronounced for oxygenated species. The first in-use light-duty gasoline vehicle study of isocyanic acid (HNCO) and hydrogen cyanide (HCN) emission factors found HNCO emissions about two times greater, and HCN emissions much lower, than those in dynamometer studies. A small fraction of vehicles account for a large fraction of HNCO/HCN emissions.

One study developed a cabin air quality index (CAQI), which may enable customers to choose vehicle heating ventilation and air conditioning (HVAC) systems that reduce their exposure to pollutants. In-use heavy-duty truck emissions measured near the Caldecott Tunnel in California and in the Ft. McHenry Tunnel in Baltimore show large decreases in emissions of oxides of nitrogen (NO_x) and PM over the past 10 years. Estimates from EPA's Motor Vehicle Emission Simulator (MOVES2014) compare well with the tunnel observations.

Air Quality and Exposure Measurements

A suite of different measurement techniques are being used to monitor air quality. Ground measurements provide detailed air quality information but lacks spatial resolution. Satellite remote sensing provides broad spatial coverage, fills spatial gaps in ground monitoring networks, and can track broad progress on various air quality management strategies.

Cooking and traffic emissions are the main sources of spatial variability in urban air pollution. Local emissions of organic aerosol and black carbon are the major contributors for PM spatial variations. Trucks are still an important source of emissions in West Oakland, CA. The centrally located monitoring site understates black carbon concentrations observed at many local monitoring sites. In the Raleigh, NC, area, biogenic emissions appear to dominate precursor emissions that lead to SOA formation, even near a busy highway, although vehicles also contribute to substantial emissions of SOA precursors. Temperature-driven partitioning has implications for primary emission exposure and SOA formed from SVOCs. Roadside vegetation can provide significant reductions in local air pollution. EPA and CARB have developed recommendations to help design and maintain roadside vegetation for air quality benefits.



Modeling of on-road diesel PM (DPM) is being conducted in California. A methodology is being developed to spatially allocate and graphically illustrate vehicle emissions on each roadway to identify localized pockets of high DPM concentrations.

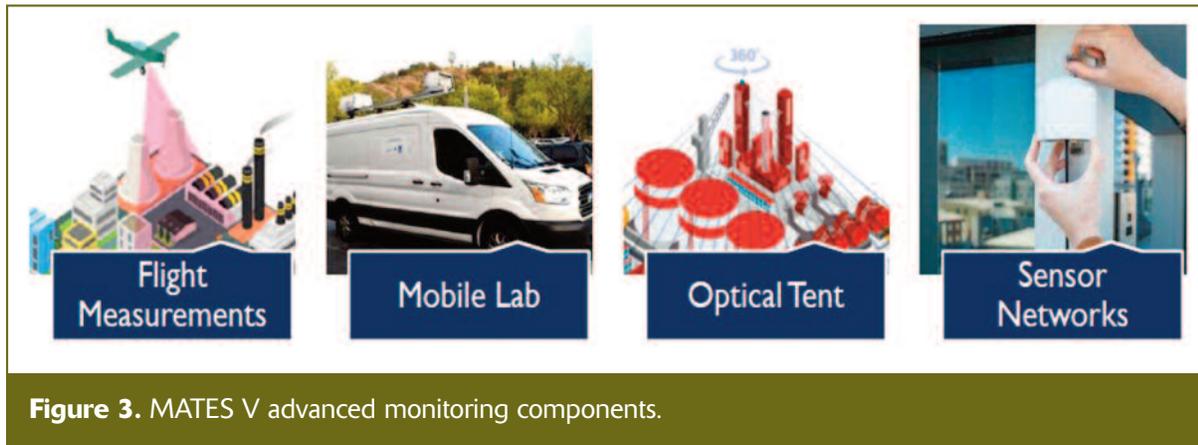


Figure 3. MATES V advanced monitoring components.

