

NADP TECHNICAL COMMITTEE MEETING ABSTRACTS OF PAPERS

Celebrating Twenty Years of Network Operations

St. Petersburg, Florida
October 26-29, 1998

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A Cooperative Research Support Program of the
State Agricultural Experiment Stations (NRSP-3)
Federal and State Agencies
and Private Research Organizations



Every year the National Atmospheric Deposition Program (NADP) fulfills thousands of requests for data, maps, and other summaries over its World Wide Web site. Researchers, policy makers, students, and other people interested in environmental data are using NADP data to address important questions about the impact of the wet deposition of nutrients on eutrophication in coastal estuarine environments, the relationship between wet deposition to unmanaged forests and the depletion of base cations from forest soils, the impact of pollutant emissions changes on precipitation chemistry, and the rate at which precipitation delivers mercury to remote lakes and streams.

NADP was organized in 1977 under the leadership of the State Agricultural Experiment Stations (SAES) to address the problem of atmospheric deposition and its effects on agricultural crops, forests, rangelands, surface waters, and other natural and cultural resources. In 1978, sites in the NADP precipitation chemistry network first began operations, collecting one-week, wet-only deposition samples analyzed by the Central Analytical Laboratory (CAL) at the Illinois State Water Survey. The network was established to provide data on the amounts, temporal trends, and geographic distributions of the atmospheric deposition of acidic chemicals, nutrients, and base cations. Initially organized as SAES North Central Regional Project NC-141, all four SAES regions endorsed the NADP as Interregional Project IR-7 in 1982. A decade later, the SAES reclassified IR-7 as National Research Support Project NRSP-3, which it remains.

In October 1981, the federally supported National Acid Precipitation Assessment Program (NAPAP) was established to increase understanding of the causes and effects of acidic precipitation. This program sought to establish a long-term precipitation chemistry network of sampling sites distant from point source influences. Because of its experience in organizing and operating a national-scale network, NADP agreed to coordinate operation of NAPAP's National Trends Network (NTN). Having common siting criteria, identical operating procedures, and sharing a common analytical laboratory, NADP and NTN merged with the designation NADP/NTN. Many sampling sites are supported by the U.S. Geological Survey (USGS), NAPAP's lead federal agency for deposition monitoring. Under the Clean Air Research Title (IX) of the federal Clean Air Amendments of 1990, NAPAP continues. Today there are nearly 200 sites in the NADP/NTN precipitation chemistry network.

In the 1990s, NADP expanded to include two additional networks. A research network, the Atmospheric Integrated Research Monitoring Network (AIRMoN), currently with ten sites, joined NADP in October 1992. AIRMoN sites collect samples daily when precipitation occurs. Samples are refrigerated until analysis at the CAL for the same constituents measured in NTN samples. AIRMoN seeks to identify pollutant source/receptor relationships and the effect of emissions changes on precipitation chemistry, combining measurements with atmospheric models. AIRMoN also evaluates new sample collection and preservation methods. Another NADP network, the Mercury Deposition Network (MDN), currently has nearly 40 sites and joined NADP in 1996. MDN sites collect one-week, wet-only deposition samples, which are sent to a lab that specializes in mercury measurements. Frontier Geosciences, Inc., analyzes all samples for total mercury and some for methyl mercury. MDN collects data on the wet deposition of mercury to surface waters, forested watersheds, and other receptors. Nearly 40 states have advisories against consuming fish from certain lakes because of high mercury concentrations in the tissues of fish from these lakes. MDN data enable researchers to investigate the importance of the atmospheric transport and deposition of mercury from distant sources as a cause of this problem.

A number of federal agencies support NADP including: U.S. Geological Survey (USGS), Cooperative State Research, Education, and Extension Service (CSREES), National Oceanic and Atmospheric Administration (NOAA), Environmental Protection Agency (EPA), National Park Service (NPS), U.S. Forest Service (USFS), Bureau of Land Management (BLM), U.S. Fish & Wildlife Service (USFWS), and Tennessee Valley Authority (TVA). Additional support is provided by various other federal agencies, State Agricultural Experiment Stations, state agencies, universities, and public and private research organizations.

For further information, contact:

**NADP Program Office
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820**

**NADP Home Page:
e-mail:**

**<http://nadp.sws.uiuc.edu>
nadp@sws.uiuc.edu**

NADP TECHNICAL COMMITTEE MEETING

ABSTRACTS OF PAPERS

Celebrating 20 years of Network Operations

St. Petersburg, Florida
October 26-29, 1998

Technical Program Chair
Dennis Lamb, Ph.D.
Penn State University
University Park, PA 16802

Prepared by

NADP Program Office
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820

October 1998

Table of Contents

Oral Presentations

Technical Session 1: Historical and Global Perspectives;

Session Chair: James Lynch

NAPAP, A National Perspective Mike Uhart, NAPAP.....	9
Progress in the Acid Rain Program and Future Integrated Air Pollution Issues Rona Birnbaum, US EPA	10
EMEP-Experience and Results of Measurements Rick Artz, NOAA.....	11
Sulfur and Nitrogen Atmospheric Budgets in the Former Soviet Union Dr. Alexey Ryaboshapko, Institute of Global Climate and Ecology.....	12
Changes in the Composition of Air and Precipitation in Canada from the Early 1980s to the Mid-1990s R.J. Vet, C.-U.Ro, A. Sirois and D. MacTavish.....	13
Acid Deposition Monitoring Activities in Japan and East Asia Hiroshi Hara, National Institute of Public Health.....	14
Nitrogen Deposition onto the United States and Western Europe: A Synthesis of Observations and Models Elisabeth Holland, NCAR; Bobby Braswell, University of New Hampshire; James Sulzman, NCAR; Jean-Francois Lamargue, NCAR.....	15
The Long-Term Changes in Precipitation and Stream Chemistry at the Hubbard Brook Experiment Forest, NH: Measurements and Model Calculations Charles T. Driscoll and Solomon Gbondo-Tugbawa, Syracuse University; John Aber, University of New Hampshire, Gene E. Likens and Donald Buso, Institute of Ecosystem Studies.....	16

Technical Session 2: Deposition and Its Effects; *Session Chair: Robert Vet*

Dry Deposition in NADP - Some Old Decisions Revisited Bruce B. Hicks, NOAA, Air Resources Laboratory.....	18
The Long, Dry Road to Total Deposition: Discovering EPA's Clean Air Status and Trends Network Gary Lear, US EPA, Acid Rain Division; Neil Frank, US EPA, Emissions, Monitoring and Analysis Division.....	19
Forest Ecoregion Sections at Relative Risk Based on Spatial Ion Deposition Patterns Interpolated across the Period 1979-1995 Kenneth W. Stolte and William D. Smith, USDA Forest Service, Casson Stallings and Luther Smith, ManTech Environmental Corporation.....	20

Assessment of Calcium Depletion in Forest Ecosystems of Southeastern USA Using a Small Watershed Approach T. G. Huntington and R. P. Hooper, USGS; C.E. Johnson, Syracuse University; B.T. Aulenbach, USGS; R. Cappellato, Emory University; A.E. Blum, USGS.....	21
Changes in Atmospheric Deposition in Eastern USA Following Enactment of Title IV of Clean Air Act Amendments of 1990 J. A. Lynch, Pennsylvania State University, V.C. Bowersox, Illinois State Water Survey, J. W. Grimm, Pennsylvania State University.....	22
Response of Streamwater Chemistry to Changes in Atmospheric Deposition at Five Headwater Basins in the Northeastern United States David W. Clow, USGS.....	23
Projected Responses of Watersheds in Southern Appalachia to Changes in Deposition of Sulfur, Nitrogen, and Base Cations P.F. Brewer, Southern Appalachian Mountains Initiative; K. Tonnessen, NPS, Air Resources Division; B.J. Cosby, University of Virginia; R.K. Munson, Tetrtech, Inc; T.J. Sullivan, E&S Environmental Chemistry, Inc.....	24

Technical Session 3: Nutrient Deposition and Hypoxia; *Session Chair: Richard Artz*

A Broad Perspective of Gulf Hypoxia Derek Winstanley, Chief, Illinois State Water Survey.....	26
Atmospheric Deposition of Nitrogen in the Mississippi River Basin G.B. Lawrence, USGS; D.A. Goolsby, USGS; W.A. Battaglin, USGS; G.J. Stensland, Illinois State Water Survey.....	27
Contributions of Atmospheric Deposition to Nitrogen Loadings in Tampa Bay: Implications for Water Quality and Living Resources Holly Greening, Tampa Bay Estuary Program.....	28
Atmospheric Deposition Contributions to Nitrogen and Phosphorus Loadings in Tampa Bay: Intensive Wet and Dry Deposition Data Collection and Analysis Ray Pribble, PBS&J.....	29
Influences of the Riparian N-fixing Shrub, <i>Alnus Incana</i> Ssp, <i>Rugosa</i> , and Atmospheric Deposition on N Concentration in Surface Waters in the Adirondack Mountains T.M. Hurd and D.J. Raynal, SUNY, Syracuse.....	30
Climate Influences on Bio-availability of Wet-deposited N in Soils: An Expansion of the NADP/NTN Database R.H. Grant and K. Scheeringa, Purdue University.....	31
Atmospheric Transport and Wet Deposition of Ammonium in North Carolina John T. Walker and Viney P. Aneja, North Carolina State University.....	32
Atmospheric Deposition of Nitrogen in a High Lightning Intensity Area C. Li, A.K. Alva, D. B. Calvert and D.J. Banks, University of Florida.....	33

Technical Session 4: Trace Metals and Toxics; *Session Chair: Mary Ann Allan*

Yearly Trends in Methyl Mercury Deposition at Selected MDN Sites in North America and Mercury Dry Deposition Methods Comparison
Eric M. Prestbo and Robert C. Brunette, Frontier Geosciences, Inc;
Colleen Caldwell, New Mexico State University.....35

