

**NADP 2003  
LONG-TERM MONITORING:  
SUPPORTING SCIENCE AND INFORMING POLICY  
AND  
TECHNICAL COMMITTEE MEETING**

October 20-22, 2003  
Washington, D.C.

**Technical Program Chair**

Gary Lear  
U. S. Environmental Protection Agency  
Clean Air Markets Division  
Washington, D.C.

**AMMONIA WORKSHOP**

October 23-24, 2003  
Washington, D.C.

**Workshop Organizer**

Margaret Kerchner  
National Oceanic and Atmospheric Administration  
Chesapeake Bay Office

**Co-Sponsors of Meeting and Workshop**

Chesapeake Bay Program's Scientific and Technical Advisory Committee  
Hubbard Brook Research Foundation  
Mid-Atlantic Regional Air Management Association  
National Oceanic and Atmospheric Administration - Air Resources Laboratory  
and Chesapeake Bay Office

**PROCEEDINGS**

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A special thank you to those responsible for making the 2003 National Atmospheric Deposition Network a success. Kathy McCormick is responsible for arranging the meeting facilities, catering and budgets. Roger Claybrooke provides the maps for the proceedings booklet as well as the maps for the annual map summaries. Bob Larson maintains the web page with meeting registration and information. Thanks also goes to Sarah Milton and Nichole Samson for their production of the CALendar. Joyce Fringer and Pamela Bedient, administrative coordinators for the NADP, provide untiring support for the staff of the NADP.



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**NADP TECHNICAL COMMITTEE MEETING AGENDA**



# NADP 2003 Long-Term Monitoring: Supporting Science and Informing Policy and Ammonia Workshop - Block Agenda Washington, D.C.

NADP 2003 Long-term Monitoring: Supporting Science and Informing Policy and Ammonia Workshop - Block Agenda Washington, D.C.			
	October 20, 2003	October 21, 2003	October 22, 2003
Time	Monday	Tuesday	Wednesday
	Registration Open	Registration Open (continental breakfast)	Registration Open (continental breakfast)
0700			
0730			
0800	Executive Committee Meeting	Annual Technical Committee Meeting	Applying NADP in the Sciences (Session Chair: Gary Lear, U.S. Environmental Protection Agency) <i>Linking Atmospheric Nitrogen Deposition to Ecological Effects along the Estuarine-Coastal Gradient</i> <i>Evaluating the Effectiveness of the Clean Air Act for Changes in Surface Water Acidification</i> (Steve Kahl, University of Maine)
0815			Multiple Roles and Effects of Ammonia Emissions (Session Chair: Dr. Jan Willem Erisman, Energy Research Centre of the Netherlands) <i>Ammonia and Air Quality</i> (Dr. Russ Dickerson, University of Maryland) <i>Effects of Ammonia Deposition</i> (Dr. Jim Galloway, University of Virginia)
0830			
0845			
0900			Effects of Atmospheric Ammonia on Terrestrial Vegetation (Dr. Sagar Krupa, University of Minnesota)
0915			
0930			Discussion
0945		(break)	(break)
1000	The Role of Long-term Monitoring in Program and Policy Evaluation (Session Chair: Rich Grant, Purdue University) <i>Role of Long-Term Monitoring for Pollution Control</i> (Rob Brenner, Deputy Assistant Administrator, OAR, U.S. Environmental Protection Agency)	Dry Deposition of Atmospheric Mercury: Models, Measurements and Future Network Design (Eric Prestbo, Frontier Geosciences)	Perspectives on Managing Ammonia Emissions (Session Chair: Dr. John Bachmann, EPA OAQPS) <i>Managing Ammonia in Europe</i> (Dr. Jim Webb, ADA S. Research)
1015			
1030	Joint Subcommittee Meeting		National Perspective <i>Managing Ammonia in the U.S.</i> (Dr. Jerry Hatfield, U.S. Department of Agriculture/Agricultural Research Service)
1045	The USGS National Water-Quality Assessment (NAWQA) Program: The Atmospheric Connection Dr. John Mimikakis, Deputy Chief of Staff, House Committee on Science	(break)	
1100		NADP in Perspective: The Next 25 Years (Session Chair: Jim Lynch, Penn State University) <i>Perspectives on Clean Air Accountability: A Look Across the Long-term Monitoring Landscape</i> <i>The North American Commission for Environmental Cooperation Perspective on Long-term Environmental Monitoring in North America</i> (Paul Miller, North American Commission for Environmental Cooperation)	State Perspective <i>Are We There Yet? Future Paths from the Past</i> (Mr. Gary Saunders, North Carolina Dept of Environment & Natural Resources)
1115			
1130	Monitoring Strategy for the National Park Service (Chris Shaver, National Park Service)	Modernizing NADP Field Equipment and On-site Data Systems (Mark Nilles, U.S. Geological Survey) <i>Preserving/Growing Long-term Monitoring</i> (Van Bowersox, Illinois State Water Survey)	Local Perspective <i>Regulating Ammonia in Clean Air Act State Implementation Plans - Do We Know Enough to Proceed?</i> (Mr. Dave Mitchell, San Joaquin Valley Air Pollution Control District)
1145			
1200	Lunch (on own)	Lunch (on own)	Lunch (on own)
1230		12:00 to 1:30	12:15 to 1:30
		Luncheon - David J. Goldston, Chief of Staff, House Committee on Science	Discussion

## NADP 2003 Long-Term Monitoring: Supporting Science and Informing Policy and Ammonia Workshop - Block Agenda Washington, D.C.

NADP 2003 Long-term Monitoring: Supporting Science and Informing Policy and Ammonia Workshop - Block Agenda Washington, D.C.		October 22, 2003 Wednesday	October 23, 2003 Thursday
Time	October 21, 2003 Tuesday	October 22, 2003 Wednesday	October 23, 2003 Thursday
	<b>Subcommittee Meetings</b>		
1300			
1315			
1330	<b>NADP in the Public Arena</b> (Session Chair: Rick Artz, National Oceanic and Atmospheric Administration) <i>NADP in the Public Arena: Nitrogen Deposition and Management of Hypoxia in Long Island Sound</i> (Paul Stacey, Connecticut Department of Environmental Quality)	<b>Hubbard Brook</b> (Session Chair: Carl Sasser Furiness, North Carolina State University)	<b>Assessing Our Ability to Quantify Ammonia</b> (Session Chair: Dr. Ray Knighton, U.S. Department of Agriculture, CSREES) <i>Measuring Ammonia Emissions from Agricultural Sources: Technical Possibilities, Applicability in Situ, Benefits and Drawbacks</i> (Dr. Gert-Jan Monteny, IMA G Wageningen University and Research Centre)
1345	<i>Native American Perspective</i> (Dwayne Beavers, Cherokee Nation)	<i>The Legacy and Future of Long-term Monitoring at the Hubbard Brook Experimental Forest, New Hampshire and the National Atmospheric Deposition Program</i> (Kathy Fallon Lambert, Science Links Consultant for the Hubbard Brook Research Foundation)	<i>Techniques for Measuring Ammonia Emissions from Land Applications of Manure and Fertiliser.</i> (Dr. Tom Misselbrook, Institute of Grassland & Environmental Research)
1400			
1415	<i>Electric Generation Perspective</i> (Rick Carlton, Electric Power Research Institute)	<i>Atmospheric Deposition at the Hubbard Brook Experimental Forest, New Hampshire: Linkages Among Long-Term Measurements, Experiments and Modeling</i> (Charles Driscoll, Syracuse University)	<i>Urban Ammonia Source Characterization Using Infrared Quantum Cascade Laser Spectroscopy</i> (Dr. Mark Zahniser, Aerodyne Research, Inc.)
1430			
1445			
1500	(break)		(break)
1515	<b>You Can't Get There from Here ... Or Can You: Monitoring as the Basis for Good Clean Air Policies</b> (Michael Shore, Environmental Defense)		<b>Quantifying Ammonia Concentrations and Exchange Fluxes: Process Interactions and Regional Generalization</b> (Dr. Mark Sutton, CEH, Edinburgh Research Station)
1530	(break)		
1545	<b>Panel Discussion</b> (Session Chair: Mark Nilles, U.S. Geological Survey) Panelist: Rona Birnbaum (U.S. Environmental Protection Agency) Tom Butler (Cornell University) Rick Carlton (Electric Power Research Institute) Bernard Melewski (Atrondack Council) Paul Stacey (Connecticut Department of Environmental Quality)	<i>Nitrogen: Linking Upland Watersheds and Coastal Ecosystems</i> (David Whittall, National Oceanic and Atmospheric Agency)	<i>Measurement of Ammonia Concentrations and Fluxes: Recent Examples Using Denuder and Chemiluminescence Technologies</i> (Mr. John Walker, U.S. Environmental Protection Agency, Office of Research and Development NRMRL)
1600			
1615			
1630			<i>Application of Micrometeorological Methods for Determining Fluxes of Nitrogen Compounds</i> (Dr. Tilden Meyers, National Oceanic and Atmospheric Administration, Office of Oceanic and Atmospheric Research, ARL)
1645			Discussion
1700			
1730			
1800			
1830			
1900			
4		<b>Poster Session and Reception/Social Mixer</b>	



**NADP Technical Committee Meeting  
Washington, D.C.  
October 20-22, 2003**

**MONDAY, October 20, 2003**

**Room Location**

Registration Desk Open All Day

8:00 a.m. to 10:15 a.m.	Executive Committee Meeting	Map
10:15 a.m. to 10:30 a.m.	Break	
10:30 a.m. to 12:00 p.m.	Joint Subcommittee Meeting	Map
12:00 p.m. to 1:00 p.m.	Lunch (on your own)	
1:00 p.m. to 3:00 p.m.	Subcommittee Meetings	
3:00 p.m. to 3:15 p.m.	Break	
3:15 p.m. to 5:00 p.m.	Subcommittee Meetings NOS DMAS Effects	Map Kalorama Jackson

**TUESDAY, October 21, 2003**

**Room Location**

7:00 a.m.	Registration	
8:00 a.m. to 9:45 a.m.	Annual Technical Committee Business Meeting	Georgetown
9:45 a.m. to 10:00 a.m.	Break	
<b>TECHNICAL SESSION:</b>	<b>THE ROLE OF LONG-TERM MONITORING IN PROGRAM AND POLICY EVALUATION</b> Session Chair: Rich Grant, Purdue University	Georgetown
10:00 - 10:45	<b><i>Accountability in Multipollutant Legislation</i></b> Rob Brenner, Deputy Assistant Administrator, OAR, USEPA	
10:45 - 11:00	<b><i>Water Resource Monitoring at the USGS</i></b> Tim Miller, U.S. Geological Survey	
11:00 - 11:30	Dr. John Mimikakis, Deputy Chief of Staff, House Committee on Science	
11:30 - 12:00	<b><i>Monitoring Strategy for the National Park Service</i></b> Chris Shaver, Natinal Park Service	
12:00 p.m. to 1:30 p.m.	Lunch (on your own)	

**TUESDAY, October 21, 2003**

**Room Location**

**TECHNICAL SESSION: NADP IN THE PUBLIC ARENA**  
Session Chair: Rick Artz, National Oceanic and Atmospheric Administration

1:30 - 2:00 ***NADP in the Public Arena: Nitrogen Deposition and Management of Hypoxia in Long Island Sound***  
Paul Stacey, Connecticut Department of Environmental Quality

2:00 - 2:30 ***Native American Perspective***  
Dwayne Beavers, Cherokee Nation

2:30 - 3:00 ***Electric Generation Perspective***  
Rick Carlton, Electric Power Research Institute

3:00 - 3:30 ***You Can't Get There from Here .... Or Can You: Monitoring as the Basis for Good Clean Air Policies***  
Michael Shore, Environmental Defense

3:30 p.m. to 3:45 p.m. Break

**PANEL DISCUSSION:** Discussion Chair: Mark Nilles, U.S. Geological Survey  
3:45-4:45 Panelists: Rona Birnbaum, U.S. Environmental Protection Agency  
Tom Butler, Cornell University  
Rick Carlton, EPRI  
Bernard Melewski, Adirondack Council  
Paul Stacey, Connecticut Department of Environmental Quality

**WEDNESDAY, October 22, 2003**

**Room Location**

7:00 a.m. Registration

**TECHNICAL SESSION: APPLYING NADP IN THE SCIENCES** Georgetown  
Session Chair: Gary Lear, U.S. Environmental Protection Agency

8:00 - 8:30 ***Linking Atmospheric Nitrogen Deposition to Ecological Effects along the Estuarine-Coastal Gradient***  
Hans Paerl, University of North Carolina

8:30 - 9:00 ***Evaluating the Effectiveness of the Clean Air Act for Changes In Surface Water Acidification***  
Steve Kahl, University of Maine

9:00 - 9:30 ***Environmental Monitoring for Model Development***  
Mark Cohen, National Oceanic and Atmospheric Administration

9:30 - 10:00 ***Linking Mercury Emissions, Environmental Cycling, and Exposure: What We Know and Where We Need to Be in the Future***  
Dave Krabbenhoft, U.S. Geological Survey

**WEDNESDAY, October 22, 2003**

**Room Location**

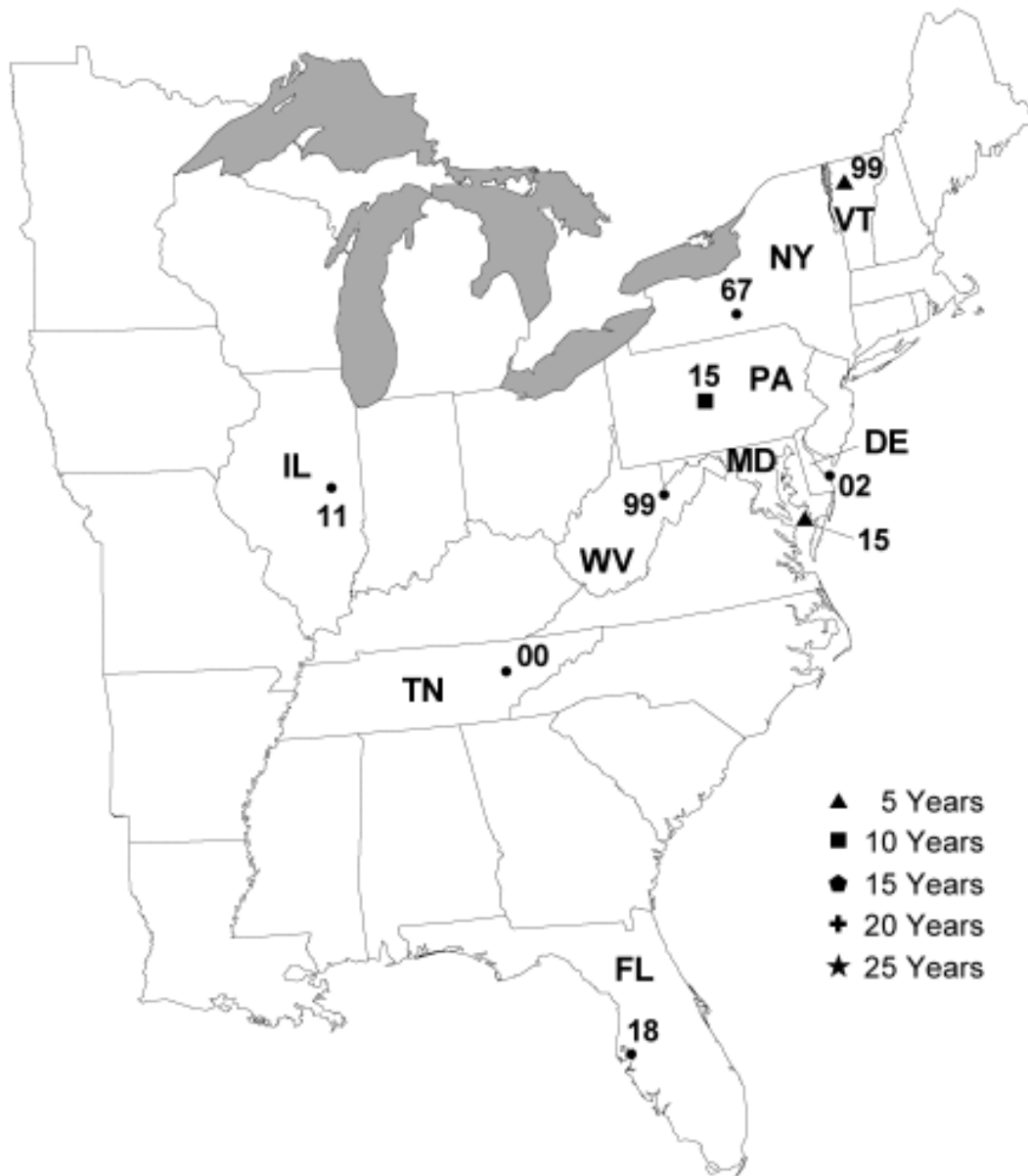
10:00 - 10:30	<b><i>Dry Deposition of Atmospheric Mercury: Models, Measurements and Future Network Design</i></b> Eric Prestbo, Frontier Geosciences	
<b>TECHNICAL SESSION:</b>	<b>NADP IN PERSPECTIVE: THE NEXT 25 YEARS</b> Session Chair: Jim Lynch, The Penn State University	
10:45 - 11:15	<b><i>Perspectives on Clean Air Accountability: A Look Across the Long-term Monitoring Landscape</i></b> David Schmeltz, U.S.Environmental Protection Agency	
11:15 -11:30	<b><i>The North American Commission for Environmental Cooperation Perspective on Long-term Environmental Monitoring in North America</i></b> Paul Miller, North American Commission for Environmental Cooperation	
11:30-11:45	<b><i>Modernizing NADP Field Equipment and On-site Data Systems</i></b> Mark Nilles, U.S.Geological Survey	
11:45 - 12:00	<b><i>Preserving/Growing Long-term Monitoring</i></b> Van Bowersox, Illinois State Water Survey	
12:00 p.m. - 1:45 p.m.	Luncheon - Invited Speaker David J. Goldston, Chief of Staff, House Committee on Science	International Ballroom East
<b>TECHNICAL SESSION:</b>	<b>HUBBARD BROOK</b> Session Chair: Cari Sasser Furiness, North Carolina State University	Georgetown
2:00 - 2:30	<b><i>Advancing Science and Affecting Change through Four Decades of Long-term Research</i></b> Kathy Fallon Lambert, Science Links Consultant for the Hubbard Brook Research Foundation	
2:30 - 3:45	<b><i>Acidic Deposition - Monitoring, Experimentation, and Modeling</i></b> Charles Driscoll, Syracuse University	
3:45 p.m. to 4:00 p.m.	Break	
4:00 p.m. to 4:45 p.m.	<b><i>Nitrogen: Linking Upland Watersheds and Coastal Ecosystems</i></b> David Whital, National Oceanic and Atmospheric Administration	
5:00 p.m. to 7:30 p.m.	<b>POSTER SESSION - SOCIAL MIXER</b>	Monroe



**2003 NADP SITE OPERATOR AWARDS**

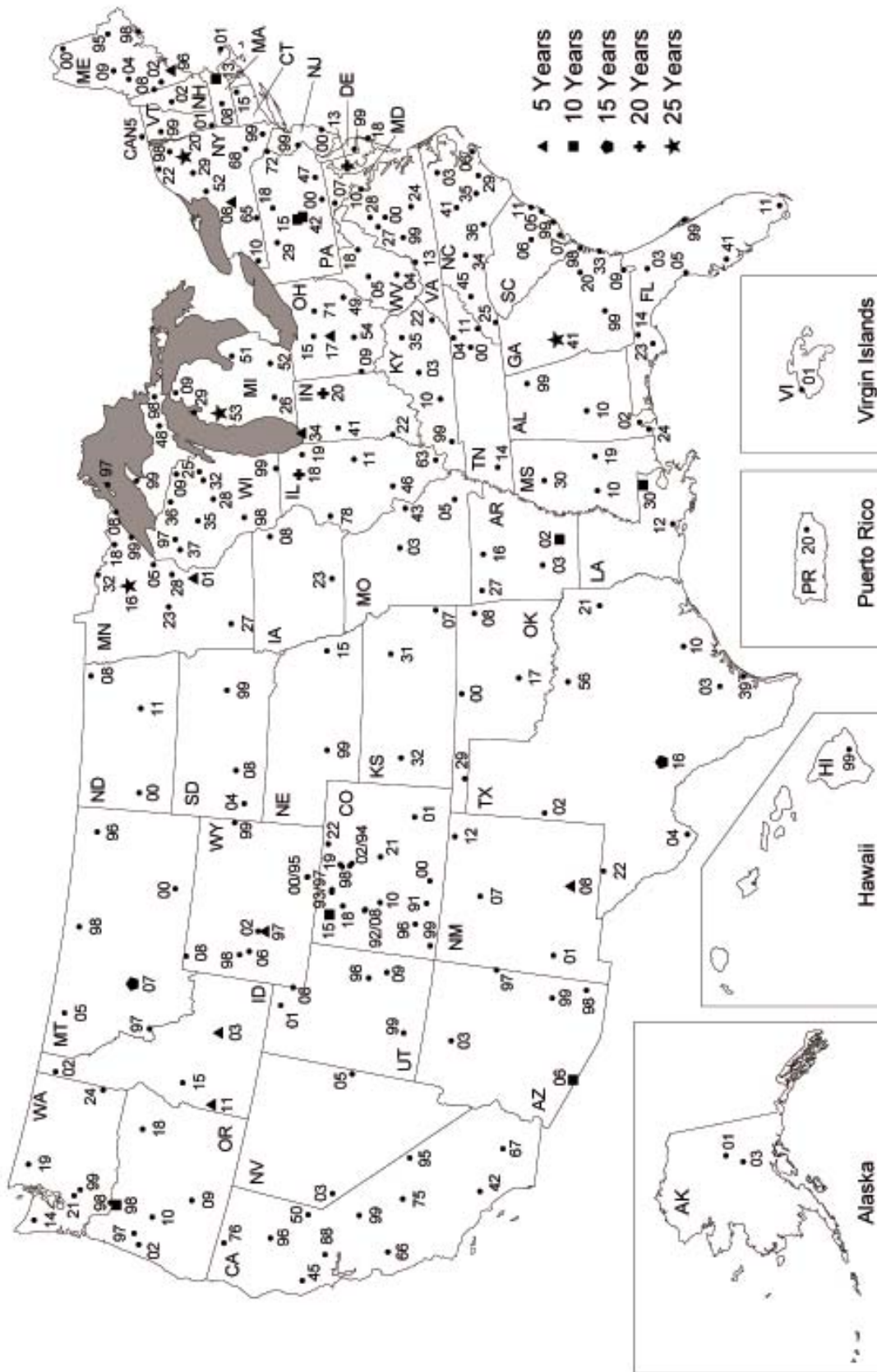


# AIRMoN Site Operator Service Awards - 2003



NTN Site/Site Name	Operator Name	Wet Start	Agency
<b>5 Year Awards</b>			
MD15 - Smith Island	Francis "Hoss" Parks	11/17/95	NOAA
VT99 - Underhill	Miriam Pendleton	1/27/93	NOAA
<b>10 Year Awards</b>			
PA15 - Penn State	Robert Zeigler	6/7/83	Penn State

# NADP/NTN Site Operator Service Awards - 2003





<b>NTN Site/Site Name</b>	<b>Operator Name</b>	<b>Wet Start</b>	<b>Agency</b>
<b>5 Year Awards</b>			
ID03 - Craters of the Moon National Monument	Michael Munts	8/22/80	NSP-ARD
ID11 - Reynolds Creek	Brenda Richards	11/22/83	USGS
IN34 - Indiana Dunes National Lakeshore	Cheryl Guster Burdett	7/15/80	NSP-ARD
ME96 - Freeport	Don Prince	1/6/98	EPA
MN01 - Cedar Creek	Dale Krueger	12/31/96	Minnesota PCA
NM08 - Mayhill	Linda Madron	1/24/84	USGS
NY08 - Aurora Research Farm	Daniel Tiffany	4/17/79	USDA/Cornell University
OH17 - Delaware	Arthur Peterson	10/3/78	USFS
WY97 - South Pass City	Liz Oswald	4/30/85	SF Phos Ltd
<b>10 Year Awards</b>			
AR02 - Warren 2WSW	Steve Tackett	5/25/82	USGS
AZ06 - Organ Pipe Cactus National Monument	Amy Pate	4/15/80	NPS-ARD
CO15 - Sand Spring	Ole Olsen	3/20/79	USGS-BRD
LA30 - Southeast Research Station	Diana Corkern	1/18/83	USGS
MA13 - East	Leslie Collyer	2/2/82	NESCAUM
OR98 - Bull Run	Verena Fabian	7/13/82	USGS/City of Portland
PA15 - Penn State	Robert Ziegler	6/7/83	NOAA-ARL
PA42 - Leading Ridge	Kevin Homer	4/25/79	SAES
<b>15 Year Awards</b>			
MT07 - Clancy	Kent Dodge	1/24/84	USGS
TX16 - Sonora	Robert Moen	6/26/84	USGS
<b>20 Year Awards</b>			
IL18 - Shabbona	David Lindgren	5/26/81	SAES/University of Illinois
IN20 - Roush Lake	Gary Zeissig	8/22/83	USGS
MD13 - Wye	Michael Newell	3/8/83	SAES/University of Maryland
<b>25 Year Awards</b>			
GA41 - Georgia Station	John Melin	10/3/78	SAES/University of Georgia
MI53 - Wellston	William Dunn	10/10/78	USFS
MN16 - Marcell Experimental Forest	Arthur Elling	7/6/78	USFS
NY20 - Huntington Wildlife	Ray Masters	10/31/78	EPA/SUNY-Syracuse



**TECHNICAL SESSION: THE ROLE OF LONG-TERM MONITORING IN PROGRAM AND  
POLICY EVALUATION**

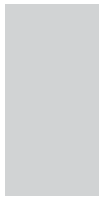
Session Chair: Rich Grant, Purdue University



## **Role of Long-Term Monitoring for Pollution Control**

Rob Brenner  
Deputy Assistant Administrator  
EPA Office of Air and Radiation

Presentation on the occasion of the 25th anniversary of the NADP provides an overview and historical context for how science and monitoring networks specifically NADP — have been instrumental in informing policy and providing accountability, using the examples of Title IV of the 1990 Clean Air Act amendments/Acid Rain Program and current multi-pollutant emission reduction proposals. Data from long-term monitoring efforts has enabled examination of regional scale problems and evaluation of control program efficacy. A singular contribution to effective policy development and implementation is the NADP network's data which establishes and verifies relationships between emissions and effects. NADP is one of the best examples of interagency collaboration and summon the lessons learned from the 25 years of experience. Challenges ahead are to maintain the long term quality and integrity of data and to be "nimble" to meet policy communities' evolving data needs.