Air Quality and Exposure Modeling

Exposure modeling was performed for various spatial levels for various air quality components to determine health risks. Using the 2014 National Air Toxics Assessment (NATA), average U.S. lifetime cancer risks from air toxics were estimated to be approximately 30 in 1 million. Formaldehyde is the highest national risk driver based on estimated cancer risk. Pollutants come from manmade sources (e.g., facilities or vehicles) and natural sources (e.g., trees). On-road vehicle emissions contribute substantially to ambient benzene and polycyclic aromatic hydrocarbon concentrations in Canada. Contributions vary widely among locations and between seasons.

Significant progress has been made in the ability to simulate and model ultrafine particles ($PM_{0.1}$) in regional and urban scales. Nucleation is a major source of ultrafine particles during photochemically active periods. Regional chemical transport models can predict the major spatial and time trends in ultrafine particle concentrations. In some California cities, mobile sources do not dominate ultrafine particle contributions.

Accountability

Accountability studies assess the effectiveness of regulatory actions. There have been large reductions (~98%) in PM and NO_x emission rates for 2007 and later heavy-duty engines compared to pre-1990 model years. California has accelerated replacement of older engines with newer engines equipped with diesel particulate filters (DPFs) and selective catalytic reduction (SCR). However, expected PM emission reductions have not been fully realized because

some heavy-duty vehicles are operating without a DPF, and because some DPF-equipped engines have performance shortfalls.

The South Coast Air Quality Management District (SCAQMD) Multiple Air Toxics Exposure Study IV (MATES IV) found DPM contributes ~70% of estimated total air pollution cancer risk. DPM emissions were reduced by 66% between 2005 and 2012. Existing regulations are expected to reduce DPM from trucks by another 90% between 2012 and 2021. MATES V will include advanced monitoring components, illustrated in Figure 3, that will enable the creation of detailed air toxics maps.

Reductions in air pollution from goods movement actions and subsequent improvements in health outcomes for 23,000 California Medicaid enrollees were studied. Enrollees with asthma in port areas or places within 500 meters of truck-permitted freeways experienced greater reductions in emergency department visits than enrollees further away from freeways.

Summary

There has been great success in reducing MSAT emissions over the past several decades despite large increases in VMT. Accelerated fleet turnover of conventional technology vehicles, influx of revolutionary vehicle technologies such as self-driving and zero-emission vehicles, and strategies for various spatial levels will ensure that the trends of decreased MSAT emissions and human exposure to the emissions will continue in coming decades. **em**

Susan Collet is an Executive Engineer with Toyota Motor North America Inc.; **S. Kent Hoekman** is an Emeritus Research Professor with Desert Research Institute; **Seungju Yoon** is manager of the Climate Change Mitigation and Emissions Research Section in the Research Division at the California Air Resources Board; and **Timothy J. Wallington** is the Senior Technical Leader in Environmental Sciences and Sustainability with Ford Motor Company.

Acknowledgment: The authors acknowledge the many presenters and organizers of the workshop, the California Air Resources Board for co-sponsoring and hosting the workshop, along with the other co-sponsors: American Petroleum Institute, Health Effects Institute, and South Coast Air Quality Management District.



Highlights from the Coordinating Research Council's

29th Real-World Emissions Workshop

by Susan Collet, Dominic DiCicco, Scott Mason, Megan Beardsley, Naveen Berry, Tom Long, Tao Huai, Matthew Thornton, Radha Purushothaman, Shirish Shimpi, and Seungju Yoon

The 29th Coordinating Research Council (CRC) Real-World Emissions Workshop was held on March 10–13, 2019, in Long Beach, CA. The workshop consisted of 56 presentations in 10 sessions, 54 posters, and 9 demonstrations of analytical and technical services by various vendors. More than 265 attendees helped set another record for the highest number of attendees. Session highlights follow.