Mercury Wet and Dry Deposition to the Chesapeake Bay
R.P. Mason, N.M. Lawson, G-R. Sheu, J-M Laporte, and S. Andres,
University of Maryland.....36

Air/surface Exchange of Mercury over Vegetation: A Reassessment of Global Biogenic Mercury Emissions
S.E. Lindberg and P.J. Hanson, Oak Ridge National Laboratory;
T.P. Meyers, NOAA/ERL.....37

Wet Deposition of Trace Metal(loid)s at Background Sites Along an East-west Transect Across The Northern United States
Dirk Wallschlager & Nicolas S. Bloom, Frontier Geosciences.....38

Mercury Deposition and Ambient Concentrations in New England: Results and Plans for the Four-site Mic-b Network
Lee Alter, Northeast States for Coordinate Air Use Management;
Dr. Gerald Keeler, University of Michigan.....39

Air Toxics in the Great Lakes Area: Regional Source Locations
Donald F. Gatz and Clyde W. Sweet, Illinois State Water Survey.....40

Technical Session 5: Technology and Methods; *Session Chair: Scotty R. Dossett*

Comparison of Chemical Loading to the Colorado Rocky Mountain Snowpack with Annual Wet Deposition Data Collected by the NADP
K. Heuer and K.Tonnessen, NPS; G. Ingersoll, USGS-WRD.....42

Monitoring Atmospheric Deposition in Seasonal Snowpacks in the Rocky Mountain Region
George Ingersoll, John T. Turk, A. Alisa Mast, Dave W. Clow and
Donald H. Campbell, USGS-WRD.....43

An Analysis of the Temporal Variation in AIRMoN Precipitation Chemistry Measurements Using Hysplit Lagrangian Trajectories
Barbara J.B. Stunder, NOAA Air Resources Laboratory.....44

The Sensitivity of Sulfur Wet Deposition to Atmospheric Oxidants
Ariel F. Stein and Dennis Lamb, Pennsylvania State University.....45

The Use of NADP Data to Ground-Truth Deposition Modeling
John Sherwell, Maryland Department of Natural Resources; Mark Garrison
and Peter Mayes, Environmental Resources Management.....46

New Jersey Atmospheric Deposition Network
Stuart Nagourney, New Jersey Department of Environmental Protection;
Steven J. Eisenreich, Rutgers University.....47

Expanding in New Directions: Wet Deposition Monitoring in Indian Country
Stephanie Bendovic, USEPA, Acid Rain Division.....48

A Comparison of NADP and CASTNet Wet Precipitation Chemistry Data
Luther Smith, ManTech Environmental Corporation.....49

Poster Presentations

Procedures for Stabilizing NH_4 and PO_4 Concentrations in Rainwater Samples Sue Bachman and Tom Bergerhouse, Illinois State Water Survey.....	51
Mercury Deposition Network: Laboratory and Field Quality Assurance Measurements Robert Brunette, Paul E. Laskowski and Eric M. Prestbo, Frontier Geosciences.....	52
Worldwide Precipitation Chemistry Collection: Current Status and Future Direction Tim Coleman, SUNY Albany.....	53
Thymol Preservation in Daily Precipitation Samples or More Mols with Thymol Brigita Demir, Jane Rother, Lori Henry and Van C. Bowersox, Illinois State Water Survey.....	54
Chassahowitzka National Wildlife Refuge - Status and Trends L. Kellie Dixon and E.D. Esteves, Mote Marine Laboratory.....	55
Comparison of Chemical Loading to the Colorado Rocky Mountain Snowpack with Annual Wet Deposition Data Collected by the NADP Kristi Heuer, Kathy Tonnessen, NPS; George Ingersoll USGS-WRD.....	56
Current Status of the Testing and Evaluation of Alternative Rain Gages for the National Atmospheric Deposition Program Laura Hult, Oak Ridge Associated Universities; John Gordon, USGS-WRD....	57
The Changing Precipitation Chemistry Picture and Hypoxia in the Gulf of Mexico-Contemporary Applications of NADP data Robert Larson, Roger Claybrooke, Gary Stensland and Van Bowersox, Illinois State Water Survey.....	58
A Comparison of Elevationally Different, Paired NADP Sites on the Front Range, Colorado Mark Losleben, University of Colorado; Nick Pepinn, University of Durham, UK; Bret Peterson, Meghan and Thomas Davinroy, University of Colorado.....	59
Projected Impacts of Acid Deposition Following Phase I of the 1990 Clean Air Act Amendments Paul Miller, Maryland Department of Natural Resources; Mark T. Southerland, Nancy E. Roth and Emily C. Rzemien, Versar, Inc; James A. Lynch, Pennsylvania State University.....	60
Major Ion and Trace Element Budgets for a Forested Watershed in Western Maryland John Sherwell, Maryland Department of Natural Resources; Mark Castro, University of Maryland Center of Environmental Science.....	61
Prediction of Ambient $PM_{2.5}$ Concentrations in Maryland John Sherwell, Maryland Department of Natural Resources; Kenneth Walsh and Richard Gardner, Science Applications International Corporation.....	62
Some Historical Aspects of the National Atmospheric Deposition Program Gary Stensland and Sarah C. Milton, Illinois State Water Survey.....	63

Wet Deposition of Total Mercury at Mercury Deposition Network (MDN) Sites in 1996 and 1997 Clyde Sweet, Illinois State Water Survey; Eric Prestbo and Robert Brunette, Frontier Geosciences, Inc.....	64
Comparison of Ionic Concentrations in Rain at Three Georgia Locations over Thirteen Years Jerry Walker and John Melin, University of Georgia.....	65
Annual Sulfur and Nitrogen, Wet and Dry Deposition in Snowy Range Wyoming Karl Zeller, USDA Forest Service.....	66

I. ORAL PRESENTATIONS

Technical Session 1

Historical and Global Perspectives

Session Chair: James Lynch

NAPAP, A NATIONAL PERSPECTIVE

Mike Uhart
1315 East-West Highway, 11419SSMC3
Silver Springs, Maryland 20910-3282

No abstract available at time of printing

Progress in The Acid Rain Program And Future Integrated Air Pollution Issues

Rona Birnbaum
Acid Rain Division, US EPA (6204J)
401 M St. S.W., Washington, DC 20460
birnbaum.rona@epa.gov

In 1995, the first phase of the Acid Rain Program was implemented. In that year alone, sulfur dioxide (SO₂) emissions from the largest, highest emitting electric power plants were reduced by 3 million tons. The total SO₂ emissions reduction under Phase I of the Acid Rain Program has been approximately 4 million tons from 1990 levels. In 1997, Phase I units emitted at approximately 23 percent below their 1997 “SO₂ allowance allocations”. Additionally, the flexibility in compliance options provided by the Acid Rain Program enabled affected units to pursue a variety of ways to meet their SO₂ reduction obligations, including scrubber installations, fuel switching, energy efficiency, and allowance trading. The Program’s flexibility significantly reduced the cost of achieving these emissions reductions as compared to early estimated costs of compliance with the program or compared with the cost of a technological mandate. Beginning in the year 2000 when Phase II begins, Phase I units will be reduced further and requirements will be extended to a greater number of smaller, cleaner power plants. In 2010, the number of SO₂ allowances will be capped at 8.95 million, a level approximating one half of industry-wide emissions in 1980.

Control of nitrogen oxides (NO_x) under the Acid Rain Program began in 1996. The Acid Rain NO_x control program establishes emissions limitations for affected units. For Phase I units, the average NO_x emission rate declined by 42 percent (from 0.69 lb/mmBtu to 0.40 lb/mmBtu). These same units exhibited about a 35 percent reduction in NO_x tons (approximately 409,000 tons between 1990 and 1997). However, NO_x mass emissions in 1997 increased slightly from 1996, attributable to greater electrical production. Without further reductions in emission rates, NO_x emissions would be expected to rise with increased utilization. In 2000, NO_x from electric utility boilers will be further reduced by over 2 million tons per year.

The EPA is also pursuing an aggressive strategy to reduce ozone transport under what is known as the “110 SIP Call”. This is a call under section 110 of the Clean Air Act to 22 states and the District of Columbia to develop state implementation plans to meet stringent summertime NO_x budgets for their jurisdiction. The regional NO_x reductions under the SIP Call combined with local ozone reduction strategies will significantly reduce ozone in the Midwest and eastern U.S. These NO_x reductions combined with those under the Acid Rain Program are also expected to incur benefits on a number of nitrogen related environmental concerns.

Nitrogen oxides and other components of atmospheric nitrogen contribute to multiple health and environmental effects including human health risks from particles and ozone formation and environmental impacts including surface water acidification, nutrient enrichment of coastal waters and large river basins, watershed nitrogen saturation, forest soil nutrient depletion and forest effects, impacts on biodiversity, and regional haze. Efforts are underway to better coordinate research, monitoring and assessment activities and develop integrated approaches to achieving reductions in nitrogen.

EMEP - EXPERIENCE AND RESULTS OF MEASUREMENTS

Jan Schaug, Arne Semb, Anne-Gunn Hjellbrekke, Sverre Solberg
Chemical Co-ordinating Centre of EMEP
Norwegian Institute for Air Research, P.O.Box 100, N-2007 Kjeller, Norway

EMEP, the European Monitoring and Evaluation Programme was started in January 1978 and has today more than 20 years of measurement results, emission data, and model calculations in its data bases. While the programme initially focused on emissions, transboundary fluxes, and deposition of acidifying substances in Europe only, other air pollution problems have been included over the years. Photochemically active substances have been a part of the measurement programme from the second half of the eighties, and during the past 3 -4 years trace metal and POP data from the participating countries have been collected and reported, although these components are not yet part of the measurement programme. The measurement programme has been extended several times over the years to meet the new requirements. Most of the measurements are based on daily sampling.