**The USGS National Water-Quality Assessment (NAWQA) Program:  
The Atmospheric Connection**

Timothy L. Miller<sup>1</sup>  
Chief, Office of Water Quality  
U.S. Geological Survey  
412 National Center  
12201 Sunrise Valley Drive  
Reston, VA 20192

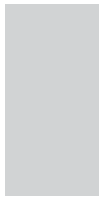
The NAWQA Program has three broad goals: 1) identify the status or condition of ambient water quality in streams and aquifers, 2) determine water-quality time trends, and 3) relate status and trends to causative factors. NAWQA works in water resource areas of the nation with high water use for municipal supply and irrigated agriculture. Together, these areas represent more than 60 percent of the population served by municipal supply and about an equal percentage of irrigated lands. NAWQA collects and analyzes data on a broad range of constituents including: nutrients, pesticides, volatile organic compounds, and trace metals.

Through this assessment program, USGS evaluates the sources, transport and fate of environmental contaminants in many environmental settings. For some of the constituents measured, atmospheric sources of contaminants are of key interest. While some of the interests are expected, e.g., nitrogen in the Northeastern United States and semi-arid watersheds of the west, other sources of atmospheric influence are more difficult to define and quantify. Specific interest centers around a volatile organic compound like MTBE (methyl tert butyl ether), and on mercury. Developing water-quality time trends by examining lake and reservoir sediment cores has led to both increasing and decreasing trends for several contaminants with significant atmospheric contributions including lead, and PAHs (polycyclic aromatic hydrocarbons). The atmospheric connections considered are often mobile sources within urban environments. Finally, atmospheric transport of some pesticides also receives attention from the NAWQA program.

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Washington, D.C.  
NADP  
2003

**Speaker: Dr. John Mimikakis  
Deputy Chief of Staff  
House Committee on Science**



## **Monitoring Strategy for the National Park Service**

Chris Shaver<sup>1</sup>  
National Park Service – Air Resources Division  
P.O. Box 25287  
Denver, CO 80225

The National Park Service (NPS) has jurisdiction over 83 million acres in more than 385 national parks and has the responsibility to preserve these areas unimpaired for the enjoyment of future generations. Included in these areas are an incredible variety of natural and cultural, biotic and abiotic resources. Many of these resources are affected by air quality and the NPS has developed an extensive program, under its Air Resources Division, to understand the origin, transport, and fate of air pollution and its impacts on resources. Part of this program includes long-term monitoring of air pollution, including deposition of air pollutants.

The NPS has participated in the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) for over 20 years and now supports over 40 monitoring sites in national parks nationwide. The information from these sites is used by the NPS to assess status and trends in air quality, identify areas of concern, and develop target and critical deposition loading values to protect sensitive areas. The information has been used to characterize deposition for 270 parks under the NPS Inventory and Monitoring Program, as well as to assess NPS goals under the Government Performance and Results Act.

The NPS faces many challenges in the coming years. Trend analyses of NADP/NTN data indicate that although sulfur deposition has decreased in most parks over the last 10 years, nitrogen deposition has increased at many parks. Levels of both sulfur and nitrogen deposition remain well above pre-industrial levels. Streams in Shenandoah and Great Smoky Mountains NPs are experiencing chronic and episodic acidification, brook trout fisheries in Shenandoah have been affected, and aquatic and terrestrial ecosystems in Rocky Mountain NP are undergoing subtle changes attributable to atmospheric deposition. Research is being conducted in other sensitive ecosystems to examine possible impacts.

Recent NPS attention has focused on the effects of mercury and organic compounds in park ecosystems. Five NPS sites now are part of the Mercury Deposition Program, with 3 more sites coming on line this year. Information from these sites will complement research on park ecosystem effects from toxics.

Long-term high quality monitoring is essential to the NPS mission to protect resources and NADP/NTN is an essential component of that effort.

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**TECHNICAL SESSION: NADP IN THE PUBLIC ARENA**

Session Chair: Rick Artz, National Oceanic and Atmospheric  
Administration



**NADP in the Public Arena: Nitrogen Deposition and Management of Hypoxia in Long Island Sound**

Paul E. Stacey<sup>1</sup>  
Connecticut Department of Environmental Protection  
Bureau of Water Management  
79 Elm Street  
Hartford, CT 06106-5127

Fossil fuel burning has increasingly been recognized as a major source of nitrogen enrichment to eastern U.S. estuaries. Long Island Sound (LIS) is a 1300 sq. mi. estuary of shared jurisdiction between Connecticut and New York that is severely impacted by nitrogen overload. Each summer an average of 200 sq. mi. of western LIS bottom waters experience dissolved oxygen levels below 3.0 mg/L with an average duration of 50 days. Less severe hypoxia in the 3.0 – 5.0 mg/L range occurs over half of the Sound's bottom waters, but is still serious enough to affect living resources and violate state water quality standards. Estimates vary, but at least 15% of the total nitrogen load to LIS is believed to originate from atmospheric deposition even when the dominant nitrogen generator, New York City sewage treatment plants (STP), is factored into the statistic. Atmospheric deposition may account for 25 - 35% of the nitrogen contributed by the Sound's major tributary, the Connecticut River. In April 2001, EPA approved Connecticut and New York's Total Maximum Daily Load (TMDL) analysis, which formalized a management plan to reduce anthropogenic nitrogen loading to LIS from the two states by nearly 60% by 2014. Much of the reduction will come from the more easily managed STPs and Connecticut has embarked on an unprecedented nitrogen trading program among 79 STPs located throughout the state. Because of uncertain load estimates and the multijurisdictional nature of its origin, the TMDL identified EPA as the appropriate authority to develop and implement a nitrogen emissions reduction plan to address nitrogen deposition to LIS. Success of that action will rely on good scientific information and a federal willingness and ability to incorporate clean water needs articulated in a TMDL into air management programs.

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## **Native American Perspective**

Dwayne Beavers  
Cherokee Nation

The state of Oklahoma's point source pollutants rank 6<sup>th</sup>, 15<sup>th</sup>, 18<sup>th</sup> and 28<sup>th</sup> nationally in carbon monoxide, nitrogen oxides, sulfur dioxide and volatile organic carbon emissions, respectively. The source emissions are primarily from coal-fired and gas-fired power plants. Of the 77 counties in Oklahoma, approximately five of those counties within the Cherokee Nation's jurisdictional boundaries (northeastern Oklahoma) repeatedly rank in the top five or upper percentile for these emissions. The Cherokee Nation's ambient monitoring program has been able to augment the state's monitoring by placing monitors in rural areas where these point sources are located. In addition, the tribal program has been able to participate in monitoring programs that address tribal, local, state, regional and national monitoring concerns. These have included criteria, PM2.5, IMPROVE, CASTNet, and mercury deposition ambient air monitoring. In addition, future monitoring may include ammonia and air toxic monitoring at identified sites.

## **Electric Generation Perspective**

Richard Carlton  
Electric Power Research Institute  
Palo Alto, California.

Increasing inputs of reactive nitrogen (N) to ecosystems in the U.S. have been linked to many environmental concerns, including acidification of ecosystems, accumulation of N in groundwater, and eutrophication of waterways. The role of atmospheric N deposition is of particular interest to land managers and policy makers, as rates of atmospheric N deposition are increasing in some areas. The sources of atmospheric N deposition include industrial, automotive, and agricultural emissions. The existing NADP program and its database have long provided value to many who endeavor to reduce the deleterious ecological effects on nitrogen deposition. Now, data regarding the relative contributions of the various sources are needed in order to develop sound strategies for managing and understanding the effects of these and other N inputs to the landscape. This presentation will discuss new approaches to source attribution and examine scenarios for future management options.



**You Can't Get There from Here .... Or Can You:  
Monitoring as the Basis for Good Clean Air Policies**

Michael Shore<sup>1</sup>  
Environmental Defense

Good environmental policy depends on sound science. As scientists monitor and model, there is broad agreement that the United States needs to make significant reductions in sulfur dioxide, oxides of nitrogen, and mercury. Additionally, the world-wide general scientific consensus on the threats of climate change tell us that the United States should play a leadership role in capping and lowering carbon dioxide and other greenhouse gas emissions. The need to reduce these pollutants — especially from undercontrolled power plants — has sparked considerable national dialogue on multi-pollutant bills in Congress. But passage of multi-pollutant legislation seems unlikely, due to the widely divergent views over the level and timing of reductions, the pollutants included, and the effect on existing Clean Air Act programs and authorities.

Though the science—the monitoring and the modeling — tells us the United States should especially clean up power plants, without Congressional action it seems as if there is no way to get there from here. On the contrary, through implementation of existing Clean Air Act authorities, the U.S. Environmental Protection Agency (EPA) has the tools in place to clean up power plant pollution.

The EPA should develop and implement a transport rule to reduce SO<sub>2</sub> and NO<sub>x</sub> pollution that contribute to fine particle and ozone non-attainment. The EPA has set March 2004 as the deadline to release a proposal. Several recent analyses support reducing emissions to levels comparable to national caps of 2 million tons for SO<sub>2</sub> and 1.5 million tons for NO<sub>x</sub>, and the agency's transport rule should lower emissions comparable to these levels. Also, this December, the EPA is required to propose standards to reduce mercury and other air toxics discharged from power plants. The agency should substantially lower these harmful contaminants. And the EPA is on a schedule to issue proposed rules and guidelines, by April 2004, establishing the "best available retrofit technology" for aging power plants and other major industrial sources that contribute to haze air pollution in protected national parks and wilderness areas.

The states also have a pivotal role. The states have been the proving ground to develop innovative policies to protect public health and the environment from air pollution. North Carolina, New York, Colorado, Connecticut, Massachusetts, Texas, New Hampshire have all put in place clean air programs for power plants that are stricter than federal requirements. And fifteen states or more have initiated policies — some modest, some bold — to start addressing the pressing problem of climate change. And, EPA does not need permission from Congress to follow the states' lead.

The science is clear: to protect public health and the environment, pollution from power plants must be reduced substantially. If we are tenacious and innovative and follow the science, we can get there. One way or another, we can achieve cleaner, healthier air.

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**PANEL DISCUSSION:** Session Chair: Mark Nilles, U.S. Geological Survey





## **Biography**

Rona Birnbaum

Rona Birnbaum is Chief of the Assessment and Communications Branch in the Office of Atmospheric Program's Clean Air Markets Division. She has been with the Division since 1991, soon after the Acid Rain Program was created. Throughout her time in the Air Office, Rona has focused on the science-policy interface relating to atmospheric deposition, assessment of human health and environmental effects, and communication of results. She holds a Masters Degree in Environmental and Natural Resource Policy.



## **Biography**

Tom Butler

Tom Butler has been an Associate of the Institute of Ecosystem Studies since its inception and is a visiting fellow in the Ecology and Evolutionary Biology Dept at Cornell University. He has been “visiting” Cornell for 20 years now! He has been actively engaged in precipitation and atmospheric chemistry research since the beginning of the MAP3S network in 1976. This was when NADP was still only a glimmer in the mind’s eye of some scientists.

He has authored several scientific articles relating the impact of changing SO<sub>2</sub> and NO<sub>x</sub> emissions on both wet and dry deposition and has worked closely with Gene Likens in much of this work.

In addition Tom has been involved in the biogeochemistry of aquatic and estuarine systems ranging from the bayous of Louisiana to the Hudson River Estuary. He is currently Chief Scientist at Cornell in an assessment of the ecology and biogeochemistry of the North Caspian Sea.

## **Biography**

Rick Carlton

Rick Carlton manages the Facilities Water Management Program in the Environment Department of the Electric Power Research Institute. Research emphases in his Program include integrated ash pond management, dry and low water cooling technologies, non-oxidizing biocides for cooling systems, plant water treatment, and constructed wetlands for waste water treatment.

Dr. Carlton manages research in diverse areas, including 1) avian interactions with power transmission and distribution structures, wind power facilities, and communication towers; 2) sources and fates of atmospheric nitrogen and mercury deposition; 3) peregrine falcon nesting on power plant stacks; 4) food-borne mercury exposure in the common loon; 5) release of pollutants from contaminated sediments; 6) and mercury and selenium cycling and food chain transfer in terrestrial and aquatic ecosystems.

Dr. Carlton earned a B.S. in Limnology and a M.S. in Ecology from the University of California, Davis, and a Ph.D. in Aquatic Ecology from Michigan State University.



## **Biography**

Bernard C. Melewski

BERNARD C. MELEWSKI has been an environmental lawyer and lobbyist in New York State for over twenty-years. A graduate of the Syracuse University College of Law, he is currently the Deputy Director and Counsel to the Adirondack Council. The Adirondack Council is a private, not-for-profit organization dedicated to protecting and enhancing the natural character and human communities of the Adirondack Park through research, education, advocacy and legal action. Prior to joining the staff of the Adirondack Council, Mr. Melewski served for five years as the Counsel to the State Legislative Commissions on Solid Waste and Hazardous Waste Management. Mr. Melewski is the author of "Acid Rain and the Adirondacks: A Legislative History," published by the Albany Law Review in 2002.

## Biography

Paul E. Stacey

Paul E. Stacey is a supervising environmental analyst with the Connecticut Department of Environmental Protection's Bureau of Water Management, Planning and Standards Division. The Planning and Standards Division has involvement in all surface water quality matters including planning, some aspects of permitting, and monitoring, and is responsible for establishing surface water quality standards and classifications for the state. Mr. Stacey has served as state coordinator for the Long Island Sound Study (LISS) since he was hired in 1985 and also supervises CTDEP's nonpoint source pollution control program. Among his responsibilities with the LISS are pollution load estimation, supervising the Long Island Sound monitoring program, management planning, implementation of nitrogen controls and nitrogen credit exchange, and technical writing of plans and literature generated by the Study. He also is involved in acid rain and nitrogen deposition programs and sits on the Steering Committee for the New England Governors/ Eastern Canadian Premiers "Acid Rain Action Plan".

The LISS is part of the federal EPA National Estuary Program, which involves more than 100 federal, state, local, and citizen participant groups. The LISS is investigating, and promoting management of, key water quality problems including: low dissolved oxygen (hypoxia), toxic contaminants, impacts on living resources and their habitats, floatable debris and pathogens. The study began in 1985 and passed major implementation milestones in 1990 with the release of its interim plan to control nitrogen, in 1994 with the release of the comprehensive management plan, and in 2001 with the adoption of the Total Maximum Daily Load for nitrogen control. The TMDL calls for major nitrogen load reductions to control hypoxia from throughout the state of Connecticut and portions of New York state that drain to Long Island Sound. A Nitrogen Credit Exchange Program has been developed to facilitate implementation of the TMDL, which is unique in the nation.

Mr. Stacey was previously employed by the Academy of Natural Sciences in Philadelphia for eight years. There, he served as project manager for studies investigating the impacts of pollution on aquatic communities and the uptake of pollutants into fish tissues.

Mr. Stacey received a Bachelor of Arts Degree from the College of the Holy Cross in Worcester, MA; a Bachelor of Science Degree from Utah State University; and a Master of Science Degree from Colorado State University. He is a member of the Estuarine Research Federation.



**TECHNICAL SESSION: APPLYING NADP IN THE SCIENCES**

Session Chair: Gary Lear, U.S. Environmental Protection  
Agency





## Linking Atmospheric Nitrogen Deposition to Ecological Effects along the Estuarine-Coastal Gradient

Hans W. Paerl<sup>1\*</sup>, David R. Whitall<sup>2</sup> and Robin L. Dennis<sup>3</sup>

Atmospheric deposition of nitrogen (AD-N) is now recognized as a major contributor of externally-supplied or “new” nitrogen (N) to estuarine and coastal waters. Watershed N export estimates indicate that AD-N can be a significant source of N flowing to estuarine and coastal waters (indirect AD-N). Direct deposition to these waters is an additionally important new N source that can bypass the terrestrial and in-stream filters that process N falling on the landscape. In coastal waters downwind of anthropogenic emission sources (US East Coast, W. Europe, E. Asia), AD-N can be the single most important source of new N. In addition, the chemical composition of AD-N is changing in response to shifts in agricultural practices, urbanization, and fossil fuel emissions. Changing proportions of reduced, oxidized and organic N in AD-N reflecting these shifts may alter the structure and function of estuarine and coastal phytoplankton communities, with potential cascading impacts on food web dynamics and nutrient cycling. Using an extension of the regional acid deposition model, a range of estuarine and coastal AD-N deposition measurements, and nutrient response bioassays with natural phytoplankton indicator communities, we have assessed the budgetary importance, spatial extent and ecological roles that AD-N plays in N cycling and eutrophication dynamics of geographically diverse coastal regions. Results indicate that AD-N plays a central role in coastal N budgets, eutrophication, trophic and biogeochemical changes. As such, this anthropogenically-dominated N source should play an important role in the development of ecosystem and regional-scale coastal water quality and habitat management strategies.

<sup>1</sup>Univ. of North Carolina at Chapel Hill, Institute of Marine Sciences, 3431 Arendell Street, Morehead City, NC 28557

<sup>2</sup>Center for Coastal Monitoring and Assessment, NOAA, N/SCI 1 SSMC4, Sta. 9222, 1305 East West Hwy, Silver Spring, MD 20910

<sup>3</sup>USEPA/NOAA, Atmospheric Modeling Division, Research Triangle Park, NC 27711

\*corresponding author



## **Evaluating the Effectiveness of the Clean Air Act for Changes In Surface Water Acidification**

Steve Kahl<sup>1</sup>, Steve Paulsen<sup>2</sup> and John Stoddard<sup>2</sup>

The Clean Air Act Amendments (CAAA) of 1990 contributed to a sub-continental scale experiment on the aquatic effects of changes in atmospheric deposition. The changes were a result of interactions at the ecosystem-scale, and thus neither deposition data or lake chemistry data were sufficient alone to address the science and policy questions. The EPA surface water research programs LTM (Long-Term Monitoring) and TIME (Temporally Integrated Monitoring of Ecosystems) were designed to quantify the changes in surface water chemistry in the northern and eastern US since 1991 and 1982, respectively. LTM is a group of sites selected for pre-existing data and specific chemical characteristics, notably low ANC (Acid Neutralizing Capacity). TIME is a statistical sub-population of lakes from EPA EMAP. The aquatic systems were used to quantify the watershed response because air deposition or precipitation chemistry monitoring are not adequate to demonstrate that the Clean Air Act has caused improvements in biologically relevant aquatic chemistry. Key support for our analysis of trends and patterns is provided by the data from the National Atmospheric Deposition Program (NADP). NADP data indicate that atmospheric deposition has improved in positive ways as intended by the CAAA. The length and continuity of record in NADP is essential for future assessments Clean Air Act related policy. Moreover, the NADP data record is fundamental to the process of providing answers to the ecological science questions posed by the results to date from LTM and TIME. The changes in sulfate concentrations in surface waters are a direct result of the decrease in atmospheric deposition. Other changes in surface water chemistry have not followed directly from changes in deposition, especially for nitrate and base cations. 'Recovery' will not be a linear process because of the complexities of ecosystem response that are influenced by a variety of confounding factors such as changes in climate.

<sup>1</sup>Senator George J. Mitchell Center for Environmental & Watershed Research  
The USGS Maine Water Resources Research Institute 102 Norm Smith Hall, University of  
Maine, Orono, ME 04469; Telephone: 207-581-3286; FAX: 581-2725; E-mail: Kahl@maine.edu;  
<http://www.umaine.edu/WaterResearch/>

<sup>2</sup>U.S. Environmental Protection Agency, Corvallis OR 97333

## Environmental Monitoring for Model Development

Mark Cohen<sup>1</sup>  
NOAA Air Resources Laboratory  
1315 East West Hwy, R/ARL, Room 3316  
Silver Spring MD 20910

The goal of this talk is to provide – from a modeler’s perspective – general ideas and specific examples of the synergisms that exist between atmospheric monitoring and modeling. The critical role that environmental monitoring plays in model development and evaluation will be discussed. General ideas regarding the characteristics of monitoring programs that make them more or less useful for different model applications will be presented, including the type of monitoring site, the frequency and duration of sampling, and the species, phases, and/or other parameters measured. The utility and limitations of existing monitoring programs will be discussed in relation to current modeling needs, including both *receptor-oriented* modeling approaches (e.g., back-trajectories) and *emissions-inventory-based* comprehensive three-dimensional dispersion modeling approaches. The utility of models to help design monitoring programs and to extend their results will also be presented. Specific examples of the above concepts from atmospheric modeling analyses will be provided (for mercury, atrazine, and/or dioxin). The take-home message of this talk is that monitoring data cannot be fully utilized without modeling, and modeling cannot be done credibly without monitoring.

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## **Linking Mercury Emissions, Environmental Cycling, and Exposure: What We Know and Where We Need to Be in the Future**

David P. Krabbenhoff<sup>1</sup>  
U.S. Geological Survey  
8505 Research Way  
Middleton, Wisconsin 53562

Since the industrial revolution, anthropogenic mercury emissions have increased atmospheric mercury levels about threefold, and caused corresponding increases in mercury levels in terrestrial and aquatic ecosystems. For most ecosystems, atmospheric deposition is the primary source of mercury, making mercury contamination a global phenomenon. Exposure to mercury can affect the viability of plants, fish, birds and mammals. Bioaccumulation within the food chain can result in sublethal or even lethal effects on piscivorous wildlife and humans, even in apparently remote and pristine environments where mercury levels in water and sediment are very low. However, our ability to predict a priori where problem areas are most likely to occur is limited by an incomplete understanding of the factors that regulate and intercede between atmospheric deposition and biological exposure. In addition, in many of areas of the US, the lack of understanding is further hampered by a paucity of data, including information on atmospheric deposition of mercury. This presentation will cover the general topic environmental mercury cycling, with special emphasis on the need to understand the linkages between atmospheric emissions, mercury methylation, and exposure to food webs by drawing upon a variety of recent or ongoing research projects. Finally, an assessment of remaining major information gaps regarding mercury contamination of the environment will be presented.

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## **Dry Deposition of Atmospheric Mercury: Models, Measurements and Future Network Design**

Eric Prestbo<sup>1</sup> and Steve Lindberg<sup>2</sup>

Current national-scale atmospheric models include estimates of the mercury dry deposition rate. For the most part, these modeled mercury dry deposition estimates are based on a relatively small set of research data and scientific judgment. Combined with past research in Europe and the North America, new ecosystem-based studies are now reestablishing the importance of quantifying the mercury dry deposition rate. In particular, the uptake of elemental mercury by foliage may be more important than previously understood. Furthermore, depending on location, the dry deposition rate of mercury is estimated to be as large or larger than the wet deposition rate. The number of sites in North America quantifying the rate of wet-deposition of mercury to sensitive aquatic ecosystems continues to grow through programs such as the NADP Mercury Deposition Network, EPA-ORD sponsored super sites and a few State sponsored networks. However, with a few exceptions that will be mentioned, the mercury dry deposition rate is not being quantified in a concerted manner. The methodologies to measure the key atmospheric mercury species have been establish. Thus, the tools are now available to quantify the mercury dry deposition rate via the inferential method. In addition some low cost options are available for the measurement of mercury dry deposition, which could be added to current wet-deposition sites. New regulations of mercury emissions in North America are expected to change the input of mercury species to the atmosphere. The measurement of the mercury dry deposition rate will be critical to provide feedback on the efficacy of the regulations and provide needed data to atmospheric and ecosystem models as well as the TMDL program, for example.

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**TECHNICAL SESSION: NADP IN PERSPECTIVE: THE NEXT 25 YEARS**

Session Chair: Jim Lynch, The Pennsylvania State  
University





**Perspectives on Clean Air Accountability:  
A Look Across the Long-term Monitoring Landscape**

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Changing national air policies and programs have compelled policy-makers to demonstrate the efficacy of these actions through the results of regional air quality and atmospheric deposition monitoring networks. While the networks offer a high quality, long-term record of environmental change across the U.S., they may not adequately fulfill evolving monitoring and assessment policy needs in a changing policy environment. This presentation offers a perspective on what a multi-pollutant accountability program could look like, and considers the capacity of the existing long-term monitoring infrastructure to address emerging policy needs.

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## **The North American Commission for Environmental Cooperation Perspective on Long-term Environmental Monitoring in North America**

Paul J. Miller  
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When the three North American countries launched the North American Free Trade Agreement (NAFTA) in 1994, they also brokered an environmental side agreement creating the North American Commission for Environmental Cooperation (CEC). One objective of the environmental side agreement is to “increase cooperation between the Parties to better conserve, protect, and enhance the environment, including wild flora and fauna.” Fundamental to meeting this objective is long-term environmental monitoring that captures information relevant to policy initiatives in each country.

This presentation will give a CEC perspective on the role of long-term environmental monitoring in North America in light of air quality priorities in Canada, Mexico and the United States. Convenient and dependable access to and dissemination of relevant, reliable, and comparable monitoring information, along with sound interpretive assessments based, in part, on that information are crucial to the confirmation and quantification of progress made with respect to air quality programs and international commitments. Some important examples are regional ozone reduction strategies, acidic deposition connected to ecological responses, and regional visibility improvement efforts. In addition, baseline surveys using monitoring information are likely to be very important when attempting to assess the nature, extent and significance of emerging transborder air pollution issues – for example potential electric power generation “clusters” arising along international boundaries to take advantage of increased trade liberalization under NAFTA. The results of such surveys using comparable data obtained across borders can help identify multi-jurisdictional spatial patterns and correlations amongst different human health and environmental parameters, and inform and guide future monitoring, research and modeling activities.

## Modernizing NADP Field Equipment and On-site Data Systems

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NADP plays a key role as one of the nation's important environmental monitoring systems. Current NADP field instrumentation and data systems are proven, with known and acceptable levels of reliability, quality assurance and serviceability. NADP has grown since 1978, when a network of 22 sites was initiated, through today, when three NADP networks comprise nearly 350 sites. Throughout the past 25 years consistency in protocols, equipment, sample analyses and quality assurance have enhanced the value of NADP data to describe the national status and temporal trends in wet atmospheric deposition of important chemical constituents.

Extensive experience with current field sampling equipment indicates current instruments exhibit under catch of light liquid precipitation and dry snow, and can exhibit reliability problems in severe cold. Because current equipment is based upon designs developed many years ago, they are not amenable to on-site digital data management and are not readily adaptable to interface with modern telemetry systems. The objective of efforts underway to develop, test and deploy modernized NADP field equipment and on-site data systems are to maintain and continue the high quality of data record while improving collector capture efficiency, increase overall system reliability, streamline site data management and provide telemetry options to enable access to near real-time precipitation data and site operational status.