Air Quality

Air quality research includes monitoring current ozone and projecting future ozone and particulate matter (PM) concentrations and determining the source apportionment, and is now expanding to decarbonizing scenarios. The 2016–2017 ozone increases in the Southern California Air Basin (see Figure 1) were primarily due to more frequent occurrence of meteorological conditions conducive to ozone formation. The fleet emission factor disparities between high- and low-socioeconomic status communities remain significant due to the different model-year distributions. Accurate source apportionment of PM emissions is needed for effective compliance with stringent regulations. A more accurate representation of secondary organic aerosol (SOA) chemistry in transport models is needed for developing efficient regulatory policies. Regarding options for decarbonizing the transportation sector, an analysis using current information found battery and fuel cell electric vehicles in California have a similar carbon dioxide (CO₂) intensity, and costs will depend on quantity sold.

Improving the Emissions Inventory

The emissions inventory can be improved by using updated in-use activity, and including volatile organic compound (VOC), nitrogen oxide (NO_x), PM, and SOA emissions information. Emissions measurements from cargo-handling

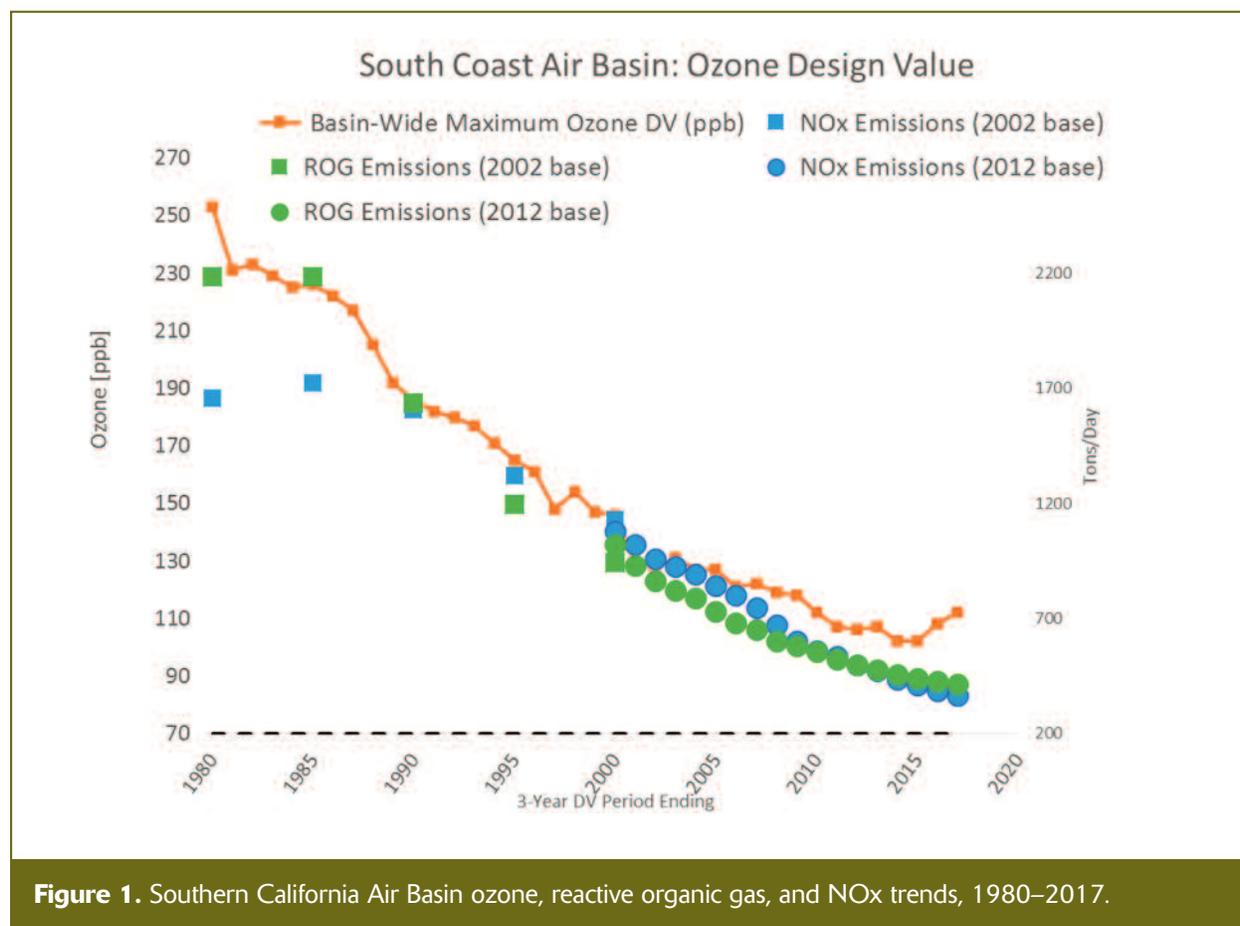
equipment during real-world operation revealed average in-use emissions were more than the certification standards, and the current inventory projections.