The programme is organised with three Centres; the Chemical Co-ordinating Centre (CCC) is responsible for recommendation of methods for sampling and chemical analysis, for quality assurance, and for the measurement data base, the Meteorological Synthesising Centre - West (MSC-W) is responsible for the modelling of acidifying and photochemically active substances, and for the emission data base, and the Meteorological Synthesising Centre - East (MSC-E) is responsible for the modelling of trace metals and POP.

In the 1995 Protocol on the reductions of sulphur emissions European countries bound themselves to reach a 30 per cent reduction in their emissions by 1993 using 1980 as a basis year. As a result of this, the total European sulphur dioxide emission was reduced 48 per cent in 1995 compared to the 1980 level, and this reduction is reflected in the measured concentration in precipitation and air, typical median annual reductions of sulphates concentrations in precipitation and air in the period being 3 -5 per cent. Similar reductions are not seen for nitrogen components.

The sulphur components in air have maxima in winter/ early spring while the precipitation components peak early in the summer. The wet deposition most often peak during the summer months. In central and southern part of the Continent ozone concentrations peak around midsummer and during the spring in the northernmost part of Europe. Measurements of light hydrocarbons and aldehydes/ketones have been operational since 1992. Hydrocarbons of anthropogenic origin peak in midwinter while the oxidised compounds have their maximum concentrations during the summer.

Concentration fields for various components are being estimated by the MSCs with their acid deposition, photooxidant, and trace metal models. Statistical modelling based on measurements is likewise carried out at the CCC. Recently the two model types, i.e. Lagrangian and kriging models, were combined into one hybrid approach for sulphur and nitrogen compounds in air and precipitation. The results gave more reliable concentration fields than each model could give separately and emphasised the need for more measurements sites.

SULFUR AND NITROGEN ATMOSPHERIC BUDGETS IN THE FORMER SOVIET UNION

Dr. Alexey Ryaboshapko
Institute of Global Climate and Ecology
Glebovskaja str., 20-B, Moscow 107258 Russia
+7 +095 / 160 58 67
ryaboshapko@ra.igce.msk.ru

The Soviet industry made a significant contribution to the world-wide atmospheric emissions of sulfur and nitrogen. It is impossible to carry out any global or hemispheric assessment of the atmosphere pollution without any regard for the situation in the former Soviet Union (FSU).

Anthropogenic emissions for 1985 and 1990 were calculated using a combination of "bottom-up" and "top-down" approaches. Overall anthropogenic emissions in 1990 (11.3 +/- 1.92 Mt S-SO₂ and 4.1 +/- 0.9 Mt N-NO_x) were spatially distributed with a 1x1 degree resolution. Long-term historic trends in anthropogenic emissions (110 years for S and 20 years for N) were estimated. Emissions from natural sources were 9.7 Mt S/yr, 1.1 Mt N(NO_x)/yr.

Monitoring data obtained since the mid-1950s were generalized and quality of the data was checked. Multi year and seasonal variations of pollutant concentrations in different parts of the FSU were established. Wet deposition in the 1980s was 14.7 Mt S/yr, 2.5 Mt N(NO_y)/yr. Estimated dry deposition values were 6.9 Mt S/yr and 2.3 Mt N(NO_y)/yr.

A three-dimensional global tracer transport model was used to calculate the budgets for the FSU. It was shown that advective fluxes of sulfur and nitrogen from the FSU exceeded the counterflows: 3.5 Mt/yr and 2.2 Mt/yr for sulfur and 1.5 and 1.1 Mt/yr for nitrogen correspondingly.

**CHANGES IN THE COMPOSITION OF AIR AND PRECIPITATION IN CANADA FROM
THE EARLY 1980S TO THE MID-1990S**

R.J. Vet, C.-U. Ro, A. Sirois and D. MacTavish
Atmospheric Environment Service, Environment Canada
4905 Dufferin Street, Downsview, Ontario, Canada M3H 5T4

Precipitation chemistry data collected in the Canadian Air and Precipitation Monitoring Network (CAPMoN) and other Canadian networks have been archived in the Canadian National Atmospheric Chemistry (NAtChem) Data Base. The data, covering the period from 1980 to 1995, have been analyzed in concert with U.S. precipitation chemistry data (predominantly from NADP/NTN) to assess changes in large scale wet deposition patterns from 1980 to 1995. As well, air and precipitation chemistry data from individual sites in the CAPMoN network have been analyzed using a time series model. The combined spatial and temporal analyses provide some fascinating insights into the changing composition of the Canadian atmosphere throughout the 1980s and 1990s, related largely to changing emission rates of acid related species in both Canada and the U.S.A. These insights will be explored in the presentation.

ACID DEPOSITION MONITORING ACTIVITIES IN JAPAN AND EAST ASIA

Hiroshi Hara
National Institute of Public Health
harahrs@iph.go.jp

Emphasis is directed towards three Japanese monitoring networks of acid deposition and an international program of the Acid Deposition Monitoring Network in East Asia (EANET). The three monitoring networks are operated by different organizations, Environment Agency (JEA), the Japanese association of prefectural laboratories of environmental science (ELA), and Meteorological Agency (JMA) whereas Central Research Institute of Electric Power Industry (CRIEPI) put an end in 1990 to its three-year long monitoring on a national scale. In 1983, JEA realized that acid deposition is an global environmental issue which could seriously damage ecosystems to launch a five-year project of wet deposition monitoring at 14 stations. After some changes in monitoring techniques, the network is currently collecting wet-only samples at 48 stations and also monitoring relevant parameters at several other stations for detecting ecological symptoms of adverse effects by acid deposition. Results show that nss-sulfate is rather uniformly deposited over the country on an annual basis and the flux is as high as those in North America. Wintertime deposition of nss-sulfate was found to increase considerably in the coastal areas of Japan Sea, which strongly suggested that sulfur compounds from Asian Continent is transported over the sea to the coast. ELA has conducted two phases of wet deposition monitoring. Phase-I survey (1991-1994) collected bulk samples on a weekly basis at 158 stations. Phase II (1995-1998) focuses on the long-range transported sulfur deposition to collect daily samples on Japan Sea coast in winter and summer months. JMA has two GAW stations of precipitation chemistry, Ryori which is located on the Pacific Ocean coast of the Mainland of Japan, and an island, Minami-Torishima, 2000 km distant from the Mainland. Measurements at the Mainland station started in 1976 whereas the remote island station in Pacific Ocean became in operation in 1996. An analysis of 1976-1994 data illustrates a rise of precipitation acidity during this period, which is explained by increased concentrations of sulfuric and nitric acids with a slight increase in ammonia. The first year result at the easternmost island of Japan divulges that the concentrations of the major ions are in the same level as those in global background stations.

EANET is an international monitoring program of atmospheric deposition and ecosystems in order to create a common understanding of the state of acid deposition problems in both northeast and southeast Asia and to provide useful inputs for decision-making aimed at preventing or reducing its adverse impacts. JEA has been advocating the need to create an international monitoring network and hosted a series of Expert Meetings of the program since 1993. The meeting in 1997 adopted a guideline for dry deposition monitoring and technical manuals for monitoring of wet deposition, soil and vegetation, and inland aquatic environment and concluded the design of the network aiming at beginning its full operation in 2000. In 1998, two-year preparatory-phase monitoring activities has been implemented in most of the participating countries. In Japan, eight stations of the national monitoring network have been assigned to be the international stations for wet deposition monitoring and several stations will be included not later than 2000. Japan has cooperative programs with several countries for the development of model strategies of acid deposition monitoring. In addition to existing major networks including EMEP, NADP, CAPMoN, and WMO/GAW, EANET will constitute another international network of national, regional, and global significance for years to come.

NITROGEN DEPOSITION ONTO THE UNITED STATES AND WESTERN EUROPE: A SYNTHESIS OF OBSERVATIONS AND MODELS

Elisabeth A. Holland^{1&2}, Bobby H. Braswell³, James Sulzman¹, and Jean-Francois Lamarque¹

¹Atmospheric Chemistry Division, National Center for Atmospheric Research

PO Box 3000, Boulder, CO, USA 80307

²Max-Planck-Institute für Biogeochemie, Postfach 10 01 64, D- 07701, Jena, Germany

³Institute for the Study of Earth, Oceans and Space, University of New Hampshire
Durham, NH 03824 USA

The documented acceleration of NH_3 and NO_x ($\text{NO} + \text{NO}_2$) emissions over the last century and a half has led to increased N deposition; thus compromising air and water quality and altering the functioning of global terrestrial and aquatic ecosystems. We mapped the deposition measured from N deposition monitoring networks in the US and in Western Europe (NADP, NDDN and EMEP) and constructed N deposition budgets for two of the most industrialized regions of the world using data. The individual deposition fields consist of measurements of wet deposition of NO_3^- and NH_4^+ and dry deposition of HNO_3 , NO_2 , particulate NO_3^- and NH_4^+ which were determined by multiplying the measured surface air concentrations of individual chemical species by a calculated deposition velocity. Deposition of the oxidized N species, NO_3^- and HNO_3 , by-products of fossil fuel combustion, dominate the N deposition budget of the U.S. whereas the reduced species, NH_x ($\text{NH}_4^+ + \text{NH}_3$), by-products of farming and animal husbandry, dominate the Western European N deposition budget. Western Europe receives five time more N in wet deposition than does the continental U.S. Nitrogen emission and deposition budgets are not balanced: total N deposition onto Europe exceeds estimated emissions and total N deposition onto the United States is less than estimated emissions.