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## Preserving/Growing Long-term Monitoring

Van Bowersox  
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*The National Atmospheric Deposition Program (NADP) will remain one of the nation's premier research support projects serving science and education and supporting informed decisions on air quality issues related to precipitation chemistry, especially acidic compounds, nutrients, base cations, and mercury. The NADP will be responsive to emerging issues requiring new or expanded measurements. Its measurement system will be efficient, its data will meet pre-defined data quality objectives, and its reports and products will meet user needs.* These statements express the vision for a program that is celebrating a quarter century of monitoring precipitation chemistry.

What has sustained the NADP for its first 25 years is providing a unique record of long-term, high-quality data on the chemicals borne by rain and snow. Making these data available on-line in a user-friendly format began in 1995, and this far-sighted approach has substantially increased interest in the program and NADP data usage. On-line data access and usage continues to grow, as the annual number of "hits" now exceeds a million, and the annual number of user sessions exceeds 150,000. Adding trend plots, expanded site information, animated time-series maps, and back trajectories are some examples of how NADP committees working with the NADP Program Office have enhanced basic on-line data in recent years. Serving user needs continues to be the emphasis of these and related efforts to expand and improve data access.

User needs change, however; and to be true to its vision, the NADP strives to accommodate emerging issues as resources are available to support new efforts. Past efforts of cooperation on special studies, such as the collaborative effort with the U.S. Geological Survey in 1991 to assess the pesticide content of precipitation, have been very successful. Today, the Program Office collaborates with nearly a dozen principal investigators from universities and federal and state agencies to provide sample aliquots for further research on chemicals not routinely measured by the NADP; isotopic concentrations of hydrogen, oxygen, nitrogen, and sulfur; and plant and animal pathogens. With its well-developed communications network and management infrastructure, together with previous experience at monitoring disasters, such as the 1986 Chernobyl nuclear accident, the NADP is well-positioned to assist in a national surveillance system to detect biological, chemical, or radiological agents. Monitoring that serves user needs is key to the enduring success of the NADP.

## **Luncheon**

Speaker: David J. Goldston  
Chief of Staff  
House Committee on Science

David Goldston was appointed to run the House Committee on Science in January 2001. As staff director, he oversees a committee with jurisdiction over most of the federal civilian research and development budget, including programs run by NASA, the National Science Foundation, the Department of Energy, the Department of Commerce and the Environmental Protection Agency. Prior to becoming staff director, Mr. Goldston was legislative director for Congressman Sherwood Boehlert (R-NY), who became chairman of the Science Committee in January 2001. Rep. Boehlert is a leading moderate Republican and has led Republican efforts to protect the environment. As legislative director, Mr. Goldston was Rep. Boehlert's top environmental aide and also oversaw the legislative and press operations of the office. Mr. Goldston came to Capitol Hill in 1983 as Boehlert's press secretary. From 1985 to 1994, he served on the Science Committee as the special assistant on the Subcommittee on Science, Research and Technology. In that role, he oversaw the programs of the National Science Foundation and the National Institute of Standards and Technology, and also directed Boehlert's efforts to shut down the Superconducting Super Collider (SSC). In 1994 and 1995, Mr. Goldston was project director at the Council on Competitiveness, a private sector group with members from industry, labor and academia. Goldston directed work on the report, "Endless Frontier, Limited Resources: U.S. R&D Policy for Competitiveness." Mr. Goldston graduated magna cum laude with a Bachelor of Arts degree in American History from Cornell University in 1978. He has completed the course work for a Ph.D. in American History at the University of Pennsylvania.



**TECHNICAL SESSION: HUBBARD BROOK**

Session Chair: Cari Sasser Furiness, North Carolina  
State University





**The Legacy and Future of Long-term Monitoring at the Hubbard Brook Experimental Forest,  
New Hampshire and the National Atmospheric Deposition Program**

K.F. Lambert\*<sup>1</sup> and C.T. Driscoll<sup>2</sup>

Long-term data play a critical role in measuring environmental change, determining its ecological consequences, and evaluating policy options and their effects. Atmospheric deposition data from the Hubbard Brook Ecosystem Study and the National Atmospheric Deposition Program (NADP) have been instrumental in documenting the occurrence and variability of acidic deposition. These programs have also played a key role in quantifying the relationship between atmospheric concentrations of sulfate and nitrate and emissions of sulfur dioxide and nitrogen oxide from anthropogenic sources. Moreover, continuous measurements of precipitation pH provide a resource for determining the impact of legislation such as the 1990 Clean Air Act Amendments.

The value of these long-term monitoring programs is well-understood within scientific community. However, distilling and communicating the results of long-term monitoring for public policy are necessary in order to build support and improve the scientific basis for decision-making. The recently created Science Links program at the Hubbard Brook Research Foundation may serve as a model for conveying the significance of NADP and other long-term monitoring programs to members of Congress, government agencies and interested citizens. Science Links combines synthesis and publications with media outreach and public policy strategies.

Finally, long-term funding for the long-term monitoring programs at both the Hubbard Brook Experimental Forest and the NADP network is a perpetual challenge. A recent review of funding for NADP and other federal programs estimates that an investment of roughly \$26 million is needed to meet current operating and infrastructure needs. Strategies for continued success and sustainability might include: (1) maintaining current high quality sample analysis, (2) documenting and communicating network needs, (3) convening panels to evaluate what measurements are needed, (4) expanding a constituency and voice in Congress, and (5) building upon links to human health and biological impacts.

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## **Atmospheric Deposition at the Hubbard Brook Experimental Forest, New Hampshire: Linkages Among Long-Term Measurements, Experiments and Modeling**

C.T. Driscoll\*<sup>1</sup>, G.E. Likens<sup>2</sup>, and T.J. Butler<sup>2</sup>

Long-term measurements of bulk deposition and stream water chemistry were initiated at the Hubbard Brook Experimental Forest (HBEF) in 1963. Since that time, additional measurements have been made at the site to better understand the structure, function and change in the northern hardwood forest and associated aquatic ecosystems in response to air pollution. Included in these measurements is wet deposition through the NADP. Long-term measurements at the HBEF provide: 1) insight into ecosystem function, 2) empirical data to test models, and generate and test hypotheses and 3) information that is relevant to regional, national and global environmental issues. There are synergistic interactions among the research activities of long-term measurements, modeling and ecosystem experiments that are critical to the success of the Hubbard Brook Ecosystem Study. Long-term measurements at the HBEF show a strong relationship between declines in concentrations of sulfate in precipitation and emissions of sulfur dioxide in the northeastern U.S. airshed. Trends in concentrations of nitrate in bulk deposition are consistent with decreases in nitrogen oxide emissions from electric utilities. Stream water chemistry measurements show long-term decreases in concentrations of sulfate, and calcium, and increases in pH in response to these changes. Long-term mass balance calculations and model hindcasts provide evidence of depletion of available calcium pools in soil due to acidic deposition. Loss of available calcium in soil is consistent with delays in the recovery of the acid-base status of stream water and long-term declines in sugar maple. To test these hypotheses an experimental addition of calcium silicate was made to Watershed 1 in 1999. This treatment has improved the base status of soil and drainage waters, and may have improved sugar maple regeneration. Model predictions of the response of soil and surface waters to anticipated future changes in acidic deposition will be presented.

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**Nitrogen Pollution in the Northeastern U.S. : Linking Upland Watersheds and Coastal Ecosystems**

D.R. Whittall<sup>1</sup>, C.T. Driscoll<sup>2</sup>, J.D. Aber<sup>3</sup>, B. Boyer<sup>4</sup>, M.S. Castro<sup>5</sup>, C.S. Cronan<sup>6</sup>, C. Goodale<sup>7</sup>, P.M. Groffman<sup>8</sup>, C. Hopkinson<sup>9</sup>, G.B. Lawrence<sup>10</sup>, K.F. Lambert<sup>11</sup>, and S.V. Ollinger<sup>3</sup>

Elevated N inputs can result in a loss of biodiversity and a degradation of ecosystem health in both forest and coastal systems. The Hubbard Brook Research Foundation has organized a study through their Science Links™ program, entitled “Status and Effects of Nitrogen Pollution in the Northeastern United States”. The Science Links program seeks to synthesize existing ecological data in the context of societal policy and management needs in order to bridge the existing gap between science and policy. In this study we present a synthesis of inputs, effects and management options for nitrogen (N) in the northeastern U.S. For this analysis we utilized many data sets compiled from across the region, including data from the Hubbard Brook Ecosystem Study LTER project and the National Atmospheric Deposition Program. In general, the northeastern U.S. receives anthropogenically elevated inputs of N largely from net imports of food and atmospheric deposition. Other inputs of N such as net feed imports, N-fixation associated with leguminous crops and fertilization are generally lower for the region. Elevated inputs of N from net food import is readily transported to surface waters via wastewater discharge, and exported from northeastern watersheds. Consequences of elevated N inputs to the Northeast include: enrichment of N pools in forest soils and increases in rates of N cycling, impacts on forest vegetation, increases in nitrous oxide production and decreases in methane consumption from forest soils, elevated leaching losses of nitrate in streams and rivers, and eutrophication of coastal areas. Biogeochemical models were used to evaluate options for N management. Model results suggest that integrated management options which target a variety of sources will be the most effective at reducing the impact of anthropogenic N to natural systems.

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**POSTER SESSION**  
**(IN ALPHABETICAL ORDER BY FIRST AUTHOR LISTED)**



**A New Gas-Particle Ion Chromatographic System for the Continuous Monitoring of Soluble Gases and Ionic Constituents of Particulate Matter**

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The chemical composition of ambient gases and particulate matter (PM) is of key interest and importance to researchers and regulators in ambient air programs worldwide. Inorganic anions and cations play a major role in the chemistry of gas and aerosols and are frequently the primary chemical species in fine PM (< 2.5 µm). Elucidating the chemistry of ambient aerosols is key to understanding their source, transport and potential health risks. A key initiative of the U.S. Environmental Protection Agency's National Ambient Air Monitoring Strategy includes development of new monitoring technologies for accelerated, real-time reporting of air quality information.

In this presentation, a new automated gas-particle ion chromatographic (GP-IC) system is described for the measurement of acid gases, ammonia and soluble ionic constituents. The instrument operates with two independent parallel channels to collect and analyse gas and fine PM constituents. A parallel plate wet denuder collects the water-soluble gaseous constituents and directs them to an IC for measurement. An optional cyclone is used to remove large particles in a second channel, with a second wet denuder used to remove potentially interfering gases. The particle constituents are then collected and extracted in a novel continuous particle collector (PC) and directed to the IC for analysis. This GP-IC system provides fully automated, continuous measurement of cations and anions in ambient aerosols with a high degree of robustness and flexibility. The limits of detection (LOD) for ammonium, sulfate, nitrate and oxalate are <0.1 ng/m<sup>3</sup> with a 15 min analytical cycle and a sampling rate of 5 L/min.

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## **Performance Characteristics of Production Model Precipitation Collectors**

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The validity of results of long term precipitation networks depends on the reliable performance of unattended sample collectors. Design and performance characteristics determine the reliability of the precipitation collectors.

These include:

- Means of sensing onset and end of a precipitation to minimize "hunting".
- Ability to perform in a wide range of temperatures and wind conditions
- Minimal contamination by splash
- Ease of field maintenance
- Simple interfacing with rain gages and data loggers.

This paper describes the development of two commercially available atmospheric deposition samplers to meet the stringent criteria of NADP/NTN, MDN and other precipitation chemistry networks, based on technical requirements and user "wish lists".



**New Wet Deposition Sampler Technology for Precipitation  
Collection Networks**

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A new atmospheric deposition sampler is described that incorporates a number of fundamental improvements over present legacy sampler/collectors. A combination of a near-IR optical and a grid impedance detectors provide faster reliable and response to changing precipitation conditions. This sensor suite is software-controlled via a low power CPU, and logged data is transferred to portable Palm devices via IrDA wireless data ports. Fundamental mechanical issues such actuator reliability and splash have been addressed through simplicity of design. The NADP program is currently evaluating this technology along side other wet deposition samplers.

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## The Relation Between $\text{NO}_x$ Emissions and Precipitation $\text{NO}_3^-$ in the Eastern USA

Thomas J. Butler<sup>\*1,2</sup>, Gene E. Likens<sup>1</sup>, Francoise M. Vermeylen<sup>3</sup>, and Barbara J. B. Stunder<sup>4</sup>

Changes in total  $\text{NO}_x$  emissions in the eastern USA have been relatively small through the 1990's, even with implementation of the Clean Air Act Amendments of 1990. The decreases in  $\text{NO}_x$  emissions from the non-vehicle sectors have been significantly offset by increases from the vehicle sector.

Different  $\text{NO}_x$  source regions impacting particular sites in the eastern USA were evaluated based on 12-hr, 24-hr and 36-hr air mass back trajectories. A 50% decline in total  $\text{NO}_x$  emissions from the appropriate source regions predicted an overall decline in precipitation  $\text{NO}_3^-$  concentration of 38%. A model based on non-vehicle  $\text{NO}_x$  emissions as the independent variable predicted that a 50% decline in non-vehicle emissions, which is a 23% decline in total emissions impacting the area, results in a 19% decline in precipitation  $\text{NO}_3^-$  concentration. Similar results are found when source areas based on 24-hr and 36-hr back trajectories are used. The several models evaluated, using the different-sized source regions and either total or non-vehicle  $\text{NO}_x$  emissions, predict that reductions in  $\text{NO}_x$  emissions should reduce  $\text{NO}_3^-$  concentrations (and deposition) with an efficiency ranging between 75% to 95%. It can be inferred that equivalent reductions (in terms of  $\mu\text{eq l}^{-1}$ ) in precipitation acidity will also occur.

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## **Wet Deposition of Total Mercury to the Piney Dam Reservoir**

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The purpose of this study is to quantify wet deposition inputs of mercury to lakes in western Maryland. In spring 2001, we started measuring total mercury concentrations in wet deposition at an upper elevation (2500 ft) site in Garrett County, Maryland. In spring 2002, we also started measuring mercury concentrations in the dissolved fraction ( $< 0.45\mu\text{m}$ ) of our precipitation samples. All samples are collected on a weekly basis using ultra clean sampling methods and analyzed in our class 100 clean room using a Tekran 2600 system. Volume-weighted total annual mercury concentrations were 8.2 ng/L in 2001 and 8.6 ng/L in 2002. Annual wet deposition rates were 7.1 and 8.9  $\mu\text{g}/\text{m}^2\text{-yr}$  in 2001 and 2002, respectively. Volume-weighted seasonal concentrations ranged from 6 to 14 ng/L. Highest concentrations occurred in the spring and summer. Comparison of total and dissolved mercury concentrations indicated that most of the mercury in our precipitation samples is in the particulate form. Particulate mercury accounted for 80% of the total mercury in the spring and summer and about 50% of the total mercury in the fall and winter.



## **Wet Deposition of Mercury in the Boston Metropolitan Area**

Ann Chalmers<sup>1</sup>, Mark Nilles<sup>2</sup>, David Krabbenhoft<sup>3</sup>, Eric Prestbo<sup>4</sup>, and Mark Olson<sup>3</sup>

Atmospheric deposition is the dominant source of mercury (Hg) input to terrestrial and aquatic ecosystems in New England. Stream water, sediment, and fish tissue data suggest relatively higher concentrations of mercury in urban areas around Boston, however, most of the previously existing deposition sites have been located in rural areas. In 2002, the U.S. Geological Survey, in collaboration with Frontier Geosciences, the New Hampshire Department of Environmental Services, and the Blue Hill Observatory began a 2-year, four-site network to monitor Hg in wet deposition. The goals of the monitoring network are to (1) assist in interpretations of Hg concentrations in water, sediment, and fish tissue in the Boston area, (2) test a new wet atmospheric deposition sampler (N-CON) that has potential use in national, multi-agency atmospheric monitoring networks, and (3) provide total and methylmercury deposition data in more urban areas of New England. Three of the 4 sites are in urban areas around Boston, the fourth is in a rural area of central New Hampshire. One N-CON collector is co-located at a NADP-MDN network site for comparison between the N-CON and the modified Aerochem collectors used by NADP.

Preliminary results from this investigation found that concentrations of total Hg in wet deposition during 2002 ranged from 2-20 ng/L (nanograms per liter) at the 4 sites. Median concentrations of Hg in the 3 urban areas around Boston were 8.8, 7.2 and 7.8 ng/L respectively, compared to 5.7 ng/L in rural New Hampshire. These results suggest that localized urban emission sources may have significant effects on concentrations of Hg in rainfall in New England, and may result in variable deposition patterns on a sub-regional scale.

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## **Environmental Technology Verification of Ammonia Monitors at Two Animal Feeding Operations**

Kenneth Cowen<sup>1</sup>, Ann-Louise Sumner<sup>1</sup>, Amy Dindal<sup>1</sup>, Karen Riggs<sup>1</sup>, Richard Pfeiffer<sup>2</sup>,  
Kenwood Scroggins<sup>2</sup>, Jerry Hatfield<sup>2</sup>, and Robert Fuerst<sup>3</sup>

The goal of the U.S. Environmental Protection Agency (EPA) Environmental Technology Verification (ETV) Program ([www.epa.gov/etv](http://www.epa.gov/etv)) is to verify the performance of commercial-ready environmental technologies through the generation of objective and quality-assured data so that potential buyers, users, and permittees of such technologies can make informed purchase and application decisions. A verification test of seven ambient ammonia monitors is being conducted as a collaborative effort between the ETV Advanced Monitoring Systems (AMS) Center and the U.S. Department of Agriculture (USDA) to generate meaningful performance information on these technologies under realistic operating conditions. The test is being conducted in two month-long phases at separate animal feedlots. The first phase of the test is being conducted in September for four weeks at a swine finishing farm in Ames, Iowa. The second phase of the test will be conducted in October at a cattle feedlot in Bushland, Texas. The monitors being tested include both open-path systems as well as point source monitors, including photoacoustic monitors, ion selective electrodes, tunable diode lasers, and chemiluminescent monitors. Each of these are continuous monitors and provide real-time or near real-time measurements of the ammonia concentration. Preliminary results from this verification test will be presented.

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## **A Comparison of Two Ion Chromatography Analytical Columns for the Determination of Chloride, Nitrate, and Sulfate in Precipitation Samples**

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The Dionex AS4A column has been used for analysis of chloride, nitrate, and sulfate in NADP/ National Trends Network (NTN) precipitation samples since 1986. This column uses a carbonate/bicarbonate eluent or mobile phase. Manufacturers have reported improved capabilities with hydroxide eluent columns, such as the Dionex AS15. The AS4A and the AS15 were tested to determine whether their detection limits, control limits for the NADP/ NTN Quality Control Samples, and separation performance are comparable. The AS15 will also be evaluated to see whether its use can improve and expand NADP/ NTN ion chromatography capabilities for other analytes of interest. The AS15 column information shows that chloride separation will be improved and that acetate, formate, and sulfite can be included with the common anions (chloride, nitrate, and sulfate) in a single run. Additionally, organic solvents can be used with this column which could allow samples containing organic preservatives to be analyzed. Comparison data will be presented along with example chromatograms.

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**Low Level Analysis of Base Cations in Precipitation Samples: Flame Atomic Absorption Spectroscopy vs. Inductively Coupled Plasma-Optical Emission Spectroscopy**

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This study was conducted to evaluate the use of ICP-AES to replace flame-AAS for ppb level base cation analysis in precipitation samples. Sodium, potassium, calcium and magnesium were investigated. A Varian SpectrAA-800 was used for flame-AAS analysis and a Varian VISTA-PRO CCD Simultaneous ICP-OES for ICP analysis. Samples analyzed were from a long-term environmental monitoring program, therefore method changes must be "equivalent or better" to minimize step function changes in the data set. Samples were filtered through 0.45  $\mu\text{m}$  Gelman polyethersulfone filters and stored at ambient temperature prior to analysis. AAS required the addition of a releasing agent (lanthanum chloride) for magnesium and calcium, and an ionization suppressant (cesium chloride) for sodium and potassium. ICP-OES did not require a releasing agent for magnesium and calcium due to the high temperature of the plasma, however, an ionization suppressant (cesium chloride) and an internal standard (yttrium) were used. These were combined and metered via a pump into the sample introduction stream to the plasma. For AAS, 50  $\mu\text{L}$  of either the ionization suppressant or the releasing agent was added to each sample prior to analysis. QA/QC and routine samples were analyzed in parallel by both methods. ICP results were plotted against AAS results for the four analytes and yielded correlation coefficients of 0.999 or better. Both instruments provided high quality results, but ICP-OES offers the advantages of speed, reduced sample volume, and an extended linear range. Alternate wavelengths can also be monitored with ICP to determine interferences. None were observed during this study.

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## **National Trends Network Ammonium Bulls-Eye in the Western Great Basin NH<sub>4</sub> Data Analysis for NADP/NTN Site CA95 Death Valley National Monument**

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Ammonium data from the National Park Service sponsored Death Valley (DEVA) NTN station show elevated concentrations when compared to other sites in the region. In both the 2001 and 2002 NADP Annual Data Summaries, these concentrations are a factor of 3-4 greater than other sites in southern California and Western Nevada. Using 10 meter wind direction, wind speed, surface wetness and concentration data from the EPA-Clean Air Status and Trends Network (CASTNet) site as well as NADP data this poster will attempt to address these questions. What source region influences the wet deposition chemistry at the DEVA site? Are the excess NH<sub>4</sub><sup>+</sup> concentration values matched by increased concentration of other analytes? Is the DEVA NTN site regionally representative?



## Daily Nitrate and Ammonium Concentration Models for the Chesapeake Bay Watershed

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The purpose of this study was to develop daily wet ammonium and nitrate concentration models for the Chesapeake Bay Watershed (CBW). Weekly measurements of ammonium and nitrate concentrations and precipitation volumes from 28 NADP/NTN sites located in or adjacent to the CBW were used for model development. Only weekly precipitation chemistry samples that were comprised of a single precipitation event were used along with the following variables: (1) the number of days since the preceding precipitation event; (2) the volume of precipitation occurring in the preceding 3, 5, 7, 10, and 14-day periods; (3) the number of days having precipitation during the preceding 7- and 14-day periods; (4) seasonality as represented by dividing each calendar year into six distinct bi-monthly periods starting with January and February; (5) local land cover (open water, forested, residential, transportation/industrial, crop land, and vegetated wetlands) as described by the 1992 National Land Cover Data (NLCD) 30-meter grids; and (6) local emission levels of ammonia and nitrous oxides obtained from the U.S. Environmental Protection Agency, National Emissions Trends (NET) database.

Precipitation volume was the strongest predictor of both ammonium and nitrate concentrations ( $p < 0.0001$ ). Both concentrations were inversely related to precipitation volume, although the dilution effect remained nonlinear after logarithmic transformation of both concentration and volume. The dilution effect also exhibited both seasonal and spatial variability. A latitudinal gradient was apparent in the concentrations for both species. Log-transformed concentrations of ammonium tended to increase linearly with latitude ( $p < 0.0001$ ). Nitrate concentrations also tended to be higher toward the north ( $p = 0.0004$ ), but the tendency was non-linear and confounded with longitudinal gradients in concentration and dilution rate. Significant long-term trends in concentration were observed for both nitrogen species. Ammonium concentrations tended to increase during the 1984 to 2001 ( $p < 0.0001$ ); whereas nitrate concentrations tended to decline during the same period ( $p < 0.0001$ ). Precipitation event history was also a significant factor affecting the concentrations of both ammonium and nitrate. Concentrations of both species were directly related to the number of days since the preceding precipitation event. This effect was more pronounced for nitrate ( $p < 0.0001$ ) than ammonium ( $p = 0.0011$ ). The volume of precipitation falling during the preceding seven days exhibited a significant, but moderate, inverse relationship to wet-fall ammonium ( $p = 0.0120$ ) and nitrate ( $p = 0.042$ ) concentrations, respectively.

Both land cover composition and emissions showed significant relationships to wet-fall concentrations of ammonium and nitrate. However, the elements of these two categories of predictors tended to displace each other in the stepwise regression selection process. As expected, ammonium concentrations were directly related to area-standardized emissions of ammonia ( $p < 0.0001$ ), and nitrate concentrations were directly related to emissions of nitrous oxides ( $p < 0.0001$ ). Ammonium concentrations were better predicted by emissions rates for the individual county containing the monitoring site than by the mean levels for the nearest three counties. Conversely, nitrate concentrations showed stronger relationships to mean emission rates for the nearest three counties than for the immediate county. The observed relationships of wet-fall concentrations to land use composition were more complex and less intuitive than for emissions rates. Concentrations of both ammonium and nitrate were strongly ( $p < 0.0001$ ), inversely related to the extent of forest cover within 8 km (5-miles) of a monitoring site; however, a weaker direct relationship exists with the amount for forest cover within 0.8 km (0.5 mile). Concentration levels of ammonium were also directly associated ( $p < 0.0001$ ) with the extent of industrial/transportation land uses within 8 km (5 miles) of a site. The stepwise predictor selection process identified the relative extent of open water in the surrounding 8- and 0.8-km (5- and 0.5 miles) proximity as a significant predictor of nitrate concentrations ( $p < 0.0001$ , and  $p = 0.0031$ , respectively). The functional relationship between nitrate concentration and the prevalence of surface water is not certain, but may reflect influences of coastal air masses on precipitation chemistry. No inflation of standard errors of regression coefficients was observed with the successive addition of land cover predictors to the models for either inorganic nitrogen species. Thus, there was no evidence of multi-collinearity of predictor variables. The decision to incorporate land cover composition rather than emissions levels into the final daily ammonium and nitrate concentration models was based on the slightly better model performance and on the consistent availability of land cover composition data for use in the model.

Estimates of mean event wet depositions from the models agreed well with observed depositions at six NADP/AIRMoN sites in operation within the CBW during 1992 through 2001 for both nitrogen species. However, measured individual event concentrations and depositions often varied widely from the estimated values. In spite of these large, single-event variations, the correlations between observed and estimated event depositions remained high, generally around 0.60 (range 0.54 to 0.72 for ammonium and 0.50 to 0.72 for nitrate). Applying the daily concentration models to the daily precipitation records from 1984 through 2001 for the 28 NADP/NTN precipitation chemistry sites located in or adjacent to the CBW and summing the deposition estimates into annual totals provides a comparison with the observed annual deposition at those sites. The mean error for ammonium and nitrate depositions were  $-0.156$  kg/ha and  $-0.85$  kg/ha, respectively. The mean percent errors were 19.0 and 15.5, respectively.