In Europe, emissions from vehicles with spark ignition engines with stop-start systems in urban traffic significantly exceeded limits for NO_x and PM under real driving conditions. After treatment designs incorporating gasoline particulate filters can be used to mitigate PM emissions.

Updates to the heavy-duty vehicle activity is anticipated to significantly improve the understanding of emissions from the heavy-duty fleet. Results from a tailpipe NO_x sensor study revealed the effectiveness of the after treatment system is dependent on the in-use duty cycle and is highly sensitive to operating temperatures. There is an ongoing assessment to determine a metric for a new paradigm of in-use NO_x emissions compliance for heavy-duty on-highway engines. The goals are to cost effectively achieve additional NO_x reductions and focus on in-use emissions, with consideration for sensor validation and durability.

Emissions Modeling

The U.S. Environmental Protection Agency (EPA) released the Motor Vehicle Emission Simulator (MOVES) version 2014b



in August 2018; updating non-road engine and diesel fuel parameters. The next MOVES major version release is in 2020 at the earliest, and will incorporate new data on emission rates and vehicle activity estimates. To refine mobile source emission inventories in the emissions factors model (EMFAC), the California Air Resource Board (CARB) is using new techniques including automated license plate monitoring and on-board diagnostic scans.

Elsewhere around the world, portable emission monitor data from an urban route was compared to four different microscale modeling approaches to explore possible upgrades to Hong Kong's EMFAC-HK. In Mexico City, remote sensing device (RSD) emission results suggest the Mexico City light-duty vehicle evaporative emissions are significant. Artificial neural networks were able to predict fuel consumption for individual gasoline and diesel vehicles. With access to velocity estimates and ambient data, such models could help optimize routing for fuel consumption and/or tailpipe emissions.

Light-Duty Vehicle In-Use Emissions

Light-duty vehicle emission variations were studied. Real-world microscale vehicle activity and emissions show large variability in emission rates between road segments. Inter-road segment variability correlated with characteristics such as average grade and vehicle activity. After 29 years, on-road vehicle emission changes at two sites in a South Los Angeles neighborhood show tailpipe carbon monoxide emissions decreased by factors of 10 and 20 and hydrocarbon emissions decreased by a factor of 25 with unchanging fleet age (see Figure 2).

In Europe, 2018 model-year pre-real driving emissions gasoline and diesel vehicles are exceeding Euro 6 limits under real driving conditions. Diesel vehicles can meet Euro 6 limits under real driving conditions using a range of exhaust treatment technology. Soot mass (or black carbon), PM mass, and solid particulate number emissions were lower from vehicles equipped with gasoline particle filters (GPFs). CO₂ emissions were not impacted by GPFs.

Heavy-Duty Vehicle In-Use Emissions

Studying in-use heavy-duty vehicles is ongoing. Preliminary results of in-use emissions testing of heavy-duty vehicles using portable emission measurement systems (PEMS) reveal the effects of three-way catalysts aging on NO_x emissions rate from older model-year stoichiometric natural gas engines. The current manufacturer heavy-duty in-use testing (HDIUT) program needs to be able to fully identify noncompliant engines.