THE LONG-TERM CHANGES IN PRECIPITATION AND STREAM CHEMISTRY AT THE HUBBARD BROOK EXPERIMENTAL FOREST, NH: MEASUREMENTS AND MODEL CALCULATIONS

Charles T. Driscoll*, Solomon Gbondo-Tugbawa, Department of Civil and Environmental Engineering, Syracuse University, Syracuse, NY 13244
John Aber, Complex Systems, University of New Hampshire, Durham, NH 03824
Gene E. Likens and Donald Buso, Institute of Ecosystem Studies, Box AB, Millbrook, NY 12545

Long-term measurements at the Hubbard Brook Experimental Forest, NH have shown declines in annual volume-weighted concentrations of sulfate in bulk deposition and streamwater, which are consistent with decreases in emissions of sulfur dioxide in the eastern U.S. There have been no long-term changes in volume-weighted concentrations of ammonium or nitrate in bulk precipitation. Following an early (~ 10 yr) increase in nitrate, there has been a long-term decline in stream concentrations. In contrast to sulfate, no relationships were evident between emissions of nitrogen oxides and volume-weighted concentrations in bulk precipitation or streamwater. These changes have resulted in limited recovery of streamwater pH. This delay in increases in stream pH is likely due to: 1) depletion of labile pools of soil basic cations, 2) additional (unmeasured) inputs of sulfate and 3) pH buffering by aluminum. Results of long-term stream measurements will be compared to results of model calculation used to evaluate the effects of acidic deposition.

Technical Session 2

Deposition and Its Effects

Session Chair: Robert Vet

DRY DEPOSITION IN NADP -- SOME OLD DECISIONS REVISITED

Bruce B. Hicks
NOAA, Air Resources Laboratory
1315 East West Highway
Silver Spring, MD 20910

In the early 1980s, there was extended debate at Technical Committee Meetings of NADP about the future of dry-bucket collections. A committee was set up to explore the options. Several recommendations arose, which have contributed to the evolution of NADP during the last two decades, and which contributed substantially to the development of the two national dry deposition arrays -- the routine Clean Air Status and Trends Network (CASTNet) of the EPA and the research-oriented Atmospheric Integrated Research Monitoring Network (AIRMoN-dry) of NOAA. It seems timely to revisit the deliberations of twenty years ago, and to see how well they have aged. It is also relevant to explore, once again, the role of surrogate-surface methods in NADP and in similar monitoring programs. In essence, these devices yield deposition of materials to their own surfaces, that are rarely representative of the surroundings. To date, no artificial collection device (or vessel) has succeeded in simulating the roles of all of the mechanisms that control deposition rates occurring in nature. But there remains no well-accepted alternative for deriving direct measurements of dry deposition rates. It remains an open question as to whether well-determined rates of deposition to non-representative surfaces are as acceptable as poorly estimated quantifications of atmospheric deposition to representative surfaces. The latter is what is yielded by CASTNet and AIRMoN.

THE LONG, DRY ROAD TO TOTAL DEPOSITION: DISCOVERING EPA'S CLEAN AIR STATUS AND TRENDS NETWORK

Gary Lear, U.S. EPA, Acid Rain Division
Neil Frank, U.S. EPA, Emissions, Monitoring and Analysis Division

In 1990, Congress amended the Clean Air Act to mandate a significant reduction in the emissions of sulfur and nitrogen oxides, to require that the environmental effectiveness of these reductions be assessed, including how emission reductions are impacting atmospheric deposition. At that time, the National Atmospheric Deposition Program/National Trends Network (NADP) had been operating for over ten years to provide information on temporal and spatial trends for wet deposition. However, information was not available on dry deposition -- that portion of deposition that occurs as adsorption or settling of particles and gaseous compounds during periods without precipitation. In 1991, the Environmental Protection Agency (EPA) established the Clean Air Status and Trends Network (CASTNET) to provide estimates of dry deposition flux for use in model validation, determination of spatial and temporal patterns of dry deposition, and for investigating the relationships between total deposition flux and ecological changes. CASTNET is considered the nation's primary source for dry deposition and ozone data for rural areas. CASTNET has also supplemented NADP and IMPROVE by making wet deposition and visibility-related measurements. EPA intends to make CASTNET data compatible with existing national databases and readily accessible to researchers and the public.

**FOREST ECOREGION SECTIONS AT RELATIVE RISK BASED ON
SPATIAL ION DEPOSITION PATTERNS INTERPOLATED ACROSS THE
PERIOD 1979-1995**

Kenneth W. Stolte and William D. Smith,
USDA Forest Service, Southern Research Station
Research Triangle Park, North Carolina

Casson Stallings and Luther Smith
ManTech Environmental Corporation
Research Triangle Park, North Carolina

The USDA Forest Service's Forest Health Monitoring (FHM) program is responsible for annual reporting of the status, changes, and trends in the health of all forested ecosystems across the United States. A recent evaluation of risk factors for forest ecoregion sections considered natural stressors, human-induced stressors, ecosystem susceptibility to impacts, and status of ecosystem sections with regard to impacts from diverse stressors. One aspect of human-induced stressors involves the deposition of sulfate, nitrate, ammonium, total nitrogen, total precipitation, precipitation pH, hydrogen, calcium, magnesium, potassium, sodium, and chloride on forest ecosystems across the U.S. Forest health issues related to human-induced stressors are high deposition of anions and hydrogen ion related to acidification of forest soils with resulting loss of cations and mobilization of aluminum; effects of S and N on diversity of lichen communities; the impacts of N fertilization on species diversity and the potential for N saturation of forest soils leading to loss of cations; and the relationship of ion deposition to forests and effects on aquatic systems and fauna populations. For this analysis we merged data from the NADP, CASTNet, and CAPMON databases for the period 1979-1995. Data not meeting specific capture criteria were eliminated. Data from each site were averaged by year, and interpolated into grids using Inverse Distance Weighting. Interpolated grids for each year were then averaged. The result was a spatial pattern of average annual deposition of each ion for the period 1979-1995 across the lower 48 U.S. states. These spatial ion deposition patterns, split into five equal interval classes, were then combined in ArcInfo with Bailey's ecoregion sections. The results are GIS maps of ecoregion sections with low-to-high relative annual deposition of each ion, and tables with the percentage of each ecoregion section receiving more than 1 interval class level of deposition of each ion. In general, average annual anion deposition was consistently highest in the Northeast, ammonium highest in the Lake States, sodium and chloride highest in coastal sections of the East and Northwest, and cations highest near the central U.S. In the near future, ion deposition GIS maps will be combined with data from the FHM program, and other programs, to evaluate the spatial correlations between high deposition of sulfate, nitrate, ammonium, total N, pH, hydrogen ion, sodium and chloride and current impacts to forest ecosystems.

ASSESSMENT OF CALCIUM DEPLETION IN FOREST ECOSYSTEMS OF SOUTHEASTERN USA USING A SMALL WATERSHED APPROACH

T. G. Huntington¹, R. P. Hooper¹, C. E. Johnson², B. T. Aulenbach¹, R. Cappellato,³ A. E. Blum⁴.
¹U. S. Geological Survey Atlanta, GA, ²Syracuse Univ., Syracuse, NY., ³Emory Univ., Atlanta GA,
⁴U. S. Geological Survey, Menlo Park, CA.

Biogeochemical mass-balance assessments of calcium status in southeastern USA forests indicate that nutrient losses from tree harvesting and soil leaching often exceed inputs from atmospheric deposition and mineral weathering. Many forest soils of the southeastern USA are particularly sensitive to calcium depletion. These highly weathered soils and the underlying saprolite from which they are derived are largely depleted of weatherable calcium. Furthermore, in many areas, forest soils were badly eroded during periods of cultivation in the late 1800's and early 1900's. At most sites, calcium uptake into merchantable wood equals or exceeds soil-leaching losses. Long-term studies at several southeastern USA sites have demonstrated declines in exchangeable soil calcium pools over the last several decades, indicating that mineral weathering and atmospheric deposition inputs together are insufficient to replenish losses through vegetation uptake and soil leaching. At the Panola Mountain Research Watershed, located in the Georgia Piedmont, and at most of the intensively studied sites in the southeastern USA, soil calcium reserves have been, or likely will be, reduced to less than twice the requirement for a merchantable forest stand in less than 120 years from the present time.

Although atmospheric deposition of sulfuric has declined in recent years, acid loading continues at rates substantially above pre-industrial levels. Acidic loading in excess of the ecosystem's capacity to retain sulfate and nitrate, results in leaching loss of base cations. At Panola Mountain, an analysis of sulfate mass balance over the last 12 years suggests that the capacity of the surface soil for sulfate adsorption has diminished. When the capacity of the surface soil to retain sulfate declines, sulfate and associated cation leaching increases. Soil acidification associated with acidic deposition and base cation uptake by trees usually results in increased aluminum and decreased calcium concentrations in soil water and stream water. Declines in atmospheric deposition of calcium over the last two decades have also accelerated calcium depletion because this source of replenishment has decreased.

Assessment of the regional extent of forest ecosystems sensitive to calcium depletion will be possible using a combination of data obtained from watershed studies, monitoring programs, and soil, geologic, and water-quality databases. A comparison between calcium storage and fluxes at intensively studied sites, with these variables estimated for larger geographic areas, strongly suggests the potential for a regional problem in forest nutrition.