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## Nitrogen in Precipitation

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Nitrogen measurements in precipitation samples from the National Atmospheric Deposition Program (NADP) have focused on soluble inorganic forms of nitrogen (such as nitrate and ammonium). Researchers have reported that a significant percentage of atmospheric deposition (up to 30%) may be present as dissolved organic nitrogen (DON). Based on these reports, TN and DON data are needed to assess the total deposition of nutrients into watersheds to determine environmental impacts and pollutant sources. In order to investigate this for NADP samples, the Central Analytical Laboratory (CAL) developed a method to measure total nitrogen (TN) using in-line persulfate digestion with a Lachat Instruments Quick Chem 8000 series flow injection analyzer. DON is determined by subtracting the inorganic nitrogen (nitrate-N and ammonium-N) concentrations from the TN concentration. This method was applied to NADP National Trends Network (NTN) samples from 5 sites in the Chesapeake Bay watershed. Samples were collected following the normal NTN weekly sampling protocol and shipped to the CAL. When excess sample was available it was refrigerated and TN analysis was performed as time allowed. In addition, samples were split and sent to the Appalachian Laboratory, University of Maryland Center for Environmental Science at Frostburg, MD for interlaboratory comparison for ~ 2 years. Results available to date from the five sites indicate good average agreement between the two labs for TN,  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, and DON values. In some cases individual sample results varied widely between the two labs. This may be attributed to sample stability, and differences in method detection limits and sample handling. Additional work will continue in order to optimize collection and analysis parameters for DON.

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**Using NADP and EMEP Deposition Data  
to Evaluate Global 3-D Chemical Transport Models**

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Over the last decade, NADP and EMEP  $\text{NH}_4^+$  and  $\text{NO}_3^-$  deposition data have been used to evaluate a series of 3-D chemical transport models. Early comparisons showed that 3 chemical transport models IMAGES, MOGUNTIA and early versions of MOZART (Model of OZone and Related Tracers) significantly underestimated  $\text{NH}_4^+$  and  $\text{NO}_3^-$  deposition (Holland *et al.* 1997; Holland *et al.* 1999). GCTM (Levy *et al.* 2000) overestimated NADP measured  $\text{NO}_3^-$  deposition but showed reasonable correlation with EMEP measured  $\text{NO}_3^-$  deposition. LMDZ-INCA, which coupled the Laboratoire de Météorologie Dynamique general circulation Model and the INCA (Interaction with chemistry and Aerosols) model, captured the overall spatial pattern of deposition in the US and Europe, but tended to underestimate European deposition.

Incorporation of an improved and physically consistent wet deposition scheme into MOZART produced a substantially improved spatial pattern of deposition for both the US and Western Europe. However, the model with the new wet deposition scheme significantly over-estimated magnitude of nitrate deposition. The new wet deposition scheme had substantial impacts on global ozone, nitric acid and hydroxyl radical budgets compared to the previously implemented wet deposition scheme. The NADP and EMEP measurements provide strong constraints on model performance that are not provided by aircraft and campaign data alone because of the spatial and temporal coverage of the network over a time period with substantial changes in the chemical system. As chemical, biogeochemical, and climate coupling of models proceeds towards Earth System modeling, extensive data sets such as these will be increasingly important constraints on model performance.

References available on request

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## Estuarine Eutrophication by Atmospheric Phosphorus

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Over the past decade, revelations about the relative importance of atmospheric nitrogen inputs to coastal waters have forced a reevaluation of estuarine nutrient budgets. However, the role of atmospheric phosphorus (P) inputs has largely been overlooked or underestimated, which is at least partially due to the paucity of atmospheric P data.

A recent examination of inputs and cycling in Rehoboth Bay, DE, reveals that there are locations and times of the year when water-column productivity is limited by P availability. As a result, P inputs can contribute significantly to problems associated with estuarine eutrophication. Annual P loading was determined at Bundicks Branch, DE, a representative catchment of the Rehoboth Bay watershed. Total P loads were determined through comprehensive baseflow and stormwater sampling, scaled up to the entire watershed, and compared with P loads from the Rehoboth Beach Wastewater Treatment Plant (RBWTP) and direct atmospheric deposition. Atmospheric P deposition was estimated from measurements of orthophosphate ( $\text{o-PO}_4^{-3}$ ) in wet deposition from the nearby Lewes NADP-AIRMoN site (DE02), and employing the approximation that dry P deposition is equal in magnitude to wet deposition (assuming that most aerosol  $\text{o-PO}_4^{-3}$  is associated with large ( $>2.5 \mu\text{m}$ ) soil or biogenic particles, which would exhibit relatively large deposition velocities).

On annual basis, the stream inputs (41%) and RBWTP (45%) provide comparable contributions to estuarine loading. Surprising is relatively large atmospheric P contribution (14%), which represents only direct inputs to the Bay surface waters, and does not include indirect transmission through the watershed (which would be reflected in the stream loading). The atmospheric term is also limited to inorganic  $\text{o-PO}_4^{-3}$ , although preliminary measurements suggest organic-P may provide a significant additional input. An examination of Lewes, DE precipitation chemistry data indicates the greatest  $\text{o-PO}_4^{-3}$  concentrations occur from the period March-Oct. Possible sources  $\text{o-PO}_4^{-3}$  consistent with this seasonality include biogenic material, as well as fugitive dusts from disturbed agricultural fields, in which P may be present in mineral phases, inorganic fertilizer residues and/or applied litter from commercial poultry houses (which typically contains 1-3% P).

To further clarify the role of atmospheric P inputs, additional information is needed to resolve existing uncertainties, including (a) analysis  $\text{o-PO}_4^{-3}$  in filtered (NADP) vs unfiltered (AIRMoN) precipitation; (b) measurements of total dissolved phosphorus (TDP) in precipitation over a complete annual cycle; and (c) determination of size-segregated aerosol-phase P, which will allow for more accurate assessment of the dry deposition contribution and provide insight into possible sources.

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**Trends in Ammonium Concentrations in Relation to Local-Scale Agriculture  
and Regional Sulfur Dioxide Emissions**

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Ammonium concentrations (in precipitation and atmospheric particles) at the Institute of Ecosystem Studies in Dutchess County, New York declined during the 12-year period between 1988-1999, but have increased between 1999 and 2002. The decline between 1988 and 1999 parallels 1) a decline in the number of cattle and calves, and especially the total milk production in Dutchess County, and 2) a decline in the concentration of particulate  $\text{SO}_4$  in the air. Concentrations of particulate ammonium correlate better with particulate sulfate concentrations than with agricultural statistics, suggesting that changes in air concentrations of ammonium are controlled more by changes in particulate sulfate concentrations, which are a product of regional  $\text{SO}_2$  emissions, than by changes in agriculture in this area. In particular, the period after 1999 is characterized by increasing particulate  $\text{NH}_4$  and  $\text{SO}_4$ , but continually declining milk production. Concentrations of ammonium in precipitation correlate with sulfate concentrations in precipitation, but not as well as air concentrations of ammonium and sulfate. In this poster we will discuss the mechanisms and implications of the observed trends.

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## **Ambient Ammonia Concentrations: A Data Review**

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Concentrations of fine particles (PM<sub>2.5</sub>) in the eastern half of the United States exceed the National Ambient Air Quality Standards in many urban areas and contribute to impaired visibility in scenic wilderness areas. Typically at least 2/3 of PM<sub>2.5</sub> consists of ammonium sulfate and ammonium nitrate, which are formed from the reactions of ammonia with sulfuric and nitric acid, respectively. Thus an accurate characterization of ambient ammonia is critical to understanding its role in the formation of PM<sub>2.5</sub>.

Despite the clearcut need for ammonia measurements, it has not been widely or routinely monitored, due partly to the difficulty of measuring ammonia at typical ambient concentrations of 1-3 ppb. This poster reviews the ammonia data currently available from EPA's Air Quality System (the national repository for aerometric data), as well as special study data from (1) the March-Midwest study sponsored by the Electric Power Research Institute, (2) urban measurements in Philadelphia, Tampa, and Houston made by researchers at Texas Tech University, (3) rural measurements by the Illinois State Water Survey, (4) source measurements made by the Minnesota Pollution Control Agency. Emission source, rural background, and urban measurements are compared. Diurnal, weekday/weekend, and seasonal patterns are characterized for each site type. Some apparent anomalies in the dataset are described and obvious gaps in spatial and temporal coverage are defined. This rudimentary review indicates that urban ammonia concentrations are typically 2 to 3 times greater than rural concentrations and exhibit weekday/weekend and diurnal variations that are consistent with mobile sources. Seasonally, ammonia is highest in the summer and lowest in the winter. Data are insufficient to determine trends over time.

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## Field Study: Intercomparison of Two Continuous Ammonia Monitors

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Measurement of ambient ammonia is becoming increasingly important because of ammonia's connection to long-term health effects on human beings and because of its precursor role in aerosol and PM formation. And yet, the research community lacks a suitable intercomparison of various instruments for ppb and sub-ppb level ammonia detection. We present preliminary intercomparison data from two new instruments for monitoring ambient gas-phase ammonia at sub-ppb concentrations that have been collocated and operated at a site in rural Illinois since July 28, 2003. One monitor, the Nitrolux™-200 is commercially available from Pranalytica Inc. of Santa Monica, CA and employs laser-based photoacoustic spectroscopy for the detection of ammonia. For this instrument gaseous samples are continuously drawn through the measurement cell, where they are interrogated spectroscopically with the output radiation of a carbon dioxide laser. The laser is line-switched between wavelengths with and without ammonia absorption to subtract out contributions from other ambient gases, yielding an updated interference-free measurement of ammonia approximately every 30 seconds. The second monitor is an ion chromatograph coupled with both a wet denuder and mist particle collector, designed and built by researchers at Texas Tech University. This instrument collects and analyzes gases and particles sequentially, at 15-minute intervals. The anions are analyzed by the ion chromatograph. Ammonia and ammonium are separated from the effluent with a membrane device and quantified by a conductivity detector. As the figure below shows, the two instruments track each other qualitatively quite well. Preliminary comparisons show excellent agreement between the two instruments: mean and maximum concentrations over the month of data collected to date are 1.4 and 9.7 ppb, respectively, for the Nitrolux™-200, and 1.6 and 7.1 ppb, respectively, for the ion chromatograph. The correlation of the measured ammonia concentrations for the two instruments when ammonia was present at levels greater than 2 ppb between July 28 and August 3 was better than 85%. During the period of August 13 to 18, when ammonia was present at even higher concentrations, the Nitrolux™-200 shows a time lag of approximately five hours relative to the IC machine, presumably because of water condensation in the unheated sampling lines exterior to the instrument, which might have trapped gas-phase ammonia until volatilized later in the day. The side-by-side consistency of these two instruments implies that researchers in the field of ambient ammonia monitoring will now have more diagnostic tools available for their field studies.

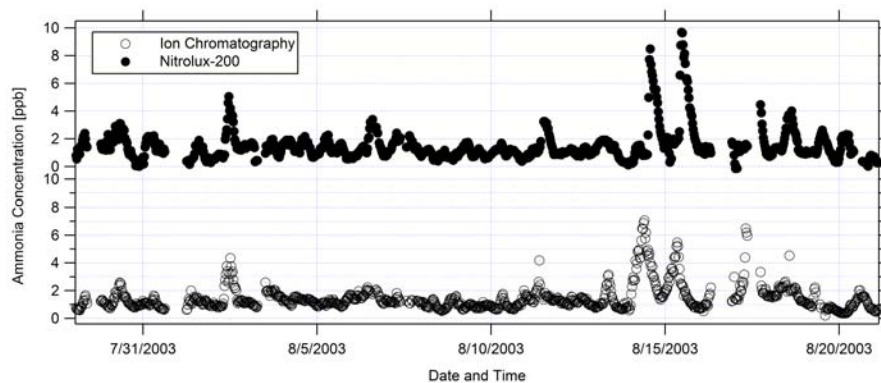


Figure 1. Measured data from collocated ammonia monitoring instruments. Top Panel: Photoacoustic instrument (Nitrolux™-200 by Pranalytica, Inc.). Bottom Panel: Ion chromatograph (Texas Tech University).

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## Using CASTNet Anion and Cation Measurements to Gauge Acidity of Regional Air Quality

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The Clean Air Status and Trends Network (CASTNet) utilizes open-face, three-stage filter packs to measure dry deposition concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{HNO}_3$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  at more than 80 locations across the United States. Dry deposition accounts for approximately 40 percent of total acid deposition. Cations play an important role in the chemical and atmospheric processes that lead to the formation of acidic compounds. Cation particles counteract the acidity of the anion particles through their ability to neutralize the anions. An analysis of the cations, anions, and cation-anion ratios can be used to gauge the acidity (cation-anion balance) of the air quality as measured by the filter packs at all CASTNet sites. Although CASTNet measures anions and cations, it was not designed to measure every ion that contributes to aerosol acidity. However, annual mean ratios of cations ( $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) to anions ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) show a dividing line between ratios greater than 1.00 and less than 1.00 roughly along the Appalachian Mountain chain from Alabama to Maine.  $\text{Na}^+$  values were excluded from the analysis because  $\text{Cl}^-$  was not measured. Deposition at western sites was generally less acidic than that measured at eastern sites. For example, Mesa Verde National Park, CO measured the highest annual ratio of 2.22 as compared with an eastern site located in Georgia Station, GA that measured an annual ratio of 0.90. Agricultural sites in the Midwest also measured quarterly ratios above 1.00. Evidently, generally dusty conditions in the West and agricultural activities in the Midwest produced surplus cations, which neutralized the acidic particles on the CASTNet filters. Air quality east of the Appalachians is dominated by acidic particles. Ratios along the East and West coasts were less than 1.00.

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## NADP Concentration and Deposition Trends

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The non-parametric Seasonal Kendall Trend Test was used to evaluate seasonal precipitation-weighted concentration and deposition trends for NADP-NTN sites in operation from 1985 to 2002 that met defined completeness criteria. Trends were also evaluated for weekly mercury concentration and deposition data from MDN stations using the standard Kendall Trend Test.

To evaluate coincident trends in concentrations and deposition, weekly concentration and deposition values from NTN and MDN stations were compared using a generalized least squares statistical analysis. Statistically significant correlations were found between mercury, sulfate, chloride, and other analytes, possibly indicating co-deposition of these species in precipitation.

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## A Field Intercomparison of Eight Ammonia Measurement Techniques

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From November 28 to December 10, 2001 the responses from eight active and passive sampling techniques designed to measure ambient gas phase ammonia ( $\text{NH}_3$ ) and particulate ammonium ( $\text{NH}_4^+$ ) were compared at a field site near Washington, DC which represented a predominantly agricultural ammonia environment. The intercomparison site was 150 m from a free-stall dairy barn facility at USDA's Beltsville Agricultural Research Center (BARC) in Beltsville, MD. The inlets of all the samplers were located within 3 m horizontally and 1 m vertically from one another, at a height of approximately 4 m. The comparison consisted of a total of eighteen sampling intervals, ranging in duration from 6 to 23 hours. The techniques under comparison included four active, batch sampling methods (cyclone separator and annular denuder/backup filter collection of  $\text{NH}_3$  and  $\text{NH}_4^+$  followed by ion chromatography (IC); honeycomb denuder/filter collection of  $\text{NH}_3$  and  $\text{NH}_4^+$  followed by IC; phosphoric acid solution impinger/IC measurements of total ammonium; and bulk filterpack collection of  $\text{NH}_3$  and  $\text{NH}_4^+$  followed by IC analysis). Two continuous techniques were also compared: a mist chamber to collect total ammonium and p- $\text{NH}_4^+$  followed by fluorescence derivitization with a liquid wavecore detector; and a commercial chemiluminescence detector. Finally, two passive sampling devices for gas-phase  $\text{NH}_3$  were deployed: a Willems badge design and an Ogawa passive sampler. A more limited comparison of the annular denuder system with the commercial chemiluminescence detector was conducted from December 18-22, 2001.

Run-averaged  $\text{NH}_3$  concentrations ranged from 0.1 to over  $30 \mu\text{g N/m}^3$  during the test period. The outputs of the continuous techniques reveal considerable temporal variation in  $\text{NH}_3$ , with concentrations ranging from almost zero (during fog and precipitation events) to over  $150 \mu\text{g N/m}^3$  in transient events. The comparison demonstrated the inherent difficulty in accurately quantifying ambient  $\text{NH}_3$  near an active  $\text{NH}_3$  source. Agreement between some of the techniques was quite good. For example, annular denuder and bulk filterpack results agreed well (regression coefficient,  $m$ , of 0.90,  $r^2 = 0.968$ ,  $n=12$ ) at integrated loadings of less than  $10 \mu\text{g N/m}^3$  on average; at higher concentrations, however, the filterpack technique suffered from breakthrough, and consistently underestimated  $\text{NH}_3$  concentrations. Average  $\text{NH}_3$  concentrations reported by the annular denuders agreed well with those measured via chemiluminescence ( $m = 0.830$ ,  $r^2 = 0.964$ ,  $n = 19$ ). The passive Ogawa and Willems samplers reported concentrations which agreed quite well with annular denuder results ( $m = 1.17$ ,  $r^2 = 0.968$ ,  $n = 3$ ). For total  $\text{NH}_4^+$ , agreement between the annular denuder and the acid scrubbers showed similar response ( $m = 0.509$ ), but with considerable scatter ( $r^2 = 0.241$ ,  $n = 18$ ), possibly due to inclusion of large particulate matter in the scrubbers but not in the denuders. Results from all the techniques will be compared using paired regression analyses. In addition, the temporal behavior of  $[\text{NH}_3]$  will be investigated at this location in close proximity to a major emission source.

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## Data Compatibility and Trends for Rainwater Chemistry for a Non-NADP Site and NADP Sites in Central Florida

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The site in Florida with the longest continuous rain-monitoring activity is located on the University of Central Florida (UCF) campus. This site has been operated from 1977 to the present with sampling intervals of 24 hours Monday through Friday and 72 hours Friday to Monday. One NADP site was established in north Florida in 1978 and four additional Florida sites were established during the early 1980's.

From early 1994 to mid-1996 split-samples from more than 90 weekly rainwater samples collected at FL99 were analyzed at UCF and results were compared to results obtained by the NADP Central Analytical Laboratory (CAL). Split samples analyzed at UCF were stored frozen for periods of one week to six months prior to analysis. Sixty-seven samples were considered valid by NADP criteria and complete analysis results for these samples are archived by NADP. Three of 67 samples were eliminated from consideration because of apparent contamination of the split sample sent to UCF.

Using the errors-in-variables model we formally tested  $H_0: \alpha = 0, \beta = 1$  and determined that  $H_0$  was true for  $H^+$ ,  $Na^+$ ,  $Cl^-$ ,  $NO_3^-$ , SAN and SCAT. The SAN and the SCAT represent total concentrations of all major anions and cations and these values are quality control parameters used in both laboratories. However,  $H_0$  was rejected for  $SO_4^{2-}$  concentration. Upon further analysis, it was determined that  $\alpha = 0$ , while  $\beta \neq 1$  for  $SO_4^{2-}$ . Hence, the measured concentrations of  $SO_4^{2-}$  at UCF differed from CAL by approximately 10 percent. In general, comparisons are quite satisfactory and suggest that both the chemical analysis schemes and laboratory quality control measures that have been implemented by both UCF and CAL are adequate. The magnesium, calcium, potassium and ammonium ion concentrations are typically quite small and combined contribute less than 25% of total cation composition in most samples. Since all composition measurements at UCF have been made using the procedures evaluated in this comparative study, it can therefore be concluded that the differences observed in rainwater composition measured at UCF are the result of composition differences and not measurement errors.

Within Florida the least acidic site is FL11 and very little change in acidity has been observed. Highest acidity has been observed at UCF with minimum acidity occurring in the late 1980's followed by a sizable increase into the mid-1990's then a leveling off to current years. Acidity at FL99 is approximately 30% less than that at UCF, however a six year shorter time frame is involved. Other Florida sites exhibit modest variability without much suggestion of substantial change. Nitrate concentrations in rainfall within Florida has increased. Modest to substantial increases are generally apparent when data from all Florida sites are considered. Most dramatic increases are noted at UCF and FL99, however a pronounced maximum is observed at UCF during the early 1990's. Recent increases in concentration do not return to the previously measured concentrations from 1980's. The recent concentrations represent a 25% increase at UCF and in excess of 50% increase at FL99. There is little evidence to suggest increasing levels of sulfate in rainwater. The only site to show increasing concentrations for non-marine sulfate is FL99 where an increase of about 25% has been observed. Other Florida sites show modest decreases.

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## **The Utilization of Ion Mobility Spectrometry and Annular Denuder Techniques to Explore the Dry Deposition of Ammonia in Coastal Ecosystems**

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Ammonia emissions contribute significantly to nitrogen inputs in aquatic and terrestrial ecosystems. Dry deposition of atmospheric ammonia may cause fundamental changes in the biological activity of an ecosystem (i.e. eutrophication). Exact concentrations of atmospheric ammonia have been difficult to quantify due to errors resulting from cross-contamination of samples and reproducibility problems. Annular denuder systems (ADS) coupled with relaxed eddy accumulation (REA) instrumentation were deployed during field experiments in Tampa, Florida, Tallahassee, Florida, and Princess Anne, Maryland to quantify atmospheric ammonia fluxes. An ion mobility spectrometer (IMS) was collocated with the ADS during several of these excursions to continuously monitor the atmospheric ammonia at two different heights to determine any concentration gradients. The utilization of the IMS system will provide increased accuracy and sensitivity of the measurements as well as the benefit of real-time data. Both methodologies will supply data concerning the magnitude of ammonia deposition in coastal areas to various atmospheric modeling efforts. The primary objectives of this study are to (1) develop an IMS protocol for atmospheric ammonia sampling; (2) utilize ADS and IMS methodologies in sampling excursions in coastal locations; (3) compare the resulting data sets from both techniques; and (4) employ the results in the development of atmospheric deposition models.

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## Sulfite in Winter AIRMoN Samples

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National Atmospheric Deposition Program/Atmospheric Integrated Research Monitoring Network-wet (NADP/AIRMoN) winter samples occasionally have higher concentrations of  $\text{SO}_4^{2-}$  when reanalyzed than the original analysis of the same samples. Several studies have indicated that during the winter, samples from the NADP/National Trends Network (NTN) have higher sulfate concentrations than do samples from the NADP/AIRMoN. AIRMoN samples are preserved using refrigeration as soon as the samples are collected, potentially slowing down natural oxidation of sulfite to sulfate. Using hydrogen peroxide to oxidize  $\text{SO}_3$  to  $\text{SO}_4^{2-}$  in NADP/AIRMoN samples for the winter of 2002/2003, this study looked at the change in concentration of sulfate in precipitation samples. Some of the samples analyzed in the study had up to four times the  $\text{SO}_4^{2-}$  concentration after oxidation than before. Samples were chosen for the study based on a  $\text{SO}_3$  peak appearing on the ion chromatograph. Ammonium also decreased in the presence of hydrogen peroxide. Changes in the nitrate concentration, however, were not consistent with the loss of ammonium indicating that some chemistry besides a simple oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  occurred. Samples were also spiked with sulfite and measured before and after spiking. These same samples were treated with hydrogen peroxide to confirm that the change in sulfate seen in NADP/AIRMoN samples was actually caused by sulfite oxidation. Graphs depicting the changes in the chemical concentrations are presented along with ion chromatograms of some of the samples.

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**Comparison of Potassium in Bulk Precipitation and Wet Deposition  
for a Twenty-Three Year Period (1979-2001) at the Hubbard Brook Experimental Forest,  
Woodstock, New Hampshire (NADP Site NH02)**

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Potassium ( $K^+$ ) in bulk precipitation at the Hubbard Brook Experimental Forest (HBEF) in Woodstock, New Hampshire has been measured weekly since 1963 by the Institute of Ecosystem Studies, while  $K^+$  in wet deposition has been measured weekly at HBEF since 1978 as part of the National Atmospheric Deposition Program (NADP). The two sites differ by approximately 4 meters in elevation and by approximately 150 meters in distance. In comparing differences in annual concentration and deposition in the years 1979 through 1988, bulk deposition of potassium at HBEF was always higher, but not significantly different from wet deposition when considering analytical error. However, since 1989 there have been significant differences between wet deposition and bulk deposition of potassium. The wet-only annual volume weighted average concentration values have remained statistically the same (slope =  $-0.0001$ ,  $r^2 = 0.05$ ,  $p = 0.30$ ) over the twenty-three year time period, while potassium concentration in bulk precipitation has increased significantly (slope =  $+0.002$  mg/yr,  $p=0.001$ ). This increase has occurred primarily in the summer months. This timeframe coincides with local inputs of pollen production from the adjacent maturing forest, although it is unknown if this is the reason for the change.

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## **NADP and the National Park Service Mission**

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The mission of the National Park Service (NPS) is to preserve unimpaired the natural and cultural resources and values of the national park system for the enjoyment, education, and inspiration of this and future generations. Integral to the preservation of resources are monitoring programs to collect information on indicators of ecosystem health and trends over time. For over 20 years, NPS has participated in the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) in order to evaluate air pollution threats to park resources and to assess trends in air pollution.

More recently, the NPS has been directed by Congress carry out a systematic, consistent, and professional inventory and monitoring program to identify resources, know where they are, how they interact with their environment and what condition they are in. This inventory and monitoring program is essential to ensure that NPS makes sound resource decisions based on sound scientific data. NADP data have been used to develop an inventory of atmospheric deposition information for the 270 park units that contain significant natural resources.

NADP data is also being used by NPS to evaluate progress towards air quality goals set under the Government Performance and Results Act (GPRA). A long-term GPRA goal is that air quality remains stable or improves in 70 percent of parks reporting data. One indicator of air quality is deposition of nitrate and sulfate in NPS areas with NADP monitoring. From 1990-1999, concentrations of sulfates in precipitation decreased at most of the 28 parks with long-term NADP monitoring; concentrations of nitrates stayed the same or increased during the period.

In addition, NADP data is being used by NPS to develop tools for protecting resources, including deposition analysis thresholds, critical loads, and target loads. Information on current deposition and trends in deposition enables NPS to identify problem areas, correlate deposition levels to observed ecosystem effects, and use information to protect resources.

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## Ammonium Wet Deposition in Eastern North America From 1980 to 1999

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Since the late 1970s, air and precipitation monitoring programs have been in place in Canada and the U.S.A. Since then, 12 Canadian precipitation-monitoring networks and 11 US networks have been operational in eastern North America. The data from the networks have been combined to produce wet deposition and concentration maps.

Annual and long-term average concentration and deposition patterns of  $\text{NH}_4^+$  were produced for eastern North America from 1980 to 1999. High values of  $\text{NH}_4^+$  concentration ( $>0.4$  mg/L) and deposition ( $>3.0$  kg/ha/yr) occurred in an area covering southern Manitoba, Ontario, Quebec, and most of the U.S. Great Plains and Midwest. The major land use in this area is agricultural, suggesting a strong influence of fertilizer and livestock on precipitation composition. This appears to be confirmed by the local concentration and deposition maxima ( $>0.5$  mg/L and 4.0 kg/ha/yr, respectively) located in the intensive agricultural areas of southwestern Ontario and South Dakota, Nebraska and Iowa. The extension of the 0.2 mg/L and 2 kg/ha/yr isopleths into northern Ontario and Quebec is somewhat surprising given the boreal forest land use that far north. This strongly suggests an influence of long-range transport from the agricultural areas to the south.