CARB has started a first-of-a-kind heavy-duty surveillance

program to verify the effectiveness of after treatment systems for in-use vehicles. Measurements on-road with PEMS and for chassis and engine dynamometer tests indicate that in a number of modes of operation NO_x emissions from 0.2g/bhp-hr NO_x vehicles will be greater than 0.2 g/bhp-hr. In addition, data may more realistically reflect real-world emissions if not-to-exceed boundaries are modified.

A study of heavy-duty diesel engine cold-start and idle NO_x emissions showed not-to-exceed emission limit exceedances. Industry proposed a cost-effective paradigm shift from prescriptive laboratory-based to performance-based compliance programs, which utilizes on-board sensors, telematics, emissions data aggregation, etc.

Particulate Emissions and Measurement

Test equipment to measure diesel PM and vehicle hardware to control diesel PM is being evaluated. A comparison of PEMS with laboratory grade particulate number systems showed similar results. Low-cost particulate number measurements for the new European inspection maintenance regulations (Periodic Technical Inspection, PTI) showed condensation particle counters are acceptable for performance and operational demands. Another study found diesel particulate filters (DPFs) effectively control diesel PM emissions and reduces the solid fraction of PM. Control of crankcase particle emissions is being researched.

Off Road/Non-Road Emissions

EPA is working to improve the non-road emissions model by collecting and analyzing real-world activity data from a variety of non-road vehicles and equipment. CARB's future off-road inventories are likely to include more idling time and load bins. Brake-specific emissions using a broad spectrum of organic compounds were analyzed from non-road diesel engines with various after treatment configurations.

Fuel Effects on Emissions and Fuel Economy

The effect of different fuel types on emissions were studied. Using premium fuel in a premium-fuel-recommended vehicle may result in increased fuel economy and increased performance. The ethanol blending effects on vehicle emissions showed predictions from a model must account for ethanol composition and properties. A decrease in test temperature has a greater impact on PM emissions for light-duty gasoline direct injection vehicles than a change to the gasoline properties T50 and RVP. Hot-running emissions from a natural gas engine were below the 0.02 g/bhp-hr heavy-duty vehicle criteria pollutant standard. Fuel blends influence exhaust and in-cylinder concentrations of polycyclic aromatic hydrocarbons. Engine-out emissions from a light-duty diesel vehicle operating on hydrogenated vegetable oil were lower than its emissions while operating on ultra-low sulfur diesel fuel.



Figure 2. On-road vehicle emissions test site in Lynwood, CA, at I-710 and Imperial Highway; top is from December 1989, bottom is May 2018.

Emission Measurement Methods

Various approaches are available to measure the emissions from vehicles and more are being explored. PEMS provides real-world emissions data by measuring vehicle emissions while the vehicle is operating under real driving conditions. Other emission measurement methods are remote sensing, and use of chassis and engine dynamometers. A European process incorporated a data collection system for “comparative” testing rather than “compliance” testing. A CARB project explored the abilities and limitations of on-road PEMS testing and measurement uncertainties. A “road-to-lab” study will be conducted to compare vehicle emissions results between PEMS and chassis dynamometer data. Other studies being conducted

are projects involving on-board monitoring; control of after treatment systems using radio frequency sensors; the sensitivity of radio frequency measurements in detecting changes in engine-out conditions; and the capability of low-cost PEMS to find high concentrations of test vehicle emissions and ambient air.

Emissions Control Measures

Characterizing heavy-duty diesel vehicle emissions and their engine after treatment operation characteristics could further assist in controlling real-world emissions and in developing effective emission control measures. Heavy-duty diesel vehicles equipped with DPFs at the Port of Los Angeles showed increases in PM emissions over time due to DPF deterioration. However, fleet-wide PM emissions decreased as older non-DPF-equipped trucks were retired and replaced by newer DPF-equipped trucks.