CHANGES IN ATMOSPHERIC DEPOSITION IN EASTERN USA FOLLOWING ENACTMENT OF TITLE IV OF CLEAN AIR ACT AMENDMENTS OF 1990

J. A. Lynch, Pennsylvania State University, School of Forest Resources
University Park, PA 16802; jal at psu.edu

V.C. Bowersox, Illinois State Water Survey, Central Analytical Lab
Champaign, IL 61820; sox at sws.uiuc.edu

J.W. Grimm, Pennsylvania State University, Environmental Resources Research Institute
University Park, PA 16802; jg4 at psu.edu

Precipitation chemistry data from the National Atmospheric Deposition Program (NADP) from 1983 through 1994 were analyzed using linear least-squares models to determine the magnitude, direction, and significance of temporal trends in cation and anion concentrations and wet depositions throughout the United States. Data from the 1983-1994 baseline period were selected to be representative of temporal trends in atmospheric deposition prior to enactment of Phase I of the Clean Air Act Amendments of 1990, Title IV (CAAA). NADP precipitation chemistry data from 1995 through 1997 were compared to the pre-CAAA linear least-squared models to assess the effectiveness of sulfur and nitrogen oxides emissions reductions on sulfate, nitrate, and hydrogen ion concentrations. The results indicated that sulfate concentrations in precipitation decreased as much as 25% at some stations in and immediately downwind of the Ohio River Valley, the same area affected most by Phase I of the CAAA, Title IV. Lower sulfate concentrations were also observed as far north and east as Maine. Concurrent, reductions in hydrogen ion concentrations were also observed. In contrast, nitrate concentrations were largely unaffected. Based on stoichiometric analyses, approximately 75% of the reduction in hydrogen ion concentrations could be attributed to reductions in sulfate concentrations in precipitation. Changes in wet sulfate, nitrate, and hydrogen ion depositions were very similar to changes in the concentrations of these ions. Significant reductions in annual wet sulfate and hydrogen depositions were observed over the Ohio River Valley and large portions of the Mid-Atlantic region and New England. Based on these results, it appears that Phase I of the CAAA, Title IV has been effective in reducing atmospheric deposition in a large portion of the Eastern USA.

**RESPONSE OF STREAMWATER CHEMISTRY TO CHANGES IN ATMOSPHERIC DEPOSITION
AT FIVE HEADWATER BASINS IN THE NORTHEASTERN UNITED STATES**

David W. Clow
U.S. Geological Survey
MS 415, Federal Center, Lakewood, CO 80225

Streamwater data from five U.S. Geological Survey Hydrologic Benchmark Network basins in the Northeastern United States and precipitation data from eight nearby National Atmospheric Deposition Program precipitation monitoring sites covering water years 1984-96 were analyzed for temporal trends in chemistry using the nonparametric seasonal Kendall test. Trends in precipitation chemistry included declines in SO_4 and Ca + Mg at seven of eight sites and declines in acidity at five of eight sites ($p < 0.1$). The magnitudes of declines in precipitation SO_4 and acidity generally were similar, and declines in Ca + Mg were much smaller. These data indicate that recent decreases in SO_4 deposition in the Northeast are now being reflected in reduced precipitation acidity. Concentrations of SO_4 declined in all of the streams, and the magnitudes of the declines generally were similar to those of precipitation SO_4 after accounting for evapotranspiration, indicating that streamwater and precipitation trends could be related. Changes in analytical methods and land use also were investigated as possible causes for the trends in streamwater SO_4 , but the analysis indicated that they were not likely to be a substantial source of the observed trends. Concentrations of Ca + Mg declined at three of five streams, and the magnitudes of the declines were much greater than those in precipitation, suggesting that changes in atmospheric deposition were not the primary cause of the changes in streamwater Ca + Mg. Reduced leaching of cations from soil, perhaps due to decreased acid inputs or depletion of cations from the cation exchange pool, may have been more important. Despite the widespread declines of SO_4 in streamwater and precipitation and the decline in precipitation acidity, alkalinity increased in only one stream, which suggests that increases in pH and alkalinity may be delayed until higher soil base-saturation levels are achieved.

PROJECTED RESPONSES OF WATERSHEDS IN SOUTHERN APPALACHIA TO CHANGES IN DEPOSITION OF SULFUR, NITROGEN, AND BASE CATIONS

P F Brewer, Southern Appalachian Mountains Initiative, 59 Woodfin Place, Asheville, NC 28801
patricia_brewer@aro.enr.state.nc.us

K Tonnessen, National Park Service, Air Resources Division, P.O.Box 25287
Denver, CO 80225-0287; kathy_tonnessen@nps.gov

B J Cosby, Department of Environmental Sciences, Clark Hall, University of Virginia Charlottesville,
VA 22903; b.j.cosby@virginia.edu

R K Munson, Tetrattech, Inc. 2696 N University Ave, Suite 255
Provo, UT 84604; munsonr@tetrattech.com

T J Sullivan, E&S Environmental Chemistry, Inc., P.O. Box 609, Corvallis, OR 97339
tsullivan@proaxis.com

The Southern Appalachian Mountains Initiative (SAMI) is a voluntary partnership among state and federal agencies, industry, environmental groups, and academia. SAMI's mission is to recommend air emissions management strategies to mitigate and prevent adverse air quality impacts to natural resources in Southern Appalachia, with particular focus on Class I national park and wilderness areas. As part of the Integrated Assessment of emissions, atmospheric transport, and effects, SAMI is evaluating the changes in impacts to aquatic and terrestrial resources as a function of changes in levels of sulfur and nitrogen emissions and deposition.

SAMI's acid deposition assessment is initially applying two watershed models, the Model of Acidification of Groundwater in Catchments (MAGIC) and the Nutrient Cycling Model (NuCM) to evaluate the responses of three watersheds (Shaver Hollow and White Oak Run in Shenandoah National Park and Noland Divide in Great Smoky Mountains National Park) to varying levels of sulfur, nitrogen, and base cation deposition. Initial results from both models suggest that the two Shenandoah streams could continue to acidify under current rates of sulfur deposition and that reductions in sulfur deposition would reduce the rate of acidification. Changes in nitrogen and base cation deposition levels were projected to have small impacts on stream chemistry in these two watersheds. For Noland Divide, a high-elevation spruce-fir watershed, MAGIC predicted greater acidification under current or reduced rates of sulfur deposition than did NuCM. The differences in model outcomes are attributable to differences in model approach to characterizing sulfate adsorption capacity for the watershed. Both models indicate that Noland Divide will be much more responsive to changes in rates of nitrogen and base cation deposition than the Shenandoah watersheds and suggest that reductions in base cation deposition could offset benefits from reduced sulfur and nitrogen deposition.

Technical Session 3

Nutrient Deposition and Hypoxia

Session Chair: Richard Artz

A BROAD PERSPECTIVE ON GULF HYPOXIA

Derek Winstanley
Chief, Illinois State Water Survey
2204 Griffith Drive, Champaign, Illinois 61820

Hypoxia (seasonal depletion of oxygen) in the northern Gulf of Mexico is the subject of a national assessment which focuses exclusively on the role of nutrients in causing hypoxia. The presentation will describe the highly dynamic conditions in the Gulf and the Mississippi/Atchafalaya River Basin and identify other major factors that contribute to water quality and ecosystem changes in the Gulf.

ATMOSPHERIC DEPOSITION OF NITROGEN IN THE MISSISSIPPI RIVER BASIN

Lawrence, G.B., U.S. Geological Survey, 424 Jordan Road, Troy, NY, 12180, glawrenc@usgs.gov
Goolsby, D.A., U.S. Geological Survey, Box 25046, Denver Federal Center, MS 406
Denver, CO, 80225-0046, dgoolsby@usgs.gov
Battaglin, W.A., U.S. Geological Survey, Box 25046, Denver Federal Center, MS 406
Denver, CO, 80225-0046, wbattagl@usgs.gov
Stensland, G.J., Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL, 61820-7495
garysten@uiuc.edu

Atmospheric deposition of N has been cited as a major factor in the overfertilization of northeastern forests (often termed N saturation) and a contributor to the eutrophication of coastal waters, including the Gulf of Mexico near the discharge of the Mississippi River. The emissions sources and spatial patterns of atmospheric deposition within the Mississippi River Basin have not been fully assessed, however. The objectives of this project were to (1) quantify the spatial distribution of atmospheric N deposition in the Mississippi River Basin and (2) evaluate the significance of atmospheric deposition as an N input to the basin by relating emission sources to spatial deposition patterns. Data collected through NADP/NTN (National Atmospheric Deposition Program/National Trends Network) and CASTNet (Clean Air Status and Trends Network) monitoring was used for this analysis.

Highest rates of wet NO_3 deposition are in the northeastern corner of the basin where electric utility plants are concentrated, whereas highest rates of wet NH_4 deposition are in Iowa, near the center of intensive agricultural activities in the basin. Lowest rates of atmospheric N deposition are on the windward (western) side of the basin, which suggests that most of the N deposition within the basin is from internal sources. Atmospheric transport eastward across the basin boundary is greater for NO_3 than NH_4 , but a significant amount of NH_4 is likely to be atmospherically transported out of the basin through formation of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 particles, that greatly increases the atmospheric residence time of NH_4 . This process may be a controlling factor in N deposition to upland forest regions in the east, such as the western Adirondack region of New York where NH_4 comprises 40% of total wet N deposition.

CONTRIBUTION OF ATMOSPHERIC DEPOSITION TO NITROGEN LOADINGS IN TAMPA BAY: IMPLICATIONS FOR WATER QUALITY AND LIVING RESOURCES

Holly Greening
Tampa Bay Estuary Program
100 8th Ave. S.E., MS 1-11NEP
St. Petersburg, FL 33701
727-893-2765
tbnep@tampabayrpc.org

Coastal waters around the United States receive large quantities of nutrients and toxic materials from various sources, including the air. As recently as 1991, scientists and resource managers assumed that atmospheric deposition had minimal effect on water quality in Tampa Bay. However, recently completed nitrogen loading estimates now suggest that up to 29 percent of the nitrogen entering the bay comes from wetfall and dryfall directly deposited to the Bay's surface alone, making this source second only to stormwater as the largest bay nitrogen loading source. Patterns of bulk nitrogen deposition indicate both localized and non-local sources.

The relationship between emissions sources and deposition in the Tampa Bay area is the subject of ongoing studies being conducted through a joint effort between EPA's Great Waters Program, the Tampa Bay Estuary Program, Florida DEP Air Management Department, and the Air Quality divisions of Hillsborough and Pinellas counties. Questions to be addressed with results from ongoing studies include: 1) How much of the nitrogen emitted annually from sources within the Tampa Bay watershed are subsequently deposited in the bay or its watershed?; 2) What are relative contributions of remote vs. local air pollution sources of NO_x to deposition in the watershed?; and 3) What are the relative contributions of mobile and stationary sources of NO_x to deposition in the watershed? Findings of ongoing work will be used to develop an action plan that includes cost-benefit analyses of options to manage atmospheric deposition.