The patterns of  $\text{NH}_4^+$  concentration and deposition and the  $\text{NH}_3$  emission patterns illustrate the relationship between precipitation chemistry and emissions, and provide evidence of long-range transport into northern Canada.  $\text{NH}_4^+$  wet deposition increased slightly between early 1980s and late 1990s. More than 40% of the total nitrogen wet deposition in eastern North America is from  $\text{NH}_4^+$  and the rest is from  $\text{NO}_3^-$ .



## Atmospheric Nitrogen Inputs to the Delaware Inland Bays: The Importance of Ammonia( $\text{NH}_3$ )

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A previous assessment of nitrogen loading to Delaware's Inland Bays indicates that atmospheric deposition provides 15-25% of the total, annual N input to these estuaries. A large and increasing fraction of the atmospheric wet flux is  $\text{NH}_4^+$ , which for most aquatic organisms represents the most readily assimilated form of this nutrient. Particularly noteworthy is the reported 60% increase in the precipitation  $\text{NH}_4^+$  concentration at Lewes, DE over the past 20 years, which parallels the increase in poultry production on the Delmarva Peninsula over this period (currently standing at nearly 585 million birds annually).

To further examine the relationship between local  $\text{NH}_3$  emissions and deposition, weekly-integrated gaseous  $\text{NH}_3$  concentrations were determined using Ogawa passive samplers deployed at 13 sampling sites throughout the Inland Bays watershed over a one-year period. Annual mean concentrations ranged from  $<0.5 \mu\text{g NH}_3/\text{m}^3$  to  $>6 \mu\text{g NH}_3/\text{m}^3$ . At most sites, highest  $\text{NH}_3$  concentrations were evident during spring and summer, when fertilizer application and poultry house ventilation rates are greatest, and seasonally elevated temperatures induce increased rates of microbial activity and volatilization from soils and animal wastes. The observed north-to-south concentration gradient across the watershed is consistent with the spatial distribution of poultry houses, as revealed by a GIS analysis of aerial photographs. Based on the average measured  $\text{NH}_3$  concentration ( $1.63 \mu\text{g NH}_3/\text{m}^3$ ) and published  $\text{NH}_3$  deposition rates to water surfaces (5-8 mm/s), the direct atmospheric deposition of gaseous  $\text{NH}_3$  to the Inland Bays is 3.0-4.8 kg N/ha/yr. This input, not accounted for in this or most other previous assessments of atmospheric loading to coastal waters, would effectively double the estimated direct dry deposition rate, and is on par with the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  wet fluxes.

A second component of this study examined spatial differences in  $\text{NO}_3^-$  and  $\text{NH}_4^+$  wet deposition within the Inland Bays watershed. In a pilot study, precipitation composition at the Lewes NADP/AIRMoN site (DE 02) was compared with that at a satellite site established on the Indian River Estuary, approximately 14 mi. southwest. While the volume-weighted mean precipitation  $\text{NO}_3^-$  concentrations did not differ significantly between sites, the  $\text{NH}_4^+$  concentration observed at Indian River ( $26.3 \mu\text{moles/L}$ ) was 73% greater than at Lewes ( $15.2 \mu\text{moles/L}$ ). More recently, a NADP site was established at Trap Pond, DE (DE 99), which was intentionally located in an area containing intense poultry production and other agricultural activities, typical of this region. A comparison of the initial 2 years (6/01-5/03) of precipitation chemistry data from Trap Pond with other nearby NADP sites (Lewes and Smith Island) indicates little ( $<10\%$ ) spatial variability in regional  $\text{NO}_3^-$  wet deposition, but fairly significant differences (50-60%) in the  $\text{NH}_4^+$  wet flux. These observations are in agreement with the pilot study, and the spatial trend in  $\text{NH}_4^+$  wet deposition is consistent with the airborne  $\text{NH}_3$  concentration gradient described above.

Overall, these results suggest that local emissions and below-cloud scavenging provide a significant contribution to regional atmospheric N deposition. This impact is exacerbated during summer, when the bay surface water productivity is most severely limited by the availability of N, and seasonally diminished stream loadings are coupled with elevated atmospheric N inputs.

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## **A Web Based Resource for Deposition Data in the Chesapeake Bay Watershed**

Dr. John Sherwell<sup>1</sup> and Ann Baines<sup>2</sup>

The Power Plant Research Program [PPRP], as well as many other regional jurisdictions have sponsored atmospheric deposition related projects. Much of this data remains unpublished or in the gray literature. PPRP undertook a program to collect, catalog and make public as much of this data as possible, especially as the data relate to the Chesapeake Bay and its watershed. A web resource has been developed where the data, or links to the data, and metadata - especially QA/QC information - are available for review and download. The site is a venue for making this type of data available to the public in a way that has not previously been possible. Excerpts from the website illustrating the range of data types will be shown.

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## **Accounting for Atmospheric Deposition in a Nutrient Cap Strategy**

Dr. John Sherwell<sup>1</sup> and Mark Garrison<sup>2</sup>

A modeling framework has been developed to link specific atmospheric emission sources of NO<sub>x</sub> to changes in the nitrate load in the Chesapeake Bay. Based on sources in the OTAG domain and listed in the EPA's 1996 NET inventory, estimates of deposition to the Bay watershed are made using the CALPUFF model. Estimates of the nitrogen load due to the predicted deposition are made using a formulation of the USGS SPARROW model specific to the Bay watershed. The Lagrangian formulation of the CALPUFF model allows impacts from individual sources to be assessed and together with SPARROW forms a transformation matrix that links a source type at a geographic location to a loading response in the Bay. This matrix allows "what if" emission reduction scenarios to be rapidly assessed. The results of several scenarios will be presented as well as implications for Clean Air and Clear Skies Acts implementation and an application for planning in the power generation sector.

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## **Evaluation of Wet Deposition Predicted by the CALPUFF Model Using NADP/NTN Historical Data**

Dr. John Sherwell<sup>\*1</sup>, Mark Garrison<sup>2</sup>, and Anand Yegnan<sup>2</sup>

The Maryland Department of Natural Resources Power Plant Research Program (PPRP) has undertaken efforts to investigate the contribution of atmospheric nitrogen to excess nutrient loading in the Chesapeake Bay. These investigations have focussed on the use of the CALMET/CALPUFF modeling system to estimate nitrogen deposition attributable to NO<sub>x</sub> emissions from both local Maryland and regional sources, onto the tidal water surface of the Bay and onto land areas in the Bay watershed. Recent work has focused on three things: 1) calculating actual loading to the Bay based on work conducted by the USGS with the SPARROW model; 2) extending the CALMET/CALPUFF predictions to a full ten-year time period; and 3) estimating ammonia-based nitrogen deposition through the use of the CALPUFF model treatment of ammonium sulfate and the observed ammonium-to-sulfate molar ratio. The proposed paper focuses on the evaluation of model vs. measured deposition over an extended (10-year) time frame, presenting comparisons for NADP stations in the eastern U.S. and providing insights into the performance of this modeling system by examining predicted and observed seasonal and spatial patterns.

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**Ammonia Measurements at an Iowa Swine Farm Using Infrared Quantum Cascade Laser Absorption Spectroscopy**

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A novel instrument using quantum cascade tunable infrared laser differential absorption spectroscopy (QC-TILDAS) has been developed for long term monitoring and source characterization of ammonia and other atmospheric trace gases. The instrument uses a long path length (56m) low volume (0.5 liters) absorption cell which provides high precision (0.2 ppb Hz<sup>-1/2</sup>), wide dynamic range (0.5 ppb to 5000 ppb) and rapid time response (0.1 s). Quantum cascade lasers operate without cryogenic cooling in the pulsed mode which makes them more robust and convenient for field measurements than conventional lead-salt tunable diode lasers. Absolute ammonia concentrations are obtained without calibration gases by real-time fitting of the measured transmission to spectroscopic line parameters from the HITRAN data base. The instrument has been recently tested at an Iowa swine farm as part of the EPA Environmental Technology Verification (ETV) Program.

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## **Characterization of Atmospheric Ammonia Plumes from Commercial Chicken Houses on the Delmarva Peninsula**

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A unique three-dimensional sampling grid using passive collectors was used to characterize the down-wind gas-phase ammonia plumes originating from a commercial chicken house on the Delmarva Peninsula in the Chesapeake Bay watershed. Inverse Gaussian plume modeling was used to determine the source strength of the chicken house and the corresponding chicken emission factors. A total of 7 field deployments were performed during 2 different flocks. The deployments occurred during weeks 3, 4 and 5 of the 6-week chicken grow out period in the months of May, June and July of 2002. The ammonia emission factors ranged from  $0.27 \pm 0.18 \text{ g NH}_3\text{-N bird}^{-1} \text{ day}^{-1}$  to  $2.17 \pm 0.30 \text{ g NH}_3\text{-N bird}^{-1} \text{ day}^{-1}$  with a mean of  $1.18 \text{ g NH}_3\text{-N bird}^{-1} \text{ day}^{-1}$ . Weighted emissions factors were also calculated to account for the nonlinear increase in ammonia emissions over the 6-week grow out period and ranged from  $0.14 \pm 0.09 \text{ g NH}_3\text{-N bird}^{-1} \text{ day}^{-1}$  to  $1.65 \pm 0.36 \text{ g NH}_3\text{-N bird}^{-1} \text{ day}^{-1}$  with a mean of  $0.74 \text{ g NH}_3\text{-N bird}^{-1} \text{ day}^{-1}$ . These weighted emission values would correspond to an annual release of approximately  $18 \times 10^6 \text{ kg NH}_3\text{-N}$  to the atmosphere from broiler production on the Delmarva Peninsula. This assumes that the emission factors in this study are representative for the entire year with varying meteorological conditions and are representative of all chicken husbandry practices. The Delmarva Peninsula could represent a significant source of nutrient nitrogen to the Chesapeake Bay and Delaware Bay watersheds through atmospheric deposition when considering the size of this annual release rate, the relative short atmospheric lifetime of ammonia due to deposition, and the proximity of the Delmarva Peninsula to the Chesapeake and Delaware Bays.

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**Have Missing Markets for Ecological Goods and Services  
Affected Progress in Modelling of Terrestrial C and N Fluxes?**

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Using the literature on modelling of C and N fluxes through cropland and other terrestrial ecosystems for the period 1991-2002, in conjunction with estimates of total economic value for both systems, we illustrate how missing markets for ecological goods and services may have biased research output in favour of croplands. Using the results of Costanza *et al* (1997) we can estimate that the total economic value for cropland is US \$0.128 trillion ( $10^{12}$ ) per year compared to US \$10.491 trillion for other terrestrial ecosystems. Fitting trendlines to the research output data we show that this 82-fold difference in value is accompanied by an average of only twice as much study (1.17 – 2.48 range) for the other terrestrial ecosystems group. Through a basic analysis, we suggest that at least 3 times as much study for other terrestrial ecosystems over cropland was justified between 1991-2002. In terms of science policy and research funding our work is a quantitative economic justification for channelling more resources into a range of natural environment research in the areas of photosynthesis, nitrogen deposition and pollution biogeochemistry in order to overcome the current bias which favours case studies in cropland.

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## **Trends of Sulfur Dioxide in Air, Sulfate in Air and Precipitation, and Sulfur Dioxide Emissions**

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Time trends of ambient air and precipitation concentrations from 1989 to 2001 are presented for 43 sites in the United States, with 37 of the sites being east of the Mississippi River. The air quality data are from the Clean Air Status and Trends Network (CASTNet) and the precipitation data are from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Both networks have as an objective to determine regional patterns and trends and thus the sites are located in rural areas as opposed to urban/suburban areas. Linear trend analysis was done on the annual median concentrations of the three sulfur species (aerosol and precipitation sulfate and gaseous sulfur dioxide) for the 43 sites to calculate the percent change over the 13-year period. Scatter plots were examined to determine that a linear trend model is reasonable. Almost all percent change values determined in this way were negative, that is, concentrations decreased over time. The median percent changes over the 13 years, by species, for 24 midwestern and northeastern sites are: -29% for aerosol sulfate, -45% for sulfur dioxide, and 29% for precipitation sulfate. It is particularly interesting that the sulfur dioxide decrease is greater than the aerosol sulfate decrease, and that the precipitation sulfate trend agrees better with the aerosol sulfate trend than with the ambient sulfur dioxide trend. The magnitude of the trends and the trend differences in space and between the three species are important features to be captured by regional sulfur models. Emissions of sulfur dioxide are compared to the air and precipitation trends. The trend in emissions appears to agree better with the aerosol sulfate trend and the precipitation sulfate trend than with the sulfur dioxide trend.

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## Measurements of Ammonia and Related Species at IL11 (Bondville)

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Between 1999 and 2003, the Illinois Water Survey has sampled ambient atmospheric gases and fine particles as part of an atmospheric fine particle (PM-2.5) characterization project at the NADP station near Bondville, IL (IL11). Gas phase ammonia, nitric acid, and sulfur dioxide were sampled for 24 hours every 6 days using coated denuders. The denuders were backed up by a filterpack with Teflon and nylon filters to collect PM-2.5. Fine particles were analyzed for sulfate, nitrate, and ammonium ions. Beginning in spring 2003, a continuous ion chromatography sampler was put in operation at IL11. This device measures the same species as the 24-hour denuder/filterpack system on a 30-minute cycle. In summer 2003, a separate commercial ammonia analyzer that measures gas-phase ammonia every 35 seconds was added to the instrumentation at IL11.

The concentration of ambient ammonia is typically around 1 ppb with fall maximum values as high as 10 ppb. Nitric acid averages about 0.3 ppb with summer maximum values of about 1.5 ppb. The average concentration of sulfur dioxide at IL11 is about 1.5 ppb. Maximum sulfur dioxide concentrations of up to 9 ppb were measured in the winter. The average concentration of PM-2.5 at IL11 is about 13  $\mu\text{g}/\text{m}^3$ . Most of the year, PM-2.5 is dominated by ammonium sulfate, which accounts for an average of 35% of the PM-2.5 mass and up to 80% of PM-2.5 mass in the summer. Ammonium nitrate accounts for about 20% of PM-2.5 on an annual basis. This species can make up more than half the ambient PM-2.5 when average ambient temperatures are below 5C.

Preliminary evaluations of the continuous samplers deployed at IL11 indicate that they can provide data equivalent to the denuder/filter method with time resolution under one minute. Continuous measurements will make it easier to evaluate the correlation of chemical parameters and meteorological data, which usually vary on a time scale much shorter than 24 hours.



**The Impact of Local Air Pollutants on Lake Tahoe's Nitrogen Budget:  
Elevated Growing-season N Deposition in a Semi-arid, N-limited Western Watershed**

Leland W. Tarnay<sup>\*1</sup>, Alan W. Gertler<sup>2</sup>, Dale W. Johnson<sup>3</sup>, and Menachem Luria<sup>4</sup>

Causes of the decline in water quality in Lake Tahoe have been attributed to nutrient additions stemming from various watershed-related changes such as urban development on the one hand and from atmospheric nutrient deposition on the other. This study addresses the latter question. A “big-leaf” inferential deposition model incorporating spatial variation in both canopy cover and concentrations nitrogen-containing pollutant gases was used to show that elevated concentrations of N containing gases in the Lake Tahoe basin are the primary source for most of the inorganic N that reaches Lake Tahoe during the summer months, when wet deposition is negligible. These fluxes, however, are small compared to total organic N fluxes from the surrounding watershed, suggesting that the watershed may control more of the Tahoe N budget than previously believed.

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**Early Results from a Study of Ammonium Ion Deposition  
in the Shenandoah Valley of Virginia**

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The Shenandoah Valley of Virginia has many poultry houses thought to be the cause of increased ammonium deposition. Rain gauges were placed at four sites in the valley and the precipitation was tested for nitrate, sulfate and ammonium ions. The first year of the study found that the valley in general has a higher than national average ammonium level in rainfall, there is a strong seasonal increase in ammonium concentration during the spring, and that close proximity to these poultry houses shows even more impact. Data also indicates that ammonium ion concentrations are higher in lower rainfall events. The study is in its early stages, with limited statistical evaluation, and expects more complete results over the next 5 years.\*

\*This project is funded by the EPA's Chesapeake Bay Program



## **Evaluating Ammonia Abatement Measures with the Use of Measurements and Models**

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Ammonia is one of the most important eutrophying components in the Netherlands. Also, ammonia deposition to the soil may contribute to soil acidification and nitrate leaching. The ammonia deposition accounts for almost 70% of the total nitrogen deposition in the Netherlands. About 75% of the ammonia deposition in the Netherlands arises from agricultural activities. Therefore the reduction of the ammonia emissions is an important national goal as well as subject in international protocols (EU, UN-ECE). Several abatement measures, like development of low emission animal housing systems, coverage of manure storage basins and incorporation of manure into the soil, have been taken since 1990. In the Netherlands the effect of the measures are evaluated using measurements and modeling of the ammonia concentrations.

The National Air Quality Monitoring Network consists of eight locations for measuring ammonia concentrations in air, seven for the ammonium aerosol concentrations and fifteen for the ammonium in precipitation. In the near future two dry deposition locations will also be operative. Ammonia concentrations in ambient air are strongly related to local ammonia emissions and can act as the most direct indicators for spatial emission differences and trends in emissions. Nevertheless, the interpretation of measured time-series in terms of emission trends is not straightforward because year-to-year differences in meteorological factors and systematic changes in the chemical composition of the atmosphere have their impact on the emission-concentration relation. These impacts can be quantified by using a transport and deposition model.

Model calculations of the ammonia concentrations on the basis of emission estimates show that the trend in the measured concentrations as well as the spatial distribution of the concentrations over the Netherlands can be simulated quite well. Conclusions on the basis of this analysis is that the emissions over the last decade have been reduced by about 35%. With the model also the reductions in the different emission categories can be shown. It is found that the emissions of animal housings and so the reductions on them have a much larger effect on the ammonia concentrations than emissions from other sources. The model, however, underestimates the measured concentrations with about 30%. The reason for this difference is not yet clear but probably point to an underestimation of the emissions as well as an overestimation of the dry deposition of ammonia by the model.

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**Comparison of Total S Deposition Measurements from 10 Sites in Eastern North America:  
NADP and CASTNet vs Throughfall**

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Samuel S. Simkin<sup>1</sup>, and Christopher Rogers<sup>3</sup>

Despite decades of research, generating accurate estimates of total deposition to ecosystems in complex terrain present significant challenges. Two methods have commonly been used: measured and modeled deposition estimates from monitoring networks (MN) (e.g., NADP and CASTNet), and the measurement of throughfall flux (TF), which, for conservative ions such as sulfate, is a measure of total deposition (wet + dry + cloud) to canopies. The TF method has the advantages of 1) being inexpensive and 2) integrating deposition over complex forest canopies and/or heterogeneous terrain where model assumptions for calculating dry deposition fluxes are tenuous, at best. The MN method allows critical temporal and spatial comparisons within and among monitoring locations. Clearly both methods have value; understanding whether and how these two methods compare allows the use of either (or both) to obtain more accurate measures of atmospheric deposition, especially in complex terrain. During the summer of 2002, we collected TF and bulk precipitation at 9 CASTNet sites in the eastern US, and at the Institute of Ecosystem Studies' (IES) Environmental Monitoring Station, to compare sulfur (S) deposition. Bulk deposition (= wet plus some component of dry deposition) and NADP wet deposition showed a strong relationship ( $r^2 = 0.80$ ). There was a strong, positive relationship between total S deposition measured via TF and MN ( $r^2 = 0.75$ ) as well. MN nitrogen (N) and S deposition were also highly correlated ( $r^2 = 0.76$ ), suggesting that TF can be used to estimate both total S and total N fluxes to ecosystems in these regions. However, net throughfall flux of S, which has been used as an estimate of dry deposition, and dry S deposition modeled at the CASTNet and IES sites showed poor correspondence, suggesting either that the TF method is confounded by sources or sinks of S in the canopy, or that the inferential method for estimating dry deposition is not very accurate.

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## Population Extinction of a Checkerspot Butterfly Driven by Vehicular Ammonia Emissions

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A population of the threatened Bay checkerspot butterfly crashed from 3500 butterflies in 1997 to likely extinction in 2003. Non-native annual grass crowded out larval host-plants over much of the habitat, primarily driven by nitrogen deposition from tailpipe emissions of  $\text{NH}_3$  from 100,000 vehicles per day on a roadway bisecting the habitat.  $\text{NH}_3$  levels (measured with passive monitors) are elevated adjacent to the roadway, but are near background levels 400 m away. Grass cover was higher closer to and downwind of the road, and hostplant cover was inversely related to grass cover. Results from a first-order model show that N-deposition levels adjacent to the roadway are similar ( $10 \text{ kg-N ha}^{-1} \text{ yr}^{-1}$ ) to levels downwind of the heavily urbanized Santa Clara Valley (where grass invasions have led to the extinction of large populations). This local butterfly extinction is unexpected fallout of the adoption of three-way catalytic converters in 1990s. The only known occurrence of an endangered plant, *Pentachaeta bellidiflora*, exists west of the freeway and may be at long term risk. The serpentine grassland ecosystem provides a model system for understanding local and regional impacts of  $\text{NH}_3$  emissions on biodiversity.

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**Spatial and Temporal Variability of the Total Error of NADP Measurements Determined by the USGS Collocated Sampler Program, Water Years 1989 – 2001**

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Office of Water Quality  
Branch of Quality Systems

The Collocated Sampler Program, operated by the U.S. Geological Survey (USGS) for the National Atmospheric Deposition Program / National Trends Network (NADP/NTN), is used to estimate the total error associated with NADP/NTN data. Precipitation sample collection, handling, shipping, and analysis errors and data processing errors are all components of the total error of the NADP/NTN data. Between 1989 through 2001, total error data were collected at a total of 41 NTN sites located across the USA, using duplicate sets of collocated NTN precipitation collectors and rain gages. All precipitation samples were collected by NTN site operators using standard NADP protocols and analyzed by the NADP Central Analytical Laboratory (CAL).

Absolute error is defined as the absolute difference between the measured or inferred value of a quantity and its actual value. The absolute errors in the NADP/NTN data are estimated by comparison of the chemical concentrations, sample volumes, and precipitation depths obtained from paired samples collected for the same precipitation events. Absolute error in the precipitation depth measurements is estimated from rain gage records obtained from collocated rain gages at each site. The absolute errors in the Collocated Sampler Program data were higher for selected chemical constituents and sample volume during water years 1989-1993 than for water years 1994 through 2001 (significant at  $\alpha=0.05$ ). This was likely due to sample-containment protocol changes implemented in 1994. However, absolute error for precipitation depth was higher during the 1994-2001 period than during the 1989-1993 period, which might indicate wear of the aging NTN precipitation gages. Higher absolute error is associated with wet-deposition samples collected during the winter months than during non-winter months for sample volume and selected constituent concentrations. The NTN collector is suspected to under-catch snow. However, no statistically significant differences were found in the comparison of absolute error for winter and non-winter months for precipitation depth.

The spatial distribution of absolute error for Collocated Sampler Program sites is generally consistent with the spatial distribution of wet-deposition concentrations across the USA. There generally is less error inherent in the concentration measurements when ion concentrations are higher and sample volumes and precipitation depths are large than when ion concentrations are low and sample volumes and precipitation depths are small. Statistically significant ( $\alpha=0.05$ ) differences in absolute error were found between western and eastern sites for sodium, chloride, nitrate, sulfate, and hydrogen ion concentrations, specific conductance, and sample volume. Statistically significant ( $\alpha=0.05$ ) differences in absolute error were also found between northern and southern sites for nitrate, hydrogen ion, and specific conductance. Results of comparisons of absolute errors obtained for dry and humid-temperate ecoregions were similar to the results from the comparison of western and eastern sites because the western sites tend to be dry.

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## **AMMONIA WORKSHOP AGENDA**



**National Atmospheric Deposition Program  
AMMONIA WORKSHOP**

October 22-24, 2003  
Hilton Washington & Towers  
1919 Connecticut Avenue, NW  
Washington, DC

**WORKSHOP OBJECTIVES**

- Provide a forum for presenting information (both national and international) on the state of the science with regard to ammonia as a precursor to the formation of PM, and its contribution to nitrogen deposition and acidification.
- Promote interaction between air quality and deposition scientists, as well as between the measurement and modeling communities.
- Provide recommendations to decision makers on future ammonia work.