Most DPF-equipped trucks emit black carbon emissions near or below their PM certification standards. About 4% of the trucks in the on-road fleet emit 50% of black carbon emission. However, NO_x emission factors from selective catalytic reduction (SCR)-equipped trucks could be three to four times higher than their certification standards. For the SCR-equipped trucks, the first 10 minutes of operation could contribute a disproportionately high percentage of NO_x emissions due to low-load and low-temperature operations.

An approach for a comprehensive heavy-duty vehicle inspection and maintenance program that could be implemented in California is being explored. One study suggests significant reductions in NO_x and PM opacity after repairing a vehicle’s faulty emission control components.

Next Workshop

The 30th Real-World Emissions Workshop is scheduled for March 15–18, 2020, in San Diego, CA. [em](#)

Susan Collet is an executive engineer at Toyota Motor North America Inc.; **Dominic DiCicco** is an environmental and energy manager at Ford Motor Company; **Scott Mason** is a fuels specialist at Phillips 66 Company; **Megan Beardsley** is an environmental scientist at the U.S. Environmental Protection Agency (EPA); **Naveen Berry** is an assistant deputy executive officer at South Coast Air Quality Management District (SCAQMD); **Tom Long** is a mechanical engineer at EPA; **Tao Huai** is a branch chief at California Air Resources Board (CARB); **Matthew Thornton** is a principal research engineer at the U.S. National Renewable Energy Laboratory (NREL); **Radha Purushothaman** is an engineering specialist at Caterpillar Inc.; **Shirish Shimpi** is a director of emissions development, at Cummins Inc.; and **Seungju Yoon** is a manager at CARB.

Acknowledgment: The Coordinating Research Council (CRC) acknowledges the many organizers, facilitators, presenters, and participants of this workshop, and especially the co-sponsors, including California Air Resources Board (CARB), National Renewable Energy Laboratory (NREL), South Coast Air Quality Management District (SCAQMD), and the U.S. Environmental Protection Agency (EPA). For more information on this workshop and others, as well as technical information regarding vehicle emissions, fuels and performance, please see the CRC website at www.crao.org.

A look back at this month 20 years ago in *EM* Magazine: July 1999.



The July 1999 issue of *EM* considered the pros and cons of implementing a then-nascent Environmental Management Information System (EMIS). When it comes to managing critical environment, health, and safety (EH&S) data for record-keeping and reporting purposes, the cover story noted that more and more companies are turning to EMISs for help. An EMIS can be as simple as a small PC-based database or as intricate as an enterprise-wide multimedia system. But whatever its size or complexity, an EMIS can improve data management, as well as the corporate bottom line.

Companies looking to improve business processes and practices regarding compliance requirements, information technology infrastructure, and budgetary concerns can benefit from implementing an EMIS. In the article, **Selecting and Implementing an Environmental Management Information System**, Jill Barson Gilbert discussed objectives and strategies that will provide the most effective and economic data management.

Quoting from the article: "A system by itself, whether automated or not, will guarantee neither compliance nor improved EH&S performance. However, a strong environmental management system is necessary to drive

improved performance. Meeting an international standard such as ISO 14001 may not be essential to having a strong environmental management system. Instead of creating separate, stand-alone environmental management systems, leading companies have integrated their environmental management processes into their broader business processes."

Elsewhere in this issue, Charles M. Wilk discussed the efficacy of solidification/stabilization (S/S) treatment of hazardous wastes in **Solidification/Stabilization Treatment: Principles and Practice**. The author suggested that its extensive use on Superfund and Resource Conservation and Recovery Act (RCRA) regulated wastes called for environmental professionals to better understand the chemical, physical, and regulatory aspects of the technology.

Quoting from the article: "Many RCRA-listed wastes require treatment to the maximum extent practical to reduce their potential hazards when land-disposed. S/S treatment is often used on RCRA-listed wastes to comply with this requirement. At remediation projects, S/S is often the only reasonably available technology to treat the large volumes of heavy metals-contaminated soil, sludge, or sediment resulting from these operations."