**ATMOSPHERIC DEPOSITION CONTRIBUTIONS TO NITROGEN AND PHOSPHORUS
LOADINGS IN TAMPA BAY: INTENSIVE WET AND DRY DEPOSITION DATA
COLLECTION AND ANALYSIS**

Ray Pribble
PBS&J
5300 W. Cypress St., Suite 300
Tampa, Fl 33607-1066
(813) 877-7275
den9@aol.com

Nitrogen and phosphorus loading estimates to Tampa Bay due to atmospheric deposition have been previously determined as part of the total estimated loadings to the bay for 1985-1991. These estimates determined that atmospheric deposition directly to the bay's surface may provide about 29% of the total nitrogen load and about 31% of the total phosphorus load to the bay. Given the relative importance of these loads in comparison to the total nutrient loads to the bay, it was determined that more accurate estimates of atmospheric deposition of nitrogen and phosphorus to the bay's surface were necessary. The Tampa Bay Atmospheric Deposition Study (TBADS), after approval by the EPA Great Waters Program, was begun in the spring of 1995, and resulted in data collection beginning in August 1996, and continuing through the present, with plans for sampling through 1999.

**INFLUENCES OF THE RIPARIAN N-FIXING SHRUB, *ALNUS INCANA* SSP. *RUGOSA*, AND
ATMOSPHERIC DEPOSITION ON N CONCENTRATION IN SURFACE WATERS IN THE
ADIRONDACK MOUNTAINS**

T. M. Hurd and D. J. Raynal
Faculty of Environmental & Forest Biology
College of Environmental Science & Forestry
State University of New York
1 Forestry Drive
Syracuse, NY 13210 USA

This study evaluates the hypothesis that shrub wetlands dominated by N-fixing alder are a major source of N export to surface waters in Adirondack watersheds. Our objectives were to quantify N fixation by alder in riparian ecosystems that receive high N deposition and to determine the relation between this biotic source of N leaching and atmospheric deposition of water and nutrients. Research was conducted at Huntington Forest in the Adirondack Park of New York State, the site of NADP/NTN NY20. Estimates of N fixation using the acetylene reduction technique show that alder in this region fixes > 25 kg N/ha/yr. Atmospheric N deposition (wet plus dry) is approximately 12 kg N/ha/yr. Streamwater NO₃⁻ concentration was measured in downstream reaches dominated by alder and upstream reaches dominated by other woody vegetation from August 1996 - May 1998. Nitrate concentrations within the main channel were consistently greatest in the alder reach, with greatest differences of 10-20 microeq/l occurring during the dormant season of both years. Similarly, NO₃⁻ in shallow groundwater was 3-6 times greater in the alder reach than the upstream reach during the dormant season of 1996-1997. The apparent mechanism responsible for this potentially important internal N source to surface waters is the build-up of mineralized and nitrified N in shallow riparian systems dominated by alder, followed by a hydrologic flush of NO₃⁻ on the rising limb of a rain or melt event. This mechanism is evidenced by greatest NO₃⁻ concentrations in the alder reach at the onset of snowmelt or a summer storm, and by similarities in NO₃⁻ and Cl⁻ concentrations between the alder reach and shallow hyporheic waters. Ongoing studies are focusing on the importance of N-fixing alder as an internal N source on a watershed or regional scale, by estimating: 1) cover of alder within, and the areal coverage of Scrub-Shrub 1 wetlands which alders dominate, and 2) alder N fixation in the field and in controlled N addition experiments.

CLIMATE INFLUENCES ON BIO-AVAILABILITY OF WET-DEPOSITED N IN SOILS: AN EXPANSION OF THE NADP/NTN DATABASE

R.H. Grant and K. Scheeringa
Department of Agronomy, Life Sciences Building
Purdue University, W. Lafayette, IN 47907

While the NADP/NTN data set provides information on the temporal and spatial distribution of annual inorganic nitrogen (N) deposition, analysis of the biological effects of the deposition requires the inclusion of climate, soils, and organism information in a GIS framework. This study developed additional GIS database layers for each NADP/NTN site east of 110 W longitude, including a weekly hydrologic budget, mean soil temperature (2 depths), and mean minimum and maximum air temperatures. With this database, the inorganic N available in the soil solution was estimated for the 10-yr period of 1986-1995. Results indicate that the estimated pool of available inorganic N varies from 0.5 to 7 kg/ha in the Eastern US during the period of study. At many locations the estimated pool of available inorganic N in the soil increases during the winter and decreases through the summer as a result of the juxtaposition of rainfall and temperature. Spatially, the pool of estimated available inorganic N in the soil varied from year to year at the regional scale. Depletion and accretion of available N did not consistently correspond to the droughtiness of a region during a given year.

ATMOSPHERIC TRANSPORT AND WET DEPOSITION OF AMMONIUM IN NORTH CAROLINA

John T. Walker and Viney P. Aneja
Department of Marine, Earth and Atmospheric Sciences
North Carolina State University
Raleigh, N.C. 27695-8208

Wet deposition and transport analysis has been performed for NH_4^+ in North Carolina, USA. Multiple regression is employed to model the temporal trend and seasonality in monthly NH_4^+ concentrations from 1983-1996 at six NADP/NTN sites. A significant ($p < 0.01$) increasing trend beginning in 1990, which corresponds to an average wet deposition increase of $0.20 \text{ kg ha}^{-1} \text{ y}^{-1}$, is detected at the rural Sampson County site (NC35), which is located within a densely populated network of swine and poultry operations. This trend is positively correlated with increasing NH_3 emissions related to the vigorous growth of North Carolina's swine population since 1990. A source-receptor regression model, which utilizes weekly NH_4^+ concentrations in precipitation in conjunction with boundary layer air mass back trajectories, is developed to statistically test for the influence of a particular NH_3 source region on NH_4^+ concentrations at surrounding NADP/NTN sites. NH_3 emissions from this area, primarily evolving from swine and poultry operations, are found to increase NH_4^+ concentration in precipitation at sites up to $\approx 100 \text{ km}$ away, allowing deposition to nitrogen sensitive coastal and estuarine ecosystems. At the Scotland County (NC36) and Wake County (NC41) sites, mean NH_4^+ concentrations show increases of at least 44% for weeks during which 25% or more back trajectories are considered influenced by this source region.

ATMOSPHERIC DEPOSITION OF NITROGEN IN A HIGH LIGHTNING INTENSITY AREA

C. Li, A. K. Alva, D. V. Calvert, and D. J. Banks

University of Florida

Intensive lightning strikes and high rainfall were assumed to increase atmospheric deposition of nitrogen (N) in the south and east coastal regions of Florida. The objective of this study was to examine the effects of lightning strikes on deposition of NO₃-N. Bulk precipitation was collected and analyzed for NO₃-N from September 1994 to August 1995. The lightning strikes significantly increased NO₃-N deposition in rainwater. Annual contribution of NO₃-N through precipitation was 3.8 kg N/ha-1. Summer season (June-October) accounted for about 53% of total annual N deposition.

Technical Session 4

Trace Metals and Toxics

Session Chair: Mary Ann Allan

YEARLY TRENDS IN METHYL MERCURY DEPOSITION AT SELECTED MDN SITES IN NORTH AMERICA AND MERCURY DRY DEPOSITION METHODS COMPARISON

Eric M. Prestbo and Robert C. Brunette
Frontier Geosciences Inc., 414 Pontius Avenue North, Suite B,
Seattle, Washington, 98109
ericp@frontier.wa.com

Colleen Caldwell
New Mexico Cooperative Fish and Wildlife Research Unit
New Mexico State University, Knox Hall, Room 132, Las Cruces, New Mexico 88003

Quantifying the concentration and wet-deposition rate of mercury (Hg) is critical to understanding the cycling of Hg in the atmosphere. However, measurement of monomethyl mercury (MMHg) is also important because of its greater toxicity and as an indicator for atmospheric Hg chemistry, even though MMHg is a small fraction (<5%) of the total Hg in rain. Furthermore, dry deposition of Hg is predicted to be approximately 50% of the total wet-deposition rate. Because of the lack of field data, the predicted dry-deposition rate of Hg is very uncertain. Both MMHg and Hg dry deposition data will be presented. There are nine Mercury Deposition Network (MDN) sites in North America, which have been collecting and analyzing monomethyl mercury (MMHg), in monthly wet-deposition composite samples for nearly 2 years. The overall seasonal pattern for MMHg at these 9 MDN sites (WI, MN and Ontario) is higher concentration and deposition during the summer months. This contrasts with MMHg deposition patterns at MDN site WA18 in Seattle where both concentration and deposition are higher in the winter. A number of other MDN and non-MDN sites with limited MMHg data sets will also be compared. We will also present new data comparing four methods for the measurement of Hg dry deposition. In order to correctly measure Hg dry deposition, unlike most metals, the method used must be able to collect and capture both particulate and gas-phase Hg, especially HgCl₂ and other oxidized forms. As part of this study, a novel method is compared to “historical” Hg dry deposition methods. The methods used in this study were: 1) plastic bag in dry bucket of an Aerochem sampler, 2) bulk deposition (minus wet-only deposition), 3) 0.25 m³ plexi-glass surface and 4) 0.05 m³ ion-exchange membrane. Dry deposition rates of Hg and a comparison of the method detection limit, ease of deployment and comparison to Hg wet deposition rates will be presented.