**AGENDA**

**THURSDAY, October 23, 2003**

**Room Location**

<b>SESSION 1:</b>	<b>MULTIPLE ROLES AND EFFECTS OF AMMONIA EMISSIONS</b> Session Chair: Dr. Jan Willem Erisman, Energy Research Centre of the Netherlands	International Ballroom West
8:00 – 8:30	<i>Ammonia and Air Quality.</i> Dr. Russ Dickerson, University of Maryland	
8:30 – 9:00	<i>Effects of Ammonia Deposition.</i> Dr. Jim Galloway, University of Virginia	
9:00 – 9:30	<i>Effects of Atmospheric Ammonia on Terrestrial Vegetation.</i> Dr. Sagar Krupa, University of Minnesota	
9:30 – 9:45	Discussion	
9:45 a.m. to 10:00 a.m.	Break	
<b>SESSION 2:</b>	<b>PERSPECTIVES ON MANAGING AMMONIA EMISSIONS</b> Session Chair: Dr. John Bachmann, Associate Director for Science & Policy, EPA OAQPS	
10:00 a.m. to 10:30 a.m.	<b>MANAGING AMMONIA IN EUROPE</b>	
10:00 – 10:30	<i>Managing Ammonia Emissions Cost Effectively.</i> Dr. Jim Webb, ADAS Research	
10:30 a.m. to 12:00 p.m.	<b>MANAGING AMMONIA IN THE U.S.</b>	

**THURSDAY, October 23, 2003**

**Room Location**

10:30 – 11:00	<b>NATIONAL PERSPECTIVE</b>  <i>Managing Ammonia in the US.</i> Dr. Jerry Hatfield U.S.Department of Agriculture	International Ballroom West
11:00 – 11:30	<b>STATE PERSPECTIVE</b>  <i>Are We There Yet? Future Paths from the Past.</i> Mr. Gary Saunders, North Carolina Dept. of Environment & Natural Resources	
11:30 – 12:00	<b>LOCAL PERSPECTIVE</b>  <i>Regulating Ammonia in Clean Air Act State Implementation Plans - Do We Know Enough to Proceed?</i> Mr. Dave Mitchell, San Joaquin Valley Air Pollution Control District	
12:00 p.m. to 12:15 p.m.	Discussion	
12:15 – 1:30	Lunch (on your own)	
<b>AMMONIA SESSION 3:</b>	<b>ASSESSING OUR ABILITY TO QUANTIFY AMMONIA</b> Session Chair: Dr. Ray Knighton, U.S. Department of Agriculture, CSREES	
1:30 p.m. to 5:00 p.m.	<b>PART 1: Current Techniques and Limitations for Measuring Ammonia/um Emissions, Ambient Concentrations, and Deposition.</b>  What measurement techniques are being used to quantify ammonia? How good are these techniques? How well can we relate ambient ammonia concentration data to emission sources and to deposition? Is there a need for standard measurement methods?	
1:30 – 2:00	<i>Measuring Ammonia Emissions from Agricultural Sources: Technical Possibilities, Applicability in Situ, Benefits and Drawbacks.</i> Dr. Gert-Jan Monteny, IMAG Wageningen University and Research Centre	
2:00 – 2:30	<i>Techniques for Measuring Ammonia Emissions from Land Applications of Manure and Fertiliser.</i> Dr. Tom Misselbrook, Institute of Grassland and Environmental Research	
2:30 – 3:00	<i>Urban Ammonia Source Characterization Using Infrared Quantum Cascade Laser Spectroscopy.</i> Dr. Mark S. Zahniser, Aerodyne Research, Inc.	
3:00 p.m. to 3:15 p.m.	Break	
3:15 – 3:45	<i>Quantifying Ammonia Concentrations and Exchange Fluxes: Process Interactions and Regional Generalization.</i> Dr. Mark Sutton, CEH, Edinburgh Research Station	

**THURSDAY, October 23, 2003**

**Room Location**

3:45 – 4:15	<b>Measurement of Ammonia Concentrations and Fluxes: Recent Examples Using Denuder and Chemiluminescence Technologies.</b> Mr. John Walker, U.S. Environmental Protection Agency	International Ballroom West
4:15 – 4:45	<b>Application of Micrometeorological Methods for Determining Fluxes of Nitrogen Compounds.</b> Dr. Tilden Meyers, National Oceanic and Atmospheric Administration	
4:45 to 5:00 p.m.	Open Floor Discussion	

**FRIDAY, October 24, 2003**

**Room Location**

<b>CONTINUATION OF SESSION 3:</b>	<b>ASSESSING OUR ABILITY TO QUANTIFY AMMONIA</b> Session Chair: Dr. Ray Knighton, U.S. Department of Agriculture, CSREES	International Ballroom West
8:00 a.m. to 9:30 a.m.	<b>PART 2: Current Modeling Tools and Limitations</b>  How well are models handling ammonia? Do we have the capability to model ammonia dispersed over local to regional scales (1-200km)? What is the quality of these models? What are the limitations? What is needed for model evaluations?	
8:00 – 8:30	<b>Modeling Atmospheric Transport and Deposition of Ammonia.</b> Dr. Willem Asman, Danish Institute of Agricultural Sciences	
8:30 – 9:00	<b>Air Quality Modeling of Ammonia: A Regional Modeling Perspective.</b> Dr. Robin Dennis, U.S. Environmental Protection Agency/NOAA Atmospheric Modeling Division	
9:00 – 9:30	<b>Measurement Techniques and Models for Ammonia Emissions at the Farm Level.</b> Dr. Lowry Harper, U.S. Department of Agriculture, Agricultural Research Service	
9:30 a.m. to 9:45 a.m.	Discussion	
9:45 a.m. to 10:00 a.m.	Break	
<b>SESSION 4:</b>	<b>THE ROLE OF ROUTINE, LONG-TERM MONITORING NETWORKS</b> Session Chair: Dr. Pam Padgett, U.S. Department of Agriculture Forest Service	
10:00 a.m. to 11:00 a.m.	<b>AMBIENT AIR MONITORING NETWORKS</b>  Is There Need to Collect Routine Ammonia Measurements in Ambient Air Monitoring Networks?	

**FRIDAY, October 24, 2003**

**Room Location**

10:00 – 10:30	<b><i>The Role of Ammonia Measurements in National Routine Ambient Air Monitoring Networks.</i></b> Mr. Rich Scheffe, U.S. Environmental Protection Agency Office of Air Quality Planning & Standards	International Ballroom West
10:30 – 11:00	<b><i>Adding Ammonia/um Measurements to Routine Monitoring Networks?</i></b> Mr. Rich Poirot, Vermont Department of Environmental Conservation	
11:00 a.m. to 12:00 p.m.	<b>DEPOSITION MONITORING NETWORKS</b>  What monitoring site density is required to give reasonable regional estimates of ammonia/um?	
11:00 – 11:30	<b><i>What Monitoring Site Density Is Required to Give Reasonable Estimates of Ammonia/ammonium?</i></b> Dr. Jan Willem Erisman, Energy Research Centre of the Netherlands	
11:30 – 11:45	<b><i>Monitoring Chemical Climate Change in America - The Case for Ammonia.</i></b> Mr. Van Bowersox, Illinois State Water Survey	
11:45 – 12:00	<b><i>Perspectives In Designing And Operating A Regional Ammonia Monitoring Network.</i></b> Mr. Gary G. Lear, U.S. Environmental Protection Agency	
12:00 p.m. to 12:30 p.m.	Discussion / Wrap-up Mr. Jim Lynch, The Penn State University	

**SESSION 1:**

**MULTIPLE ROLES AND EFFECTS OF AMMONIA EMISSIONS**

Session Chair: Dr. Jan Willem Erisman, Energy Research  
Centre of the Netherlands





**Washington, D.C.  
Ammonia Workshop  
2003**

**Ammonia and Air Quality**

Russell R. Dickerson, Professor & Chairman  
Department of Meteorology  
Affiliate of Chemistry & Chemical Physics  
The University of Maryland, College Park, MD

The US EPA and USDA recently commissioned the National Research Council to review the state of the science of emissions from animal feeding operations in the US. That study concluded that these agricultural activities are a major, or even dominant source of several pollutants including ammonia. It further concluded that it is not currently possible to quantify accurately emissions factors, or, as would be more appropriate, quantify emissions as a function of local meteorology, climate, geography and farming practices. Mass balance approaches to the N budget of animal feeding operations, however, provide substantial evidence for the loss of large quantities of ammonia from the system. In the troposphere, ammonia plays only a minor role in the NO<sub>x</sub> budget and smog chemistry, although it may be a source of N<sub>2</sub>O under some circumstances. In the condensed phase, however, ammonia is a major component of aerosols, and aerosols have major effects on human health, visibility, and climate. Ammonia can alter the microphysical properties of aerosols to increase the rate of new particle formation. Ammonium can make particles more hydroscopic and alters their properties as cloud condensation nuclei - changing climate through what is called the indirect effect. Haze from ammonia-containing aerosols not only limits visibility but alters the radiative balance of the atmosphere with implications for atmospheric stability, precipitation, photochemistry, and climate.



## Effects of Ammonia Deposition

James N. Galloway  
University of Virginia

On a global basis, the deposition of ammonia to continents has increased about 4-fold, from ~11 Tg N/yr in 1860, to ~39 Tg N/yr in the mid-1990s. The primary driver of the increased deposition is food production, especially animal production. The most immediate effect of additional ammonia deposition is altered productivity of N-limited terrestrial and aquatic ecosystems. In addition, as the deposited N atom cascades through environmental reservoirs, there are numerous secondary and tertiary effects. In addition to impacting productivity, the deposited N can also increase soil acidity and decrease biodiversity. If the N atom is discharged to an aquatic ecosystem, it can increase surface water acidity, and then lead to coastal eutrophication. If the N atom is converted to  $N_2O$ , and emitted back to the atmosphere, it can then first increase greenhouse warming potential, and then decrease stratospheric ozone. The only effective way to reduce the magnitude of these effects is to decrease ammonia deposition by adopting a total-system approach to N management in food and energy production.

## Effects of Atmospheric Ammonia (NH<sub>3</sub>) on Terrestrial Vegetation

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At the global scale, among all N (nitrogen) species in the atmosphere and their deposition on to terrestrial vegetation and other receptors, NH<sub>3</sub> (ammonia) is considered to be the foremost. The major sources for atmospheric NH<sub>3</sub> are agricultural activities and animal feedlot operations, followed by biomass burning (including forest fires) and to a lesser extent fossil fuel combustion. Close to its sources, acute exposures to NH<sub>3</sub> can result in visible foliar injury on vegetation. NH<sub>3</sub> is deposited rapidly within the first 4–5 km from its source. However, NH<sub>3</sub> is also converted in the atmosphere to fine particle NH<sub>4</sub><sup>+</sup> (ammonium) aerosols that are a regional scale problem.

Much of our current knowledge of the effects of NH<sub>3</sub> on higher plants is predominantly derived from studies conducted in Europe. Adverse effects on vegetation occur when the rate of foliar uptake of NH<sub>3</sub> is greater than the rate and capacity for in vivo detoxification by the plants. Most to least sensitive plant species to NH<sub>3</sub> are native vegetation > forests > agricultural crops. There are also a number of studies on N deposition and lichens, mosses and green algae. Direct cause and effect relationships in most of those cases (exceptions being those locations very close to point sources) are confounded by other environmental factors, particularly changes in the ambient SO<sub>2</sub> (sulfur dioxide) concentrations.

In addition to direct foliar injury, adverse effects of NH<sub>3</sub> on higher plants include alterations in: growth and productivity, tissue content of nutrients and toxic elements, drought and frost tolerance, responses to insect pests and disease causing microorganisms (pathogens), development of beneficial root symbiotic or mycorrhizal associations and inter species competition or biodiversity. In all these cases, the joint effects of NH<sub>3</sub> with other air pollutants such as all-pervasive O<sub>3</sub> or increasing CO<sub>2</sub> concentrations are poorly understood.

While NH<sub>3</sub> uptake in higher plants occurs through the shoots, NH<sub>4</sub><sup>+</sup> uptake occurs through the shoots, roots and through both pathways. However, NH<sub>4</sub><sup>+</sup> is immobile in the soil and is converted to NO<sub>3</sub><sup>-</sup> (nitrate). In agricultural systems, additions of NO<sub>3</sub><sup>-</sup> to the soil (initially as NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup>) and the consequent increases in the emissions of N<sub>2</sub>O (nitrous oxide, a greenhouse gas) and leaching of NO<sub>3</sub><sup>-</sup> into the ground and surface waters are of major environmental concern.

At the ecosystem level NH<sub>3</sub> deposition cannot be viewed alone, but in the context of total N deposition. There are a number of forest ecosystems in North America that have been subjected to N saturation and the consequent negative effects. There are also heath lands and other plant communities in Europe that have been subjected to N-induced alterations. Regulatory mitigative approaches to these problems include the use of N saturation data or the concept of critical loads. Current information suggests that a critical load of 5–10 kg ha<sup>-1</sup> yr<sup>-1</sup> of total N deposition (both dry and wet deposition combined of all atmospheric N species) would protect the most vulnerable terrestrial ecosystems (heaths, bogs, cryptogams) and values of 10–20 kg ha<sup>-1</sup> yr<sup>-1</sup> would protect forests, depending on soil conditions. However, to derive the best analysis, the critical load concept should be coupled to the results and consequences of N saturation.

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**SESSION 2: PERSPECTIVES ON MANAGING AMMONIA EMISSIONS**

Session Chair: Dr. John Bachmann, Associate Director for  
Science & Policy, U.S. Environmental Protection  
Agency, OAQPS



## Managing Ammonia Emissions Cost Effectively

J. Webb\*<sup>1</sup> and U. Dämmgen<sup>2</sup>

Critical levels of acidification and nutrient-N deposition are still exceeded in many parts of Europe. Even with further reductions in emissions of NO<sub>x</sub>, significant exceedance of critical loads and levels will continue due to NH<sub>3</sub> deposition. Hence, a requirement to reduce NH<sub>3</sub> emissions has been included in a multi-pollutant, multi-effects protocol to reduce acidification and eutrophication in Europe, agreed by the UNECE Convention on Long-Range Transboundary Air Pollution. Agriculture is recognised as the source of c. 80-90% of European NH<sub>3</sub> emissions, with c. 70-80% of the total emitted during livestock production.

Emissions of NH<sub>3</sub> take place at all stages of manure management: from buildings; during storage; following application of manures to land and during grazing. Measures to reduce NH<sub>3</sub> emissions at the various stages of manure management are interdependent, and combinations of measures are not simply additive when combining their emission reduction. Reducing NH<sub>3</sub> emissions following application of manures to land is particularly important, as these are a large component of NH<sub>3</sub> emissions and land application is the last stage of manure management. Without abatement at this stage much of the benefit of reducing emissions from buildings and stores may be lost. In order to estimate the cumulative effects of a series of abatement measures, a mass-flow approach is needed. The source of NH<sub>3</sub> emission from livestock excreta and manure is regarded as a pool of total ammoniacal-N (TAN) which is not significantly added to during manure management. At each stage of manure management, a proportion of TAN may be lost, mainly as NH<sub>3</sub>, and the remainder passed to the next stage. This approach enables rapid and easy estimation of the consequences of abatement at one stage of manure management (upstream) at later stages (downstream). Such a model enables scenario analysis of abatement options and cost-curve production. The approach provides an unbiased assessment of the costs of abatement so that priority can be given to the most cost-effective measures.

The resulting cost-curve analysis indicates that these are generally the rapid incorporation of slurry or litter-based manures (FYM) into arable land, and the application of slurry to grassland by trailing shoe or injection equipment. These methods rank highly because of their large potential for abatement (60-90% of NH<sub>3</sub> emissions), relatively small cost and because once manure is incorporated into soil there is little further potential for abatement. Some approaches earlier in manure management may also be cost-effective. In particular allowing the surface of slurry stores to congeal (crusting) and storing FYM prior to spreading instead of spreading to land immediately the manure is removed from buildings. However, the adoption of even the most cost-effective measures may have serious adverse effects on farm budgets. The costs need to be assessed against affordability.

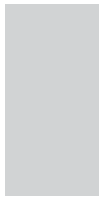
There is a need to ensure that measures taken to reduce emissions of NO<sub>x</sub> and NH<sub>3</sub> do not, so far as possible, increase other emissions of reactive-N. Early indications from modeling studies in the UK indicate that significant reductions in NH<sub>3</sub> emissions can be obtained while leading to only small total increases in nitrate leaching. However, locally abatement may lead to significant increases in nitrate concentrations in water.

A group of modelers are working together in Europe to produce a harmonised TAN-flow model, and to produce simple integrated, N and C mass-flow approaches for all gaseous emissions from livestock excreta.

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## **Managing Ammonia in the U.S.**

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Ammonia is both a critical component and byproduct of production agricultural systems. It is an important source form of nitrogen in crop production when applied to the soil as anhydrous ammonia. Ammonia is also released from agricultural systems as a gas. The release occurs from both animal production through excretion of urine and the near-immediate conversion to ammonia and the continual release of ammonia from animal housing and manure storage systems and the release from manure application. Reduction of ammonia from various components of agricultural systems requires the development of methods that modify the ammonia formation process or reduce the emission rate of ammonia to the boundary layer of the atmosphere. In animal production systems reductions in ammonia production can be achieved through maintaining the manure in an acidic state that reduces the conversion of nitrogen into ammonia. Reductions in ammonia emission from manure storage facilities are possible through either changing the storage environment from an anaerobic to an aerobic one or by covering the storage surface with an impermeable cover. Reductions in ammonia release from agricultural systems will require adoption of treatment methods that reduce the formation, emission, or transport. Direct comparisons of treatment technologies will result in quantifying how ammonia flux or emissions into the atmosphere can be reduced. Combinations of direct measurements and emission models from agricultural systems are being used to define how agricultural systems affect ammonia levels in the environment.

Throughout USDA in the Agricultural Research Service (ARS) and Cooperative States Research Education and Extension Service (CSREES) there are ongoing activities to determine the ammonia emission from beef, dairy, poultry, and swine operations. These efforts are helping define the variation in emission rates across different production systems. Coupled with these measurement studies are ongoing efforts in dairy, poultry, and swine facilities to evaluate potential treatment technologies that reduce ammonia emissions. Ammonia emissions and treatment technologies are being addressed through combinations of scientists that understand the components of agricultural systems and how they can be managed for improved performance efficiency and reduced environmental impact.

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**Washington, D.C.  
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**Are We There Yet? Future Paths from the Past**

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North Carolina has experienced several periods of extremely rapid expansion in the number of animals raised for commercial purposes. Two of the most recent periods occurred in the late 1980's with poultry (turkeys) and in the mid-1990s with hogs. This large expansion of the "animal inventory," as tallied by the US Department of Agriculture, tells only part of the story about the effects of this growth and the impact of on the environment.

North Carolina's most recent experience with the animal industry has focused on hog production, it's rapid expansion and the subsequent moratorium that remains in effect today because of the environmental consequences. While the increase in ammonia emissions was substantial, North Carolina eventually regulated on the basis of nitrogen load (from the water quality perspective) and objectionable odor (from the air quality perspective). But the focus of the work under the Smithfield/ Premium Standards/ Frontline Agreements, conducted under the guidance of NC State University, focuses on the control of ammonia and the Environmentally Superior technologies identified and developed under the agreements should provide an array of choices for the control of ammonia.

From a regulatory standpoint, the number of factors to be considered have a much broader perspective than simply "controlling ammonia." These factors include traditional air pollution issues such as PM-fine and ozone precursors, cross media transfer, and exposure levels resulting from emissions. More recently, issues like the cost for natural gas (as a feedstock for ammonia) and the increased demand for ammonia for NO<sub>x</sub> reduction from combustion sources have entered the regulatory equation. This presentation looks at potential future regulatory issues as they deal with these broader energy, environmental and supply issue as well as some of impacts that the current data suggest for more traditional air pollution control strategies and approaches.



## **Regulating Ammonia in Clean Air Act State Implementation Plans - Do We Know Enough to Proceed?**

Dave Mitchell<sup>1</sup>  
San Joaquin Valley Air Pollution Control District

The San Joaquin Valley has a serious particulate pollution problem that is caused in large part by ammonium nitrate and ammonium sulfate during winter stagnation events. Ammonium nitrate alone measured between 54 and 110 micrograms per cubic meter at monitoring sites throughout the air basin during episodes captured by the California Regional Particulate Air Quality Study (CRPAQS) field study in 2000-2001. The San Joaquin Valley has a \$15 billion diversified farm economy and is California's leading dairy region. Agriculture is estimated to contribute over 90 percent of the 397 ton per day ammonia emission inventory.

The San Joaquin Valley Air Pollution Control District (District) submitted a Particulate Matter less than 10 micrometers in diameter (PM10) State Implementation Plan to United States Environmental Protection Agency (EPA) in June 2003. The plan relies upon controls of oxides of nitrogen (NOx) and oxides of sulfur (SOx) to reduce nitrate and sulfate concentrations. This is based on field measurements that indicated that ammonia was nearly always in excess and NOx/nitric acid was the limiting pollutant in the reaction. Modeling conducted by the California Air Resource Board using UAM-Aero was inconclusive regarding the benefit of control of each precursor. These inconclusive results led environmental groups following the process to comment that ammonia controls should be pursued immediately. EPA has so far allowed the District to forego ammonia controls pending the results of final CRPAQS reports due in 2005 and with a commitment to pursue controls should convincing evidence of their benefit be identified in the interim. The District also made the case that knowledge regarding the effectiveness of ammonia controls for agricultural sources was not sufficiently advanced to proceed with regulations. To resolve this situation satisfactorily, the District needs answers to three questions: 1. Are ammonia emission factors from all sources reliable enough to accurately identify the true causes of the problem? 2. Would ammonia emission reductions result in expedited attainment of PM10 and PM2.5 standards? 3. Are ammonia controls for agricultural sources effective and, if so, at what cost? The expenditure of millions of dollars by the agriculture industry and by government may hinge on the answer.

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**SESSION 3: ASSESSING OUR ABILITY TO QUANTIFY AMMONIA**

Session Chair: Dr. Ray Knighton, U.S. Department of Agriculture,  
CSREES



**Measuring Ammonia Emissions from Agricultural Sources:  
Technical Possibilities, Applicability in Situ, Benefits and Drawbacks**

Gert-Jan Monteny and Julio Mosquera  
IMAG Wageningen University and Research Centre

Ammonia emissions are an important environmental issue and especially in regions with high animal densities (e.g. the Netherlands). Ammonia contributes not only to soil acidification, but it also leads to disruption of the nutrient cycle and disappearance of sensitive natural ecosystems. In order to comply with the ammonia emission reduction assigned to the Netherlands, fast and accurate measurements are necessary to get new estimates of the ammonia emission from each agricultural category.

For years, the basic components of emission measurement strategies for mechanically ventilated houses have been based upon a detailed measurement of the ventilation rate using calibrated anemometers (measurement fans), combined with an accurate measurement of the gas concentration in the exhaust air. Naturally ventilated houses were measured using a gas mass balance method, either using a natural (e.g. CO<sub>2</sub>) or an introduced (SF<sub>6</sub>) tracer gas to estimate the ventilation rate, combined with a continuous measurement of the NH<sub>3</sub> concentration in the air leaving the building. Although various theoretical possibilities exist for NH<sub>3</sub> emission measurements from non-point sources, like land spread slurry or grazing cattle, full-scale measurements have been limited due to high costs, large labour requirement or insufficient accuracy. Small-scale (micro meteorological mass balance methods, laboratory scale methods) measurements have been conducted on a large scale to yield emission estimates for practical situations.

New insights in measurement equipment for ventilation rate determination, concentration measurement and flux measurements have yielded a basis for new measurement systems and protocols. Statistics and mechanistic models can be promising aspects of these new protocols, aiming at a reduction of the labour and money input, yet maintaining accuracies and offering possibilities for conducting repetitive measurements.

During campaigns to measure emissions from animal houses, it became clear that management is an important factor in determining the emission level. Differences between animal houses of the same type and kind of animal may differ more than the variation in time and season within one animal house. These management related differences in emission factors point at the need of measuring more animal houses. The newly formulated protocols (partly based upon new measurement techniques) can offer possibilities for a more dense data collection, thus leading to a more accurate average emission level per source type (housing system, storage facility, field application of slurry, grazing) and an improved insight in the variation and its influencing factors. This will eventually benefit the development of emission reduction strategies and more accurate legislation.

The paper will focus on developments in the techniques to measure ventilation rates, gas concentrations and fluxes, and on their applicability in practical and research situations. Benefits and drawbacks are highlighted and discussed. Furthermore, the role of models and statistics will be briefly addressed.



## **Techniques for Measuring Ammonia Emissions from Land Applications of Manure and Fertiliser**

T. H. Misselbrook<sup>\*1</sup> and F. A. Nicholson<sup>2</sup>

Land application of manures represents a major source of ammonia (NH<sub>3</sub>) emissions to the atmosphere in Europe, often accounting for 30-40% of the total national emission. A number of techniques have been developed to quantify NH<sub>3</sub> emissions for the construction of national inventories, so that the impacts on the environment can be assessed and the effectiveness of abatement strategies evaluated. These techniques are equally applicable to the measurement of emissions from fertiliser applications. Generally, the techniques fall into one of two categories: micrometeorological methods (usually used for large land areas) and enclosure methods (commonly used on small plots). Most techniques require the measurement of NH<sub>3</sub> concentration and air flow or wind speed, or, alternatively, direct measurement of NH<sub>3</sub> flux. This paper will briefly present a range of available techniques and then concentrate on the three techniques most often used in Europe.

The integrated horizontal flux (IHF) mass balance technique is the most widely used micrometeorological measurement technique, employing either acid-filled absorption flasks ('bubblers') for measurement of NH<sub>3</sub> concentration or, more commonly now, passive flux samplers ('shuttles') for direct NH<sub>3</sub> flux measurement. Wind tunnels are the most commonly used small-plot technique, with acid-filled absorption flasks employed to measure NH<sub>3</sub> concentration. The equilibrium concentration technique lies somewhere between a classical micrometeorological technique and an enclosure technique and uses passive diffusion samplers (PDS) for the measurement of NH<sub>3</sub> concentration. A series of experiments was conducted to assess the variability and accuracy of the samplers used in each technique and the variability of the techniques as a whole in measuring emissions from different manure types. For the samplers, coefficients of variation (CVs) were 21, 10 and 14% and limits of detection were 70, 50 and 2.5 µg N for 'bubblers', 'shuttles' and PDS, respectively. For the emission measurement techniques as a whole, CVs following spreading of different manure types were in the ranges of 23-57, 31-76 and 22-39% for the IHF, wind tunnels and equilibrium concentration techniques, respectively. Lower CVs were associated with measurements following slurry application compared with solid manure application. The equilibrium concentration technique was considered to be the least robust of the methods as the PDS were susceptible to under- or over-exposure. The development of a reliable, non-intrusive technique for measuring emissions from small plots is still required.

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**Urban Ammonia Source Characterization Using  
Infrared Quantum Cascade Laser Spectroscopy**

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Ammonia in cities can be an important source of particulates due to elevated levels of nitrogen oxides in urban areas. Instrumentation using quantum cascade (QC) infrared laser absorption has been developed to characterize sources of ammonia. QC lasers operate without cryogenic cooling which makes them much more robust and convenient for field measurements than conventional lead-salt tunable diode lasers. An extractive sampling version of the instrument has been mounted in a mobile van for fast response (sub-second), high precision (0.5 ppb) mapping of emission sources. The van is also equipped with an aerosol mass spectrometer for measurements of ammonium in particles. Simultaneous measurements of CO<sub>2</sub> are used to distinguish combustion sources of ammonia associated with automobile traffic from other sources. An open-path, retro-reflector version of the instrument has been developed to measure ammonia emissions in automobile exhaust as individual vehicles pass through the laser beam. Data from recent studies in Mexico City and in Boston will be presented and compared with other measurement techniques including long path FTIR spectroscopy.

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## **Quantifying Ammonia Concentrations and Exchange Fluxes: Process Interactions and Regional Generalization**

M.A. Sutton<sup>1</sup>, Y.S. Tang<sup>1</sup>, C. Milford<sup>1</sup>, T. Dore<sup>1</sup>, E. Nemitz<sup>1</sup>, M.R. Theobald<sup>1</sup>,  
U. Dragosits<sup>1</sup>, D. Fowler<sup>1</sup>, A. van Pul<sup>2</sup> and J.W. Erisman<sup>3</sup>

Quantifying the amounts and fate of ammonia in the environment requires measurements at a range of spatial and temporal scales. The measurement task can be distinguished into three levels: 1) Application of low-cost sampling methods for the assessment of spatial patterns and long term trends in  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations, 2) Detailed measurements using basic techniques, including basic monitoring of dry deposition, 3) Process studies on  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations and biosphere-atmosphere exchange. In relation to air concentration monitoring, the emphasis needs to be on Levels 1 and 3. Low-cost denuders and passive sampling at a monthly frequency provide data on spatial patterns and temporal trends cheaply, while expensive continuous monitoring techniques for  $\text{NH}_3$  and  $\text{NH}_4^+$  can concentration and/or flux data with a 10-minute to hourly resolution for the investigation of process controls. Conversely, traditional daily sampling using manual methods fails to meet either of these objectives optimally.