In another article, **Back to the Drawing Board: Now That the Court of Appeals Has Remanded Its Air Quality Standards for Ozone and Particulate Matter, What Next for the EPA?**, Lucinda Minton Langworthy considered the ramifications for the U.S. Environmental Protection Agency's (EPA) implementation of new National Ambient Air Quality Standards (NAAQS) for ozone and particulate matter after the U.S. Court of Appeals for the District of Columbia Circuit remanded the standards back to the agency in May 1999.

Quoting from the article: "Because the U.S. Clean Air Act requires EPA to base ambient standards on a criteria document that summarizes evidence of 'all identifiable effects' of a pollutant in the ambient air on public health and welfare, from the court's point of view, EPA was wrong in refusing to consider possible health benefits of ozone in the air." **em**

EM Archive

Access to A&WMA's complete *EM* back issues archive through 2013 is available online at www.awma.org/empastissues. If you are searching for a particular issue or article from our pre-2013 archived back catalog, please send a request e-mail to lbucher@awma.org.

Staff and Contributors

A&WMA Headquarters

Stephanie M. Glyptis

Executive Director
Air & Waste Management Association
Koppers Building
436 Seventh Ave., Ste. 2100
Pittsburgh, PA 15219
1-412-232-3444; 412-232-3450 (fax)
em@awma.org
www.awma.org

Advertising

Jeff Schurman

1-412-904-6003
jschurman@awma.org

Editorial

Lisa Bucher

Managing Editor
1-412-904-6023
lbucher@awma.org

Editorial Advisory Committee

Teresa Raine, Chair

ERM
Term Ends: 2022

Leiran Biton

U.S. Environmental Protection Agency
Term Ends: 2022

Gary Bramble, P.E.

Retired
Term Ends: 2021

James Cascione

SABIC Innovative Plastics
Term Ends: 2022

Bryan Comer

International Council on Clean Transportation
Term Ends: 2020

Prakash Doraiswamy, Ph.D.

RTI International
Term Ends: 2020

Ali Farnoud

Ramboll Environ
Term Ends: 2020

Steven P. Fryinger, Ph.D.

James Madison University
Term Ends: 2021

Keith Gaydosh

Affinity Consultants
Term Ends: 2021

Jennifer K. Kelley

General Electric
Term Ends: 2020

John D. Kinsman

Edison Electric Institute
Term Ends: 2022

Mingming Lu

University of Cincinnati
Term Ends: 2022

David H. Minott, QEP, CCM

Arc5 Environmental Consulting
Term Ends: 2020

Brooke A. Myer

Indiana Department of Environmental Management
Term Ends: 2022

Brian Noel, P.E.

Trinity Consultants
Term Ends: 2020

Golam Sarwar

U.S. Environmental Protection Agency
Term Ends: 2022

Melanie L. Sattler

University of Texas at Arlington
Term Ends: 2022

Anthony J. Schroeder, CCM, CM

Trinity Consultants
Term Ends: 2022

Justin Walters

Southern Company Services
Term Ends: 2022

Susan S.G. Wierman

Johns Hopkins University
Term Ends: 2021

Layout and Design: Clay Communications, 1.412.704.7897

EM, a publication of the Air & Waste Management Association, is published monthly with editorial and executive offices at The Koppers Building, 436 Seventh Ave., Ste. 2100, Pittsburgh, PA 15219, USA. ©2019 Air & Waste Management Association (www.awma.org). All rights reserved. Materials may not be reproduced, redistributed, or translated in any form without prior written permission of the Editor. A&WMA assumes no responsibility for statements and opinions advanced by contributors to this publication. Views expressed in editorials are those of the author and do not necessarily represent an official position of the Association. A&WMA does not endorse any company, product, or service appearing in third-party advertising.

em

The Magazine for Environmental Managers