MERCURY WET AND DRY DEPOSITION TO THE CHESAPEAKE BAY

R.P Mason, N.M. Lawson, G-R. Sheu, J-M Laporte and S. Andres
Chesapeake Biological Laboratory
The University of Maryland
Solomons, MD 20688

Atmospheric deposition is an important source of mercury to the Chesapeake Bay. We have been collecting wet deposition at a number of rural sites in Maryland (Frostburg and Solomons) as well as urban sites in and around Baltimore. In Frostburg, in addition to both wet and throughfall deposition, stream samples have been collected to understand the transport of Hg, and other metals/metalloids, through forested watersheds. Biota from the streams have also been analyzed for Hg and other trace metals/metalloids. From our studies we estimate the regional wet flux as 10-20 (micro)g m⁻² yr⁻¹. Higher fluxes are found close to Baltimore. Our recent measurements on the roof of the Science Center in downtown Baltimore, for example, yield a yearly wet flux of 35 (micro)g m⁻² (1997/8 data); compared to 25 (micro)g m⁻² yr⁻¹ (1996/7 data) at Hart-Miller Island, about 10 miles away. Atmospheric Hg speciation has been measured at a number of sites and these studies indicate that gaseous ionic Hg could be an important source of dry deposition, especially close to the city. Overall, direct wet and dry deposition to the Chesapeake Bay contribute about half the mercury entering the Bay.

AIR/SURFACE EXCHANGE OF MERCURY OVER VEGETATION: A REASSESSMENT OF GLOBAL BIOGENIC MERCURY EMISSIONS

S. E. Lindberg and P. J. Hanson
Environmental Sciences Division, Oak Ridge National Laboratory,
PO Box 2008, Oak Ridge, TN 37831

T. P. Meyers
Atmospheric Turbulence and Diffusion Laboratory, NOAA/ERL
Oak Ridge, TN

Atmospheric sources are significant in the cycling of Hg in the biosphere, but there are few reliable data on air/surface exchange of Hg in terrestrial systems. We developed a tower-based micrometeorological gradient method for measuring gas-phase HgE fluxes over soils and vegetation. We describe here results of the modified Bowen ratio approach from three separate flux sampling campaigns: over a mature deciduous forest at the Walker Branch Watershed in Tennessee, over a young pine plantation in Tennessee, and over the boreal forest floor at the Lake Gardsjon watershed in Sweden. Our data show that Hg exchange over these surfaces is bidirectional, but is dominated by emissions from plants and soil. Dry deposition is less frequent, of generally lower magnitude, and is enhanced by surface wetness. We measured emissions over tree canopies in Tennessee in the range of $\sim 10\text{-}300\text{ ng}^{-2}\text{ h}^{-1}$, and over the boreal forest floor in Sweden of $\sim 1\text{-}4\text{ ng}^{-2}\text{ h}^{-1}$. Fluxes were influenced by temperature, solar radiation, and atmospheric turbulence. The ability of trees to emit Hg from soil pools is now well established. There exists a significant biotic re-emission of HgE from the oceans, and our data provide the first direct evidence of a similar process in terrestrial systems. These data have been combined with results from chamber studies to estimate the overall flux of gas-phase HgE between the atmosphere and terrestrial systems. Transpiration of HgE represents a previously unmeasured mobilization of Hg from the continents to the troposphere, one which may increase current estimates of so-called natural emissions by over 100%.

We have recently begun new studies of Hg emissions over open water and the predominant emergent wetland vegetation of the Florida Everglades (*Typha domingensis*, *Cladium jamaicense*). Emission over Everglades waters averaged $\sim 3\text{--}4\text{ ng mg}^{-1}\text{ h}^{-1}$, lower than fluxes measured in Swedish boreal lakes which averaged 8-9 $\text{ng mg}^{-1}\text{ h}^{-1}$. During the recent summer campaign, we completed the first ever study of Hg⁰, CO₂, and water vapor fluxes over vegetation in the Everglades. Transpiration is now realized as an appropriate term for the phenomenon of Hg emission from plants, as the patterns of the emission of water vapor and Hg are clearly similar, with the latent energy flux explaining $\sim 40\%$ of the variance in Hg flux ($r=0.62$, $p<0.001$, $n>200$). Transpiration far exceeds Hg emission from open water, averaging $47\text{--}66\text{ ng}^{-2}\text{ h}^{-1}$ in daytime and $-0.5\text{--}6\text{ ng}^{-2}\text{ h}^{-1}$ at night. Mercury fluxes are influenced by solar radiation and temperature, and cool, cloudy days consistently yield the lowest fluxes. We now have sufficient data in hand to allow us to make preliminary estimates of Hg fluxes over the Everglades resulting from air/surface exchange processes for gas-phase Hg⁰, and the approaches will be presented at the meeting.

**WET DEPOSITION OF TRACE METAL(LOID)S AT BACKGROUND SITES
ALONG AN EAST-WEST TRANSECT ACROSS THE NORTHERN UNITED STATES**

Dirk Wallschläger & Nicolas S. Bloom
Frontier Geosciences, 414 Pontius Ave. N, Seattle WA 98109
DirkW@Frontier.WA.com

Precipitation samples were collected at six stations of the mercury deposition network (MDN), representing an East-West transect from Seattle, WA to Nova Scotia, from May to October 1997. The samples were analyzed for total mercury by CV-AFS, and for methylmercury compounds by direct ethylation - TD-GC-AFS. We also determined As and Se by HG-AFS and HG-CT-GC-AAS, and measured Na, Mg, Ca, Al, Mn, Ba, Zn, Ni, Cu, Cd, Sb and Pb by ICP-MS. Geographical trends along the transect and temporal variation of concentrations and wet deposition rates are presented and discussed. Statistical analysis also revealed significant correlations between certain groups of elements. These are discussed with regard to identifying potential sources of trace elements to the atmosphere. The potential environmental significance of these trace metal(loid) wet depositions is evaluated. Finally, we balance the benefits and cost of adding trace metal capabilities to the existing MDN.

**MERCURY DEPOSITION AND AMBIENT CONCENTRATIONS IN NEW ENGLAND:
RESULTS AND PLANS FOR THE FOUR-SITE MIC-B NETWORK**

Lee Alter
Air Quality Specialist
Northeast States for Coordinate Air Use Management
129 Portland Street
Boston, MA 02114
P: 617-367-8540 F: 617-742-9162
e: lalter@nescaum.org

Dr. Gerald Keeler
University of Michigan
School of Public Health
Department of Environmental and Industrial Health
109 South Observatory
Room 25118
Ann Arbor, MI 48109-2029

A number of field studies have been initiated during the past few years to measure mercury deposition and ambient concentrations in the northeast states and eastern Canadian provinces. Among these is a study sponsored by the U.S. EPA under the Regional Ecological Monitoring and Assessment Program (REMAP). Data collection for the REMAP study began in June 1997. Wet deposition samples will be collected for two years at four sites. These sites are distributed among urban, rural, coastal, and mountainous environments. Samples are collected on an event basis using the MIC-B precipitation collector and analyzed at the University of Michigan (UMI). Wet deposition results from the network will be presented for one full year. Results will be compared to data from other sites operated inside and outside the region during this period.

One of the four REMAP sites is collocated with an Aerochem collector operating as part of the NADP-Mercury Deposition Network (MDN). Results from the first year of this comparison study will be presented. The remaining three sites also measure ambient gas and particle phase mercury concentration. Samples are collected every sixth-day over a 24-hour period and analyzed at the UMI. Results for gas- and particle-phase concentrations will be presented for a nine-month period. Plans for the second year of the REMAP study will be outlined, including cloud water, additional collocated measurements, and source-receptor studies.

AIR TOXICS IN THE GREAT LAKES AREA: REGIONAL SOURCE LOCATIONS

Donald F. Gatz and Clyde W. Sweet

Illinois State Water Survey, 2204 Griffith Dr., Champaign, Illinois 61820

Because atmospheric deposition is an important mode of input of persistent bio-accumulating toxic chemicals to the Great Lakes, any efforts to reduce their concentrations in the lakes should be based on knowledge of the nature and location of their sources. The purpose of this investigation was to examine recent measurements of airborne toxic materials at a remote site on Lake Superior for clues to the locations of regional sources. Principal components analysis (PCA) and a back-trajectory analysis technique known as the potential source contribution function (PSCF) were used to gain information on the location of potential sources. The PCA identified four separate groups of toxic materials that behave independently and likely have separate sources. These groups were 1) PCBs, 2) chlorinated pesticides, 3) light PAHs, and 4) heavy PAHs. The PSCF results need careful interpretation, especially in areas distant from the receptor where high values can occur by chance when there were few overall occurrences of back-trajectory endpoints. PSCF patterns were different for compounds with high loadings on different components, and suggest several likely source areas for PCBs, the PAH chrysene, and g-HCH affecting Eagle Harbor. These areas are primarily in Wisconsin, Michigan, Minnesota, and northern Illinois.

Technical Session 5

Technology and Methods

Session Chair: Scotty R. Dossett

**COMPARISON OF CHEMICAL LOADING TO THE COLORADO ROCKY MOUNTAIN
SNOWPACK WITH ANNUAL WET DEPOSITION DATA COLLECTED BY THE NATIONAL
ATMOSPHERIC DEPOSITION**

K. Heuer
National Park Service
P.O. Box 25287, Denver, CO 80225
kristi_heuer@nps.gov;

K. Tonnessen
National Park Service
P.O. Box 25287, Denver, CO 80225
kathy_tonnessen@nps.gov

G. Ingersoll
USGS-WRD, MS 415, DFC, Denver, CO 80225
gpingers@usgs.gov.

The National Park Service and the U.S. Geological Survey have cooperatively monitored snowpacks along the Continental Divide in the Rocky Mountains from 1993-1998, measuring total chemical loads at maximum accumulation. At 62 snow survey sites, adjacent to SnoTel sites, we dug snowpits in late March-early April to estimate the chemical concentrations of major anions, cations, trace metals, and sulfur isotopes. The objective of this work is to amass long-term data on the distribution of pollutants to snowpacks to allow us to set critical loads for nitrogen and sulfur. These are the chemicals that can cause changes in surface water chemistry of high-elevation lakes, streams and ponds in sensitive watersheds. NADP sites in the Rocky Mountains provide us with weekly chemical loading estimates during all seasons of the year. Our comparison of the NADP and snow survey data at a number of high elevation sites in the Colorado Rockies has shown that winter frontal storms deposit larger amounts of chemicals in snow on the western slope. During the spring and summer seasons, upslope meteorological conditions result in more loading of nitrogen and sulfur to eastern slope locations. We have also been able to identify interannual patterns of chemical deposition related to total rain and snowfall.