Substantial advances in quantifying ammonia interactions have been made in the UK and Europe based on these approaches. While Level 3 measurements have aided the development of bi-directional  $\text{NH}_3$  exchange models, and feed into improving the process description in regional emission, dispersion and deposition models, the Level 1 measurements provide a resource to test the  $\text{NH}_3$  and  $\text{NH}_4^+$  concentration outputs of the regional models, both spatially and against long term trends. This is demonstrated from a comparison of data from the UK and Dutch national monitoring networks with the respective national models. A key challenge for  $\text{NH}_3$  is that of local spatial variability, which leads to serious errors in the national risk assessments of ecological impacts. Here there is an ongoing need for fine scale investigations (e.g. 50 m resolution, within example 5 km grid squares), to better quantify impacts, improve sampling representativity and refine  $\text{NH}_3$  abatement strategies.

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<sup>2</sup>RIVM, Bilthoven, NL

<sup>3</sup>ECN, Petten, NL



**Measurement of Ammonia Concentrations and Fluxes: Recent Examples  
Using Denuder and Chemiluminescence Technologies**

John Walker<sup>1</sup>  
U.S. Environmental Protection Agency  
National Risk Management Research Laboratory  
Air Pollution Prevention and Control Division  
Atmospheric Protection Branch  
Research Triangle Park, NC 27711

This presentation will describe selected ongoing research projects that employ commercially available technologies for determination of atmospheric concentrations and fluxes of ammonia. Annular denuders are used in an ambient monitoring project to measure ammonia, ammonium aerosol, and acid gases at agricultural and non-agricultural sites in eastern North Carolina. Another project examines spatial gradients of ammonia concentrations in the vicinity of a swine production facility using passive diffusion samplers. A third project investigates air/surface exchange of ammonia above crop canopies using chemiluminescence analyzers as part of a modified Bowen-ratio flux measurement system. Methodology and selected results will be presented for each project and advantages/disadvantages of the respective ammonia measurement technologies will be discussed.

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## **Application of Micrometeorological Methods for Determining Fluxes of Nitrogen Compounds**

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Atmospheric Turbulence and Diffusion Division  
Oak Ridge, TN

For many applications of determining the deposition or emission of a trace gases or aerosols the landscapes, micrometeorological methods are often employed to determine the flux. These methods are often used because the fluxes can be resolved at time scales that are on the order of hours. This is particularly important because there is often a diurnal pattern of trace gas fluxes and measurements are needed in order to resolve the diurnal nature of the flux. The particular method used depends on the accuracy of the concentration measurement and the frequency at which the measurement can be made. For those gases in which concentrations can be measured at a frequency of at least 1 Hz, the eddy covariance method is the preferred technique and fluxes are usually computed at 30 minute intervals. Although newer cutting edge methodologies, are being developed for fast measurements, there are relatively few chemical species for which fast response sensors are available. Those include O<sub>3</sub>, SO<sub>2</sub>, CO<sub>2</sub> and NO. There are more sensors available that can measure trace gas concentrations, but that are not fast response. Flux/gradient methods are then often employed with such sensors to determine fluxes. These include the Bowen ratio, modified Bowen ratio, and aerodynamic method. Essentially, the fluxes and corresponding gradients of well known surrogates such as heat and water vapor, are used to compute the fluxes of other constituents based on their gradients over some specified interval. These methods require accurate measurements such that small differences in concentrations can be resolved. Typically, differences less than 5% of the mean concentration are required.

More recently, the conditional sampling (relaxed eddy accumulation) method has been used to measure trace gas and aerosol fluxes. With this method, sample collectors or “accumulators” are used to selectively sample large “updrafts” and “downdrafts” of which the difference is proportional to the flux. Filterpacks and annual denuders are often used in this configuration. Similar to gradient methods, accurate differences are required in order to obtain a statistically significant flux. Special care must be made to monitor flow rates and extraction volumes. Examples of each will be presented with a focus on the application towards nitrogen compounds, especially ammonia.

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**Modeling Atmospheric Transport and Deposition of Ammonia**

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8830 Tjele, Denmark

An overview is given on modeling of the atmospheric transport and deposition of ammonia and ammonium for different purposes on different scales and the problems associated with the validation of such models. The various processes that are part of such models are discussed as well as the problems with obtaining the relevant information. The issue of short vs. long distance transport will be discussed. An example is given of local modeling of ammonia deposition.

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## **Air Quality Modeling of Ammonia: A Regional Modeling Perspective**

Robin L. Dennis  
U.S. Environmental Protection Agency  
National Oceanic and Atmospheric Administration  
Atmospheric Science Modeling Division

The talk will address the status of modeling of ammonia from a regional modeling perspective, yet the observations and comments should have general applicability. The air quality modeling system components that are central to modeling ammonia will be noted and a perspective on their contribution to the overall uncertainty will be given. Special attention to the overall importance of ammonia emissions and their uncertainty will be given with illustrations from inverse modeling. The capability of our physical and chemical modeling of the ammonia part of the inorganic system will be put in perspective vis a vis the overall inorganic system uncertainties. Issues related to estimating the dry deposition of ammonia will be noted. The large uncertainty in interpretations of the ammonia budget will then be raised, including our poor understanding of the regional or continental budget. Perspectives on local versus long-range transport from regional analyses will be given, modeled budget analyses will be presented and some discrepancies with conventional wisdom noted. This leads into a further discussion of issues that can affect attribution and introduce biases. The talk concludes with a set of recommendation of research directions that will help improve the modeling of ammonia, support better evaluation of models and aid interpretation of the ammonia system.

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**Measurement Techniques and Models for Ammonia Emissions At the Farm Level**

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Agricultural Research Service  
U.S. Department of Agriculture  
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The unique chemical and physical properties of ammonia make it difficult to obtain accurate atmospheric measurements of concentrations and to determine representative emission rates. Ammonia is a diffusive gas and emissions are driven by the chemical and physical factors of solution concentration, solution hydrogen ion concentration (pH), solution temperature, and ambient air turbulence (represented by windspeed). Influencing these factors during measurement results in non-representative estimates of concentrations and emissions. Mathematical relationships and field measurements of the effects of these factors have shown the problems associated with measurement influence. Non-interference techniques should be used in determination of emissions and for the verification of models; however, use of inappropriate, non-interference techniques will also give erroneous results. We made comparisons of emissions using appropriate and inappropriate measurement technologies. Large differences were obtained in emissions rates. Available statistical emissions models showed good fit to data although the geographical extent of usefulness was limited. A process model had slightly poorer fit to data but was not geographically limited.

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**SESSION 4: THE ROLE OF ROUTINE, LONG-TERM MONITORING NETWORKS**

Session Chair: Dr. Pam Padgett, U.S. Department of Agriculture  
Forest Service

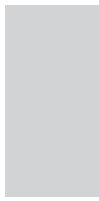




**The Role of Ammonia Measurements in National Routine  
Ambient Air Monitoring Networks**

Richard D. Scheffe  
Office of Air Quality Standards and Planning  
U.S. Environmental Protection Agency

The role of ammonia in air program management is gaining more attention as secondarily formed particulate matter is now a principal focus in the air quality agenda. Ammonia also cuts across environmental media with impacts related to watershed eutrophication and neutralization that demand comprehensive integration across media and effects pathways when considering ammonia mitigation strategies. Although the fate and transport processes governing ammonia through the atmosphere are relatively well understood, our ability to characterize ammonia emission processes and ambient air concentrations are compromised given: 1) the pervasiveness and highly variable nature of several agricultural and industrial emission sources; 2) complex interactions between ammonia gas and nearby landscape (which can either be a source or sink to uptake ammonia and re-release some or all of it at a later time); and 3) by the thermodynamic properties of ammonia which partitions across particle and gaseous phases at typical environmental conditions. Collectively, the relative importance of ammonia in environmental management practice combined with characterization difficulties pose substantial questions regarding a national approach to more routine monitoring of airborne ammonia. This presentation discusses design considerations accommodating ammonia measurements in the national air monitoring strategy.



## **Adding Ammonia/um Measurements to Routine Monitoring Networks?**

Richard Poirot<sup>1</sup>  
Air Quality Planner  
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One important consequence of ammonia emissions and concentrations in the atmosphere is their critical role in the formation and modification of secondary aerosols. Particle-phase ammonium is one of the most important constituents of fine particles (PM-2.5) and gaseous ammonia is a key aerosol precursor, yet the emissions, atmospheric chemistry, ambient air concentrations, effects on human health, visibility and radiation budgets and implications for alternative control strategies remain poorly characterized. This presentation will consider the question of adding ammonium and/or ammonia measurements to routine monitoring networks by providing several examples illustrating the value that such measurement can provide, or have provided when included in aerosol measurement programs. At the same time several cautionary issues or questions are raised regarding appropriate methods for conducting such measurements on a routine network basis.

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**Deposition Monitoring Networks: What Monitoring Site Density Is Required to Give Reasonable Estimates of Ammonia/ammonium?**

Jan Willem Erisman<sup>1,\*</sup>, Arjan Hensen<sup>1</sup>, Mark Sutton<sup>2</sup>, and Addo van Pul<sup>3</sup>

Deposition is one of the main loss terms for ammonia and ammonium from the atmosphere. It is also the input for ecosystems that can lead to drastic changes and effects. Deposition networks are needed to evaluate the need and the effect of policies to reduce emissions, but also for studying deposition parameters and develop deposition models. As with the ambient concentration of ammonia, deposition, especially dry deposition, varies strongly in space and in time. Furthermore, the bi-directional surface – atmosphere exchange of ammonia makes the combination of ambient concentration measurements with inferential models inadequate. Developing deposition monitoring networks with reasonable accuracy and representativity is therefore not straightforward. In Europe several projects have addressed deposition monitoring. From these results it is concluded that a monitoring strategy should consist of a network with a limited amount of super sites combined with a larger number of sites where cheap methods are applied, together with models for generalization.

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## Monitoring Chemical Climate Change in America - The Case for Ammonia

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National Atmospheric Deposition Program  
Illinois State Water Survey  
Champaign, IL 61820

The National Atmospheric Deposition Program - National Trends Network (NTN) has measured the acids, nutrients, and base cations in U.S. precipitation for more than two decades, long enough to identify a “chemical climate” and observe its changes. Much as climatologists describe the physical characteristics of our average weather (i.e., climate) and use long-term temperature records to evaluate climate change, scientists use NTN data to calculate mean chemical concentrations and deposition fluxes to evaluate chemical climate changes. Precipitation chemistry is an indicator of chemical climate, since precipitation scavenges airborne gases and particles, which are affected by emissions, chemical transformations, and weather. NTN data indicate that significant changes have occurred in precipitation chemistry, particularly for the ammonia/ammonium system and important related chemical species.

A Seasonal Kendall Trend Test was applied to precipitation-weighted concentration data from 139 NTN sites operational from 1985 to 2002 (see Nilles and Conley, *Water, Air, Soil Pollution* **130**:409-414, 2001). Ammonium increased over this 18-year period at 124 sites (89%) and the increases were statistically significant ( $p < 0.05$ ) at 58 sites (42%). Central and northern Midwestern states generally had the largest ammonium increases. Significant decreases occurred at just two sites. The median annual ammonium change over all 139 sites was 0.17 microequivalents/liter/year; the median ammonium concentration increased ~30% from 1985 to 2002. Citing U.S. Environmental Protection Agency data ([www.epa.gov/ttn/chief/trends/inex.html](http://www.epa.gov/ttn/chief/trends/inex.html)), ammonia emissions increased, as well, from 3.9 teragrams (Tg) in 1990 to 4.5 Tg in 2001. Ammonia emissions and ammonium concentrations have increased, signaling important changes in our chemical climate over the last 15 - 20 years.

Generally higher ammonium concentrations in precipitation have been accompanied by significant sulfate decreases (e.g., Lynch, et al., *Environmental Science & Technology* **34**:940-949) and locally significant nitrate increases and decreases. The relative amounts of sulfate, nitrate, and ammonium in precipitation have changed markedly. This signals a change in the mix of gases and particles being scavenged by precipitation. This change is important to our understanding of the changing chemical climate of America.

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**Perspectives in Designing and Operating A Regional Ammonia Monitoring Network**

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Washington DC 20460

Ammonia emissions are increasingly recognized as a major contributor to nitrogen deposition and aerosol formation. Some research indicating that ammonia gas contributes up to 30 percent of total nitrogen deposition in regions with high ammonia concentrations. However, the magnitude and geographic extent of elevated ammonia concentrations are currently unknown, with most estimates based on measurements of relatively limited geographic extent and duration. Accurate determinations of the magnitude and extent of pollutants require a uniform network of monitoring locations with sufficient density to detect trends and gradients in pollutant concentrations. However, the behavior of ammonia gas in the atmosphere may be sufficiently different from other gaseous pollutants like sulfur dioxide and nitric acid to preclude it from the traditional characterization methods of existing regional monitoring networks. For example, the removal rates of ammonia gas are orders of magnitude greater than those of sulfur dioxide and nitric acid, which may result in extremely steep concentration gradients of the gas. In addition, the bidirectional nature of ammonia gas flux and the ammonia-ammonium equilibrium may require covariant measurements and inferential models to estimate net flux. This presentation will examine these and other design considerations for an ammonia gas monitoring network.

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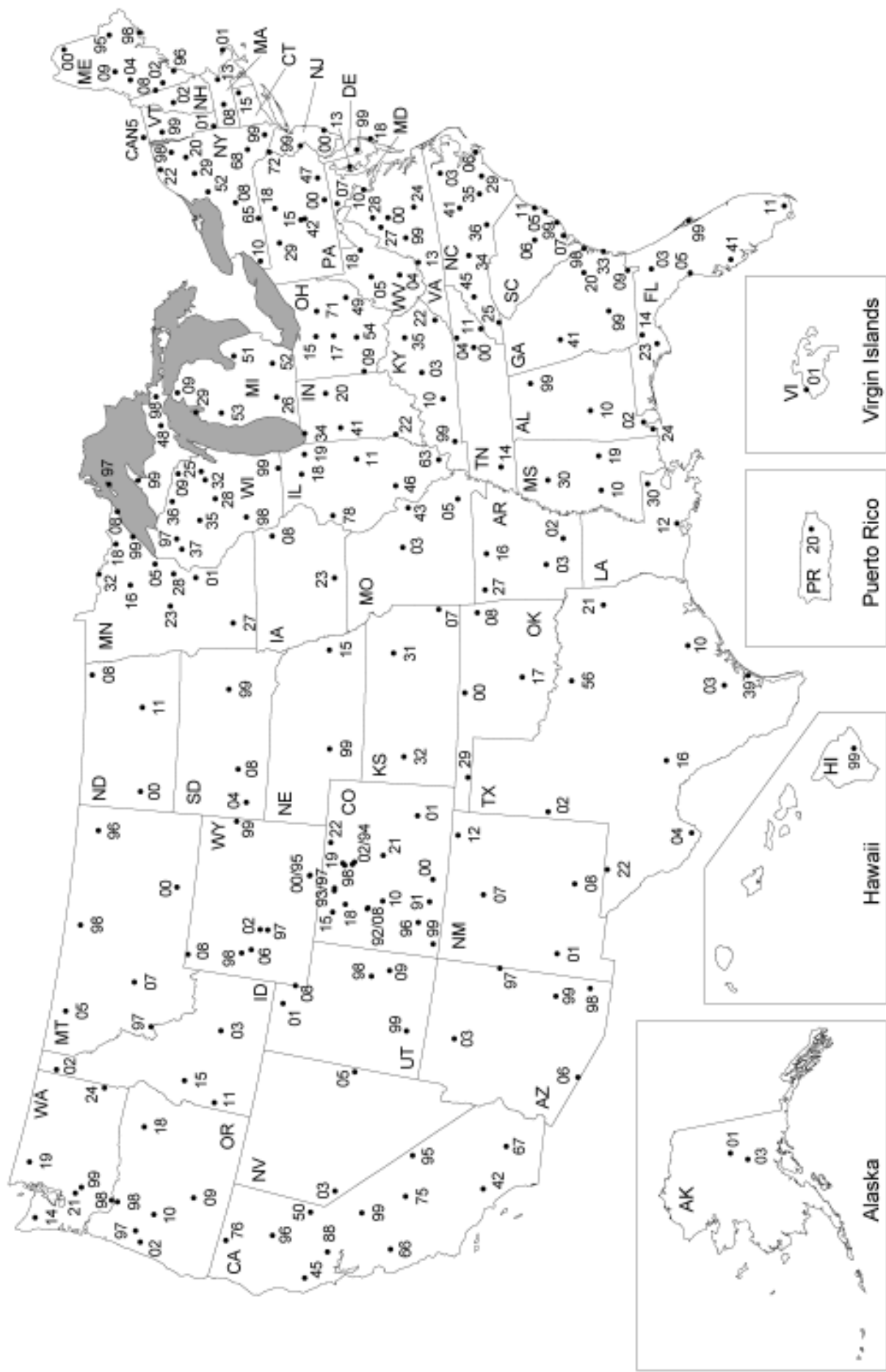


## **NTN MAP AND SITE LISTINGS**





# National Atmospheric Deposition Program National Trends Network



**National Atmospheric Deposition Program/National Trends Network Sites**  
**August 31, 2003**

State	Site Code	Site Name	Collocation	Sponsoring Agency	Start Date
<b>Alabama</b>					
	AL02	Delta Elementary	MDN	Mobile Bay National Estuary Program	06/01
	AL10	Black Belt Agricultural Experiment Substation		US Geological Survey	08/83
	AL24	Bay Road	MDN	Mobile Bay National Estuary Program	05/01
	AL99	Sand Mountain Agricultural Experiment Substation		Tennessee Valley Authority	10/84
<b>Alaska</b>					
	AK01	Poker Creek		USDA Forest Service	12/92
	AK03	Denali NP - Mount McKinley		National Park Service - Air Resources Div	06/80
<b>Arizona</b>					
	AZ03	Grand Canyon NP - Hopi Point		National Park Service - Air Resources Div	08/81
	AZ06	Organ Pipe Cactus NM		National Park Service - Air Resources Div	04/80
	AZ97	Petrified Forest National Park-Rainbow Forest		National Park Service - Air Resources Div	12/02
	AZ98	Chiricahua		US Environmental Protection Agency-CAMD	02/99
	AZ99	Oliver Knoll		US Geological Survey	08/81
<b>Arkansas</b>					
	AR02	Warren 2WSW		US Geological Survey	05/82
	AR03	Caddo Valley		US Geological Survey	12/83
	AR16	Buffalo NR - Buffalo Point		National Park Service - Air Resources Div	07/82
	AR27	Fayetteville		US Geological Survey	04/80
<b>California</b>					
	CA42	Tanbark Flat		USDA Forest Service	01/82
	CA45	Hopland		US Geological Survey	10/79
	CA50	Sagehen Creek		US Geological Survey	11/01
	CA66	Pinnacles NM - Bear Valley		National Park Service - Air Resources Div	11/99
	CA67	Joshua Tree NP - Black Rock		National Park Service - Air Resources Div	09/00
	CA75	Sequoia NP - Giant Forest	MDN	National Park Service - Air Resources Div	07/80
	CA76	Montague		US Geological Survey	06/85
	CA88	Davis		US Geological Survey	09/78
	CA95	Death Valley NP - Cow Creek		National Park Service - Air Resources Div	02/00
	CA96	Lassen Volcanic NP - Manzanita Lake		National Park Service - Air Resources Div	06/00
	CA99	Yosemite NP - Hodgdon Meadow		National Park Service - Air Resources Div	12/81
<b>Colorado</b>					
	CO00	Alamosa		US Geological Survey	04/80
	CO01	Las Animas Fish Hatchery		US Geological Survey	10/83
	CO02	Niwot Saddle		NSF-INSTAAR/University of Colorado	06/84
	CO08	Four Mile Park		US Environmental Protection Agency-CAMD	12/87
	CO10	Gothic		US Environmental Protection Agency-CAMD	02/99
	CO15	Sand Spring		Bureau of Land Management	03/79
	CO18	Ripple Creek Pass		Air Science, Incorporated	05/03
	CO19	Rocky Mountain NP - Beaver Meadows		National Park Service - Air Resources Div	05/80
	CO21	Manitou		USDA Forest Service	10/78
	CO22	Pawnee		NSF-LTER/Colorado State University	05/79
	CO91	Wolf Creek Pass		USDA Forest Service	05/92
	CO92	Sunlight Peak		US Environmental Protection Agency-CAMD	01/88
	CO93	Buffalo Pass - Dry Lake		USDA Forest Service	10/86
	CO94	Sugarloaf		US Environmental Protection Agency-CAMD	11/86
	CO96	Molas Pass		USDA Forest Service	07/86
	CO97	Buffalo Pass - Summit Lake	MDN	USDA Forest Service	02/84
	CO98	Rocky Mountain NP - Loch Vale		USGS/Colorado State University	08/83
	CO99	Mesa Verde NP - Chapin Mesa	MDN	US Geological Survey	04/81
<b>Connecticut</b>					
	CT15	Abington		US Environmental Protection Agency-CAMD	01/99
<b>Delaware</b>					
	DE99	Trap Pond State Park		US Environmental Protection Agency-CAMD	05/03
<b>Florida</b>					
	FL03	Bradford Forest		St. John's River Water Management District	10/78
	FL05	Chassahowitzka NWR	MDN	US Fish & Wildlife Serv - Air Quality Branch	08/96
	FL11	Everglades NP - Research Center	MDN	National Park Service - Air Resources Div	06/80
	FL14	Quincy		US Geological Survey	03/84
	FL23	Sumatra		US Environmental Protection Agency-CAMD	01/99
	FL41	Verna Well Field		US Geological Survey	08/83
	FL99	Kennedy Space Center		NASA/Dynamac Corporation	08/83

State	Site Code	Site Name	Collocation	Sponsoring Agency	Start Date
<b>Georgia</b>					
	GA09	Okefenokee NWR	MDN	US Fish & Wildlife Serv - Air Quality Branch	06/97
	GA20	Bellville		US Environmental Protection Agency-CAMD	04/83
	GA33	Sapelo Island		Georgia Department of Natural Resources	11/02
	GA41	Georgia Station		SAES-University of Georgia	10/78
	GA98	Skidaway		NSF/Skidaway Institute of Oceanography	06/02
	GA99	Chula		US Geological Survey	02/94
<b>Hawaii</b>					
	HI99	Hawaii Volcanoes NP - Thurston		National Park Service - Air Resources Div	11/00
<b>Idaho</b>					
	ID02	Priest River Experimental Forest		USDA Forest Service-Rocky Mountain Res. Stn.	12/02
	ID03	Craters of the Moon NM		National Park Service - Air Resources Div	08/80
	ID11	Reynolds Creek		US Geological Survey	11/83
	ID15	Smiths Ferry		US Geological Survey	10/84
<b>Illinois</b>					
	IL11	Bondville	AIRMoN/MDN	SAES-University of Illinois	02/79
	IL18	Shabbona		SAES-University of Illinois	05/81
	IL19	Argonne		DOE-Argonne National Laboratory	03/80
	IL46	Alhambra		US Environmental Protection Agency-CAMD	01/99
	IL63	Dixon Springs Agricultural Center		SAES-University of Illinois	01/79
	IL78	Monmouth		US Geological Survey	01/85
<b>Indiana</b>					
	IN20	Roush Lake	MDN	US Geological Survey	08/83
	IN22	Southwest-Purdue Agricultural Center		US Geological Survey	09/84
	IN34	Indiana Dunes NL	MDN	National Park Service - Air Resources Div	07/80
	IN41	Agronomy Center for Research and Extension		SAES-Purdue University	07/82
<b>Iowa</b>					
	IA08	Big Springs Fish Hatchery		US Geological Survey	08/84
	IA23	McNay Memorial Research Center		US Geological Survey	09/84
<b>Kansas</b>					
	KS07	Farlington Fish Hatchery		US Geological Survey	03/84
	KS31	Konza Prairie		SAES-Kansas State University	08/82
	KS32	Lake Scott State Park		US Geological Survey	03/84
<b>Kentucky</b>					
	KY03	Mackville		US Geological Survey	11/83
	KY10	Mammoth Cave NP-Houchin Meadow	MDN	National Park Service - Air Resources Div	08/02
	KY22	Lilley Cornett Woods		NOAA-Air Resources Lab	09/83
	KY35	Clark State Fish Hatchery		US Geological Survey	08/83
	KY99	Mulberry Flats		TVA/Murray State University	12/94
<b>Louisiana</b>					
	LA12	Iberia Research Station		US Geological Survey	11/82
	LA30	Southeast Research Station		US Geological Survey	01/83
<b>Maine</b>					
	ME00	Caribou		NOAA-Air Resources Lab	04/80
	ME02	Bridgton	MDN	EPA/Maine Dept of Environmental Protection	09/80
	ME04	Carrabassett Valley		US Environmental Protection Agency-CAMD	03/02
	ME08	Gilead		US Geological Survey	09/99
	ME09	Greenville Station	MDN	SAES-University of Maine	11/79
	ME95	Wolapomomqot Ciw Wocuk		EPA/Passamaquoddy Tribe	06/02
	ME96	Casco Bay - Wolfe's Neck Farm	MDN	EPA/Maine Dept of Environmental Protection	01/98
	ME98	Acadia NP - McFarland Hill	MDN	National Park Service - Air Resources Div	11/81
<b>Maryland</b>					
	MD07	Catoctin Mountain Park		National Park Service - Air Resources Div	05/03
	MD13	Wye		SAES-University of Maryland	03/83
	MD18	Assateague Island NS - Woodcock		Maryland Department of Natural Resources	09/00
<b>Massachusetts</b>					
	MA01	North Atlantic Coastal Lab	MDN	National Park Service - Air Resources Div	12/81
	MA08	Quabbin Reservoir		N.E. States for Coord. Air Use Management	03/82
	MA13	East		N.E. States for Coord. Air Use Management	02/82

State	Site Code	Site Name	Collocation	Sponsoring Agency	Start Date
<b>Michigan</b>					
	MI09	Douglas Lake - University Michigan Biological Station		USDA/Michigan State University	07/79
	MI26	Kellogg Biological Station		USDA/Michigan State University	06/79
	MI29	Peshawbestown		US Environmental Protection Agency-CAMD	01/02
	MI48	Seney NWR - Headquarters		US Fish & Wildlife Serv - Air Quality Branch	11/00
	MI51	Unionville		US Environmental Protection Agency-CAMD	01/99
	MI52	Ann Arbor		US Environmental Protection Agency-CAMD	01/99
	MI53	Wellston		USDA Forest Service	10/78
	MI97	Isle Royale NP - Wallace Lake		National Park Service - Air Resources Div	05/85
	MI98	Raco		US Environmental Protection Agency-CAMD	05/84
	MI99	Chassell		National Park Service - Air Resources Div	02/83
<b>Minnesota</b>					
	MN01	Cedar Creek		Minnesota Pollution Control Agency	12/96
	MN05	Fond du Lac		EPA/Fond du Lac Reservation	11/96
	MN08	Hovland		Minnesota Pollution Control Agency	12/96
	MN16	Marcell Experimental Forest	MDN	USDA Forest Service	07/78
	MN18	Fernberg	MDN	US Environmental Protection Agency-CAMD	11/80
	MN23	Camp Ripley	MDN	US Geological Survey	10/83
	MN27	Lamberton	MDN	Minnesota Pollution Control Agency	01/79
	MN28	Grindstone Lake		Minnesota Pollution Control Agency	12/96
	MN32	Voyageurs NP - Sullivan Bay		National Park Service - Air Resources Div	05/00
	MN99	Wolf Ridge		Minnesota Pollution Control Agency	12/96
<b>Mississippi</b>					
	MS10	Clinton		US Geological Survey	07/84
	MS19	Newton		NOAA-Air Resources Lab	11/86
	MS30	Coffeeville		Tennessee Valley Authority	07/84
<b>Missouri</b>					
	MO03	Ashland Wildlife Area		US Geological Survey	10/81
	MO05	University Forest		US Geological Survey	10/81
	MO43	Tyson Research Center		Washington University	08/01
<b>Montana</b>					
	MT00	Little Bighorn Battlefield NM		US Geological Survey	07/84
	MT05	Glacier NP - Fire Weather Station		National Park Service - Air Resources Div	06/80
	MT07	Clancy		US Geological Survey	01/84
	MT96	Poplar River		EPA/Ft. Peck Tribes	12/99
	MT97	Lost Trail Pass		USDA Forest Service	09/90
	MT98	Havre - Northern Agricultural Research Center		US Geological Survey	07/85
<b>Nebraska</b>					
	NE15	Mead		SAES-University of Nebraska	07/78
	NE99	North Platte Agricultural Experiment Station		US Geological Survey	09/85
<b>Nevada</b>					
	NV03	Smith Valley		US Geological Survey	08/85
	NV05	Great Basin NP - Lehman Caves		National Park Service - Air Resources Div	01/85
<b>New Hampshire</b>					
	NH02	Hubbard Brook		USDA Forest Service	07/78
<b>New Jersey</b>					
	NJ00	Edwin B. Forsythe NWR		US Fish & Wildlife Serv - Air Quality Branch	10/98
	NJ99	Washington Crossing		US Environmental Protection Agency-CAMD	08/81
<b>New Mexico</b>					
	NM01	Gila Cliff Dwellings NM		EPA/New Mexico Environment Dept.	07/85
	NM07	Bandelier NM		DOE-Los Alamos National Lab	06/82
	NM08	Mayhill		US Geological Survey	01/84
	NM12	Capulin Volcano NM		EPA/New Mexico Environment Dept.	11/84
<b>New York</b>					
	NY08	Aurora Research Farm		USDA/Cornell University	04/79
	NY10	Chautauqua		US Geological Survey	06/80
	NY20	Huntington Wildlife	MDN	EPA/State Univ of New York-Syracuse	10/78
	NY22	Akwasasne Mohawk - Fort Covington		US Environmental Protection Agency-CAMD	08/99
	NY29	Moss Lake		U.S. Geological Survey	07/03
	NY52	Bennett Bridge		EPA/State Univ of New York-Oswego	06/80
	NY65	Jasper		US Geological Survey	02/80
	NY68	Biscuit Brook		US Geological Survey	10/83
	NY98	Whiteface Mountain		US Geological Survey	07/84
	NY99	West Point		US Geological Survey	09/83

State	Site Code	Site Name	Collocation	Sponsoring Agency	Start Date
<b>North Carolina</b>					
	NC03	Lewiston		North Carolina State University	10/78
	NC06	Beaufort		US Environmental Protection Agency-CAMD	01/99
	NC25	Coweeta		USDA Forest Service	07/78
	NC29	Hofmann Forest		North Carolina State University	07/02
	NC34	Piedmont Research Station		North Carolina State University	10/78
	NC35	Clinton Crops Research Station		North Carolina State University	10/78
	NC36	Jordan Creek		US Geological Survey	10/83
	NC41	Finley Farms		North Carolina State University	10/78
	NC45	Mount Mitchell		North Carolina State University	11/85
<b>North Dakota</b>					
	ND00	Theodore Roosevelt NP-Painted Canyon		National Park Service-Air Resources Div	01/01
	ND08	Icelandic State Park		US Geological Survey	10/83
	ND11	Woodworth		US Geological Survey	11/83
<b>Ohio</b>					
	OH09	Oxford		US Geological Survey	08/84
	OH15	Lykens		US Environmental Protection Agency-CAMD	01/99
	OH17	Delaware		USDA Forest Service	10/78
	OH49	Caldwell		US Geological Survey	09/78
	OH54	Deer Creek State Park		US Environmental Protection Agency-CAMD	01/99
	OH71	Wooster		US Geological Survey	09/78
<b>Oklahoma</b>					
	OK00	Salt Plains NWR		US Geological Survey	12/83
	OK08	Lake Eucha		EPA/Oklahoma Conservation Commission	02/00
	OK17	Great Plains Apiaries		NOAA-Air Resources Lab	03/83
	OK29	Goodwell Research Station		US Geological Survey	01/85
<b>Oregon</b>					
	*OR02	Alsea Guard Ranger Station		US Environmental Protection Agency-CAMD	12/79
	OR09	Silver Lake Ranger Station		US Geological Survey	08/83
	OR10	H J Andrews Experimental Forest	MDN	USDA Forest Service	05/80
	OR18	Starkey Experimental Forest		US Geological Survey	03/84
	OR97	Hyslop Farm		US Environmental Protection Agency-CAMD	04/83
	OR98	Bull Run		USGS/Portland Water Bureau, OR	07/82
<b>Pennsylvania</b>					
	PA00	Arendtsville	MDN	US Environmental Protection Agency-CAMD	01/99
	PA15	Penn State	AIRMoN	NOAA-Air Resources Lab	06/83
	PA18	Young Woman's Creek		US Geological Survey	04/99
	PA29	Kane Experimental Forest		USDA Forest Service	07/78
	PA42	Leading Ridge		SAES-Pennsylvania State University	04/79
	PA47	Millersville	MDN	PA Dept of Env. Protection/Penn State Univ.	11/02
	PA72	Milford	MDN	USDA Forest Service	12/83
<b>Puerto Rico</b>					
	PR20	El Verde		USDA Forest Service	02/85
<b>South Carolina</b>					
	SC05	Cape Romain NWR		US Fish & Wildlife Serv - Air Quality Branch	11/00
	SC06	Santee NWR		US Geological Survey	07/84
	SC07	Ace Basin NERR		NOAA/SC Department of Natural Resources	12/01
	SC11	North Inlet-Winyah Bay NERR		EPA/SC Dept. of Health and Env. Control	01/02
	SC99	Fort Johnson		EPA/SC Dept. of Health and Env. Control	03/02
<b>South Dakota</b>					
	SD04	Wind Cave National Park-Elk Mountain		National Park Service - Air Resources Div	11/02
	SD08	Cottonwood		NOAA-Air Resources Lab	10/83
	SD99	Huron Well Field		US Geological Survey	11/83
<b>Tennessee</b>					
	TN00	Walker Branch Watershed	AIRMoN	DOE/Oak Ridge Natl Lab/Lockheed-Martin	03/80
	TN04	Speedwell		US Environmental Protection Agency-CAMD	01/99
	TN11	Great Smoky Mountain NP - Elkmont	MDN	National Park Service - Air Resources Div	08/80
	TN14	Hatchie NWR		Tennessee Valley Authority	10/84

State	Site Code	Site Name	Collocation	Sponsoring Agency	Start Date
<b>Texas</b>					
	TX02	Muleshoe NWR		US Geological Survey	06/85
	TX03	Beeville		NOAA-Air Resources Lab	02/84
	TX04	Big Bend NP - K-Bar		National Park Service - Air Resources Div	04/80
	TX10	Attwater Prairie Chicken NWR		US Geological Survey	07/84
	TX16	Sonora		US Geological Survey	06/84
	TX21	Longview	MDN	Texas Commission on Environmental Quality	06/82
	TX22	Guadalupe Mountains NP-Frijole Ranger Stn		US Geological Survey	06/84
	TX39	Texas A & M Corpus Christi		EPA/Texas A&M University	01/02
	TX56	LBJ National Grasslands		US Geological Survey	09/83
<b>Utah</b>					
	UT01	Logan		US Geological Survey	12/83
	UT08	Murphy Ridge		BP Amoco	03/86
	UT09	Canyonlands NP - Island in the Sky		National Park Service - Air Resources Div	11/97
	UT98	Green River		US Geological Survey	04/85
	UT99	Bryce Canyon NP - Repeater Hill		National Park Service - Air Resources Div	01/85
<b>Vermont</b>					
	VT01	Bennington		US Geological Survey	04/81
	VT99	Underhill	AIRMoN	US Geological Survey	06/84
<b>Virgin Islands</b>					
	VI01	Virgin Islands NP - Lind Point		National Park Service - Air Resources Div	04/98
<b>Virginia</b>					
	VA00	Charlottesville		US Geological Survey	10/84
	VA10	Mason Neck Wildlife Refuge		VA Department of Environmental Quality	08/03
	VA13	Horton's Station		Tennessee Valley Authority	07/78
	VA24	Prince Edward		US Environmental Protection Agency-CAMD	01/99
	VA27	James Madison University Farm		US Environmental Protection Agency-CAMD	07/02
	VA28	Shenandoah NP - Big Meadows	MDN	National Park Service - Air Resources Div	05/81
	VA99	Natural Bridge Station		Virginia Department of Environmental Quality	07/02
<b>Washington</b>					
	WA14	Olympic NP - Hoh Ranger Station		National Park Service - Air Resources Div	05/80
	WA19	North Cascades NP-Marblemount Ranger Stn		US Geological Survey	02/84
	WA21	La Grande		US Environmental Protection Agency-CAMD	04/84
	WA24	Palouse Conservation Farm		US Geological Survey	08/85
	WA98	Columbia River Gorge		USDA Forest Service - Region 6	05/02
	WA99	Mount Rainier NP - Tahoma Woods		National Park Service - Air Resources Div	10/99
<b>West Virginia</b>					
	WV04	Babcock State Park		US Geological Survey	09/83
	WV05	Cedar Creek State Park		US Environmental Protection Agency-CAMD	01/99
	WV18	Parsons		USDA Forest Service	07/78
<b>Wisconsin</b>					
	WI09	Popple River	MDN	Wisconsin Department of Natural Resources	12/86
	WI25	Suring		Wisconsin Department of Natural Resources	01/85
	WI28	Lake Dubay		Wisconsin Department of Natural Resources	06/82
	WI32	Middle Village	MDN	EPA/Menominee Indian Tribe	01/02
	WI35	Perkinstown		US Environmental Protection Agency-CAMD	01/99
	WI36	Trout Lake	MDN	Wisconsin Department of Natural Resources	01/80
	WI37	Spooner		Wisconsin Department of Natural Resources	06/80
	WI97	Lac Courte Oreilles Reservation		EPA/Lac Courte Oreilles Conservation Dept	11/01
	*WI98	Wildcat Mountain		Wisconsin Department of Natural Resources	08/89
	WI99	Lake Geneva	MDN	Wisconsin Department of Natural Resources	06/84
<b>Wyoming</b>					
	WY00	Snowy Range - West Glacier Lake		USDA Forest Service	04/86
	WY02	Sinks Canyon		Bureau of Land Management	08/84
	WY06	Pinedale		Bureau of Land Management	01/82
	WY08	Yellowstone NP - Tower Falls		National Park Service - Air Resources Div.	06/80
	WY95	Brooklyn Lake		USDA Forest Service	09/92
	WY97	South Pass City		SF Phosphates Ltd/Bridger Teton NF	04/85
	WY98	Gypsum Creek		Exxon Mobil Corporation/Bridget-Teton NF	12/84
	WY99	Newcastle		Bureau of Land Management	08/81
<b>Canada</b>					
	CAN5	Frelighsburg		US Geological Survey	10/01

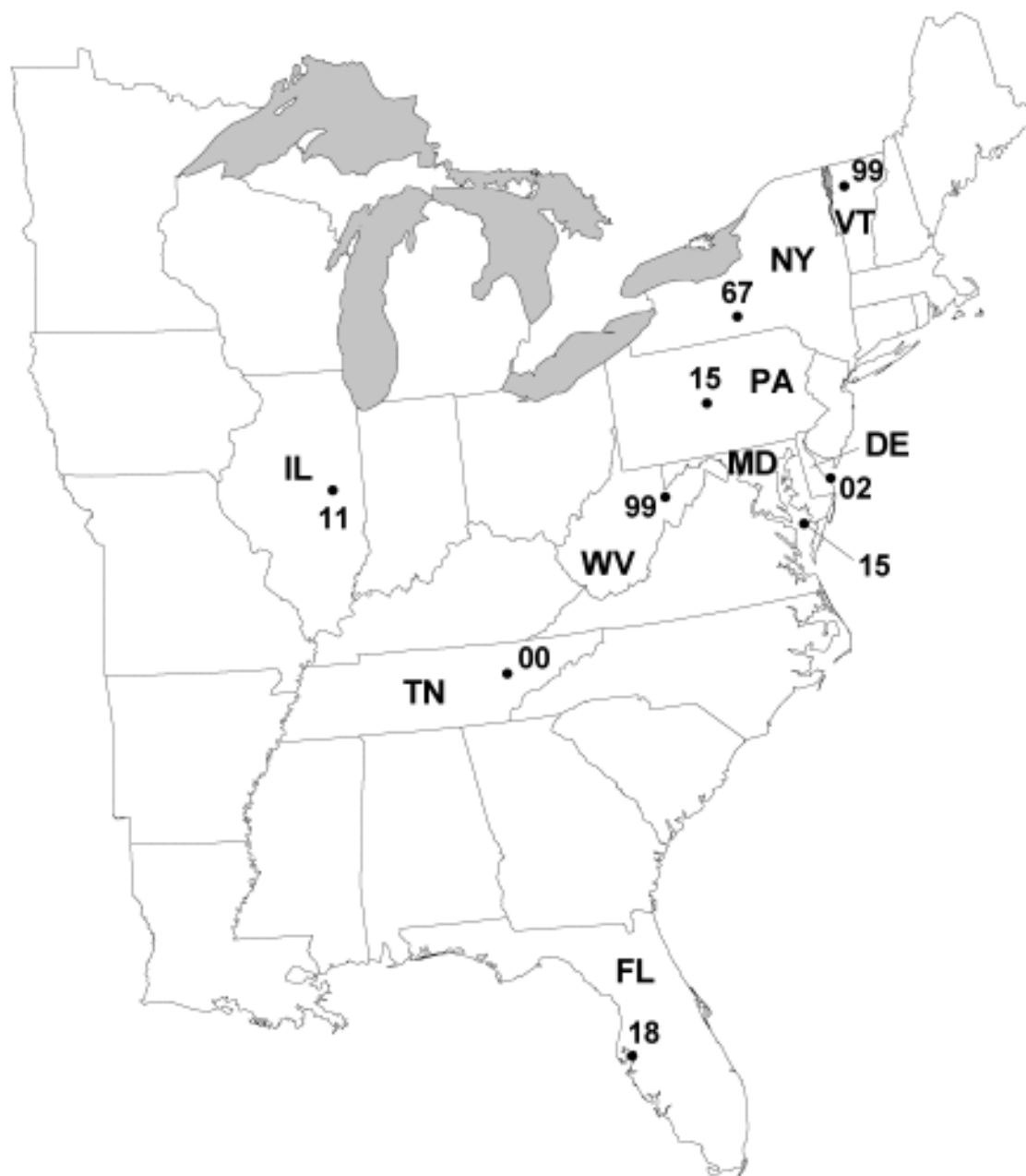
\* At these sites the USGS sponsors a second collector for the purpose of measuring network precision.

**AIRMoN MAP AND SITE LISTINGS**





# National Atmospheric Deposition Program Atmospheric Integrated Research Monitoring Network



**NADP/Atmospheric Integrated Research Monitoring Network Sites**  
**August 31, 2003**

State Site Code	Site Name	Collocation	Sponsoring Agency	Start Date
<b>Delaware</b>				
DE02	Lewes		NOAA-Air Resources Laboratory	09/92
<b>Florida</b>				
FL18	Tampa Bay		FL Department of Env. Protection	08/96
<b>Illinois</b>				
IL11	Bondville	MDN & NTN	NOAA-Air Resources Laboratory	10/92
<b>Maryland</b>				
MD15	Smith Island		NOAA-Air Resources Laboratory	11/95
<b>New York</b>				
NY67	Cornell University		NOAA-Air Resources Laboratory	09/92
<b>Pennsylvania</b>				
PA15	Penn State	NTN	NOAA-Air Resources Laboratory	10/92
<b>Tennessee</b>				
TN00	Oak Ridge National Lab	NTN	NOAA-Air Resources Laboratory	09/92
<b>Vermont</b>				
VT99	Underhill	NTN	NOAA-Air Resources Laboratory	01/93
<b>West Virginia</b>				
WV99	Canaan Valley Institute		NOAA-Air Resources Laboratory	06/00

## **MDN MAP AND SITE LISTINGS**



# National Atmospheric Deposition Program Mercury Deposition Network



**National Atmospheric Deposition Program/Mercury Deposition Network Sites  
August 31, 2003**

State/Providence Site Code	Site Name	Collocation	Sponsoring Agency	Start Date
<b>Alabama</b>				
AL02	Delta Elementary	NTN	Mobile Bay Nat'l Estuary Prog.-Dauphin Island Sea Lab	
06/01				
AL03	Centreville		Southern Company/Atmospheric Research and Analysis, Inc.	06/00
AL24	Bay Road	NTN	Mobile Bay National Estuary Program-Dauphin Island Sea Lab	05/01
<b>California</b>				
CA72	San Jose		San Francisco Estuary Institute	01/00
CA75	Sequoia NP-Giant Forest	NTN	National Park Service - Air Resources Division	07/03
<b>Colorado</b>				
CO97	Buffalo Pass - Summit Lake	NTN	USDA Forest Service-Rocky Mountain Research Station	09/98
CO99	Mesa Verde NP-Chapin Mesa	NTN	National Park Service - Air Resources Division	12/01
<b>Florida</b>				
FL04	Andytown		S FL Water Mgt Dist & FL Dept of Environmental Protection	01/98
FL05	Chassahowitzka NWR	NTN	US Fish and Wildlife Service - Air Quality Branch	07/97
FL11	Everglades NP - Research Center	NTN	S FL Water Mgt Dist & FL Dept of Environmental Protection	*12/95
**FL34	ENRP		S FL Water Mgt Dist & FL Dept of Environmental Protection	07/97
<b>Georgia</b>				
GA09	Okefenokee NWR	NTN	US Fish and Wildlife Service - Air Quality Branch	07/97
GA22	Atlanta - Jefferson Street		Southern Company/Atmospheric Research and Analysis, Inc.	06/02
GA40	Yorkville		Southern Company/Atmospheric Research and Analysis, Inc.	06/00
<b>Illinois</b>				
IL11	Bondville	AIRMoN/NTN	Illinois State Water Survey	*12/95
<b>Indiana</b>				
IN20	Roush Lake	NTN	Indiana Department of Environmental Management/USGS	10/00
IN21	Clifty Falls State Park		Indiana Department of Environmental Management/USGS	01/01
IN26	Indianapolis		Indiana Department of Environmental Management/USGS	04/03
IN28	Bloomington		Indiana Department of Environmental Management/USGS	12/00
IN34	Indiana Dunes NL	NTN	Indiana Department of Environmental Management/USGS	10/00
<b>Kentucky</b>				
KY10	Mammoth Cave NP-Houchin Meadow	NTN	National Park Service - Air Resources Division	08/02
<b>Louisiana</b>				
LA05	Lake Charles		Louisiana Department of Environmental Quality	10/98
LA10	Chase		Louisiana Department of Environmental Quality	10/98
LA23	Alexandria		Louisiana Department of Environmental Quality	02/01
LA28	Hammond		Louisiana Department of Environmental Quality	10/98
<b>Maine</b>				
ME02	Bridgton	NTN	EPA/Maine Department of Environmental Protection	06/97
ME09	Greenville Station	NTN	EPA/Maine Department of Environmental Protection	09/96
ME96	Casco Bay - Wolfe's Neck Farm	NTN	EPA/Maine Department of Environmental Protection	01/98
ME98	Acadia NP - McFarland Hill	NTN	NPS-Acadia NP & EPA/ME Dept of Environmental Protection	*01/96
<b>Massachusetts</b>				
MA01	North Atlantic Coastal Lab	NTN	NPS-Cape Cod National Seashore	08/03
<b>Minnesota</b>				
MN16	Marcell Experimental Forest	NTN	USDA Forest Service-North Central Res. Station & MNPCA	*12/95
MN18	Fernberg	NTN	USDA-FS - Superior NF & MN Pollution Control Agency	*01/96
MN22	Mille Lacs Band of Ojibwe		EPA/Mille Lacs Band of Ojibwe	04/02
MN23	Camp Ripley	NTN	Minnesota Pollution Control Agency	07/96
MN27	Lamberton	NTN	Minnesota Pollution Control Agency	07/96
<b>Mississippi</b>				
MS22	Oak Grove		Southern Company/Atmospheric Research and Analysis, Inc.	06/00
<b>Missouri</b>				
MO46	Mingo NWR		Missouri Department of Natural Resources	03/02
<b>Nevada</b>				
NV02	Lesperance Ranch		EPA/University of Nevada	02/03
NV99	Gibb's Ranch		EPA/University of Nevada	02/03
<b>New Hampshire</b>				
NH00	Laconia		New Hampshire Department of Environmental Services	04/98
<b>New Mexico</b>				
NM10	Caballo		USGS/New Mexico State University	05/97

State/Providence	Site Code	Site Name	Collocation	Sponsoring Agency	Start Date
<b>New York</b>					
	NY20	Huntington Wildlife	NTN	EPA/State University of New York - Syracuse	12/99
<b>North Carolina</b>					
	NC08	Waccamaw State Park		North Carolina Dept of Environment & Natural Resources	*12/95
	NC42	Pettigrew State Park		North Carolina Dept of Environment & Natural Resources	*12/95
<b>Oklahoma</b>					
	OK99	Stilwell		EPA/Cherokee Nation	04/03
<b>Oregon</b>					
	OR01	Beaverton		U.S. Geological Survey	04/03
	OR10	H. J. Andrews Experimental Forest	NTN	U.S. Geological Survey	12/02
<b>Pennsylvania</b>					
	PA00	Arendtsville	NTN	PA Dept of Environmental Protection/Penn State University	11/00
	PA13	Allegheny Portage Railroad NHS		PA Dept of Environmental Protection/Penn State University	01/97
	PA30	Erie		PA Dept of Environmental Protection/Penn State University	06/00
	PA37	Holbrook		Electric Power Research Institute	05/99
	PA47	Millersville	NTN	PA Dept of Environmental Protection/Penn State University	11/02
	PA60	Valley Forge		PA Dept of Environmental Protection/Penn State University	11/99
	PA72	Milford	NTN	PA Dept of Environmental Protection/Penn State University	09/00
	PA90	Hills Creek State Park		PA Dept of Environmental Protection/Penn State University	01/97
<b>South Carolina</b>					
	SC19	Congaree Swamp State Park		South Carolina Dept of Health & Environmental Control	*12/95
<b>Tennessee</b>					
	TN11	Great Smoky Mountains NP-Elkmont	NTN	National Park Service - Air Resources Division	01/02
<b>Texas</b>					
	TX21	Longview	NTN	Texas Commission on Environmental Quality	*12/95
	TX50	Fort Worth		EPA/City of Fort Worth	08/01
<b>Virginia</b>					
	VA08	Culpeper		U.S. Geological Survey	11/02
	VA28	Shenandoah NP-Big Meadows	NTN	National Park Service - Air Resources Division	10/02
<b>Washington</b>					
	WA18	Seattle - NOAA		Frontier Geosciences, Inc	03/96
<b>Wisconsin</b>					
	WI08	Brule River		Wisconsin Department of Natural Resources	*12/95
	WI09	Popple River	NTN	Wisconsin Department of Natural Resources	12/95
	WI22	Milwaukee		U.S. Geological Survey	10/02
	WI31	Devil's Lake		Wisconsin Department of Natural Resources	01/01
	WI32	Middle Village	NTN	EPA/Menominee Indian Tribe	01/02
	WI36	Trout Lake	NTN	Wisconsin Department of Natural Resources	*12/95
	WI99	Lake Geneva	NTN	Wisconsin Department of Natural Resources	01/97
<b>Wyoming</b>					
	WY07	Yellowstone NP - Yellowstone Lake		National Park Service - Air Resources Division	02/02
<b>CANADA</b>					
<b>British Columbia</b>					
	BC06	Reifel Island		Environment Canada - Pacific and Yukon Region	03/00
<b>New Brunswick</b>					
	NB02	St. Andrews		Environment Canada - Atmospheric Environment Branch	07/96
<b>Newfoundland</b>					
	NF09	Cormak		Environment Canada - Atmospheric Environment Branch	05/00
<b>Nova Scotia</b>					
	NS01	Kejimikujik NP		Environment Canada - Atmospheric Environment Branch	07/96
<b>Ontario</b>					
	ON07	Egbert		Environment Canada	03/00
<b>Quebec</b>					
	PQ04	Saint Anicet		Environment Canada-Public Works and Government Service	04/98
	PQ05	Mingan		Environment Canada-Public Works and Government Service	04/98
<b>Saskatchewan</b>					
	SK12	Bratt's Lake BSRN		Environment Canada - Prairie and Northern Region	08/01

\*These dates mark the official start of NADP/MDN operations. Data for a transition network operating in 1995 are available from the NADP web site at <http://nadp.sws.uiuc.edu>.

\*\*At this site the NADP Program Office sponsors a second collector for the purpose of measuring network precision.





## PROCEEDINGS NOTES



