MONITORING ATMOSPHERIC DEPOSITION IN SEASONAL SNOWPACKS IN THE ROCKY MOUNTAIN REGION

George P. Ingersoll, John T. Turk, M. Alisa Mast, Dave W. Clow, and Donald H. Campbell
US Geological Survey, Mail Stop 415, Federal Center, Denver, CO 80225

Regional snowpack water-quality data for the Rocky Mountains are sparse. In the past, data from National Atmospheric Deposition Program (NADP) sites provided the only regional estimates of meteoric deposition. Although the NADP network is extensive nationwide, coverage for high-elevation sites in the Rocky Mountains is limited. Thus, little was known of the chemical concentrations of precipitation in mountainous ecosystems throughout the region, and new methods to define snowpack quality were needed.

Our technique determines the seasonal snowpack chemistry in single samples at 52 sites in the Rocky Mountain region. During 1993-97, the U.S. Geological Survey and other sponsoring agencies collected snow samples representing most of the annual precipitation at high-elevation sites in New Mexico, Colorado, Wyoming, and Montana. The sampling network was designed to provide long-term information about atmospheric deposition in snowpacks to complement the NADP.

Snowpack chemistry appears to be a robust substitute for NADP-wetfall chemistry. Concentrations of ammonium, nitrate, and sulfate in snowpacks were similar to NADP wet deposition values during several years at several collocated sites across the region. These results suggest this technique can be useful for improving the coverage and resolution for monitoring atmospheric deposition in the Rocky Mountains.

**AN ANALYSIS OF THE TEMPORAL VARIATION IN AIRMON PRECIPITATION
CHEMISTRY MEASUREMENTS USING HYSPLIT LAGRANGIAN TRAJECTORIES**

Barbara J.B. Stunder
NOAA Air Resources Laboratory
1315 East West Highway, Rm 3151
Silver Spring, MD 20910
barbara.stunder@noaa.gov

HYSPLIT back-trajectories were computed for the years 1993 and 1996, from the State College, Pennsylvania AIRMoN site, using National Weather Service meteorological model output. Trajectory origin times corresponded to times of observed precipitation. The trajectories were statistically clustered as a means of grouping the trajectories by meteorological flow pattern. Statistics, by cluster, of the precipitation chemistry data were computed. Differences in cluster chemistry between similar clusters in the two years may indicate differences in pollutant emissions.

THE SENSITIVITY OF SULFUR WET DEPOSITION TO ATMOSPHERIC OXIDANTS

Ariel F. Stein and Dennis Lamb
__Meteorology Department
___503 Walker Bldg.
___Penn State University
___University Park, PA 16802
FAX: __814-865-3663

The wet deposition of sulfate in eastern North America is chemically linked to the abundance of oxidants and therefore also to the emissions of nitrogen oxides within the region. The impact that future NO_x controls will have on acidic deposition depends in part on the resulting changes in oxidant levels and the competition that naturally exists between clear-air and in-cloud oxidation. This issue is addressed here using a meteorological transport model (HY-SPLIT) coupled to a detailed chemical reaction scheme in order to interpret air and precipitation chemistry data (AIRMoN) obtained at the Penn State research sites. A case study of a high-deposition event in June 1996 is used to gain an understanding of the linkages between sulfur deposition and oxidant chemistry and transport. Interactions among VOC/ O_3 / NO_x chemistry, meteorological transport, and SO_2 oxidation pathways need to be considered together in order to understand the occurrence of such extreme acid rain episodes. This study shows that the deposition of sulfate is likely to decrease in response to decreases in oxidant levels. However, because the connection between NO_x and oxidant concentrations is strongly dependent on the VOC/ NO_x ratio, a linear relationship between NO_x emissions and oxidant levels does not generally exist. Nevertheless, under conditions typically found in large regional areas of the eastern U.S., decreases in NO_x emissions would lead to lower oxidant concentrations and reductions in sulfate deposition.

THE USE OF NADP DATA TO GROUND-TRUTH DEPOSITION MODELING

John Sherwell
Power Plant Research Program
Maryland Department of Natural Resources
Tawes Building B-3
Annapolis, MD 21401
jsherwell@dnr.state.md.us

Mark Garrison and Peter Mayes
Environmental Resources Management
855 Springdale Drive
Exton, PA 19341

The Maryland Department of Natural Resources Power Plant Research Program (PPRP) has an ongoing interest in environmental issues affecting water quality in the Chesapeake Bay. Among other activities, PPRP has undertaken efforts to investigate the contribution of atmospheric nitrogen to excess nutrient loadings in the Bay. These investigations have focused on the use of the CALMET/CALPUFF modeling system to estimate nitrogen deposition attributable to NO_x emissions from both local Maryland and regional sources onto the surface of the Bay and onto land areas in the Bay watershed. The Model has been implemented with both a full year of 3-dimensional gridded meteorological data based on MM4 to identify deposition contributions from several different categories of sources and with longer-term, readily available NWS data to analyze climatological deposition trends. The evaluation of the estimates produced by CALPUFF are compared to measured deposition rates. PPRP has used NADP/NTN data on nitrogen deposition to perform evaluations of wet deposition rates, and has used CASTNet data, or comparisons of observed vs. predicted NO_x concentrations as a surrogate for, dry deposition rates. These development and evaluation efforts have enabled PPRP to initiate analyses of the effects of different environmental and electric utility regulatory programs, including NO_x trading, restructuring of the electric utility industry, and various Clean Air Act NO_x reduction requirements. The present paper will provide a summary of the use of NADP data for model evaluation, and will present the results of deposition estimates segregated into the ten Tributary Regions in Maryland that are the focus of the State's strategy for complying with the Chesapeake Bay Agreement on nutrient reductions. The paper will also provide estimates of the reduction in nitrogen loading due to selected Clean Air Act and restructuring initiatives.

NEW JERSEY ATMOSPHERIC DEPOSITION NETWORK

Stuart Nagourney
New Jersey Department of Environmental Protection
PO Box 409, 401 East State St.
Trenton, NJ 08625

Steven J. Eisenreich
Rutgers University
Department of Sciences
New Brunswick, NJ 08903

The effect of non-point source pollution and the composition and magnitude of out-of-state sources are critical to scientists and policy makers as we develop watershed-based management strategies and regional solutions to environmental issues. To examine the impact of atmospheric deposition, the New Jersey Department of Environmental Protection, in collaboration with the United States Environmental Protection Agency, has contracted with Professor Steven J. Eisenreich of Rutgers University to implement the New Jersey Atmospheric Deposition Network (NJADN) a nine-site network to quantify organics, metals and nutrients in wet and dry deposition with the twin goals of assessing the extent of non-New Jersey impacts and their influence on critical watersheds.

This paper will discuss what is known about deposition in New Jersey, expand upon the goals of the NJADN and present some anticipated outcomes of the results.

EXPANDING IN NEW DIRECTIONS: WET DEPOSITION MONITORING IN INDIAN COUNTRY

Stephanie Benkovic, Senior Environmental Policy Analyst
U.S. Environmental Protection Agency
Acid Rain Division

EPA's Acid Rain Division and Office of Air and Radiation and the National Atmospheric Deposition Program are working collectively with Tribes to broaden the spatial distribution of the wet deposition monitoring network in Indian Country. This initiative will increase the number of wet deposition monitors by 10 over the next two years. Enhancing the spatial distribution of the monitoring network will help in achieving a greater understanding of the changes and trends in wet deposition chemistry. It will also facilitate a more comprehensive partnership with Tribes by increasing their use and understanding of the wet deposition monitoring network. Training and materials will be offered to participating and interested Tribes in developing skills and tools to examine ecological resources that may be impacted by acidic deposition in Indian Country.

A COMPARISON OF NADP AND CASTNET WET PRECIPITATION CHEMISTRY DATA

Luther Smith
ManTech Environmental Corporation
Research Triangle Park, North Carolina

The Clean Air Status and Trends Network (CASTNet) operated by the U. S. EPA has, with minor exceptions, been implemented with very similar protocols to the NADP weekly sampling network. The question of merging the two networks has recently been raised. Prior to the integration of the two networks, one would like to ascertain the comparability of the data collected thus far.

Here the comparability of the data from the two networks is examined. Comparisons are made using data from collocated (both intra- and internetwork) sites and from sites that are not collocated, but separated by varying degrees of distance. Both summary statistics and weekly data are used in the assessment, and both measures of central tendency and variability are considered.

II. POSTER PRESENTATIONS

PROCEDURES FOR STABILIZING NH₄ AND PO₄ CONCENTRATIONS IN RAINWATER SAMPLES

Sue Bachman and Tom Bergerhouse
Illinois State Water Survey
2204 Griffith Dr., Champaign, IL 61820
E-mail:bachman@sun.sws.uiuc.edu

Many studies over the past two decades have examined the chemical stability of the main ionic components in precipitation. A variety of techniques including refrigeration, acidification, filtration and biocide addition have been tested. A study undertaken at the Illinois State Water Survey, Champaign, Illinois, has combined two of these techniques (filtration and refrigeration) to evaluate the preservation effects on rainwater samples collected in central Illinois. Fifteen wet-only event samples, collected in July and August of 1997 and April through June of 1998, were processed and analyzed for pH, NH₄ and PO₄. A Lachat Flow Injection Analyzer (FIA) was used for the nutrient analyses. At the time of collection, samples were prepared according to the following protocol: Set **A** samples were filtered immediately after collection and remained at room temperature throughout the study. Set **B** samples were filtered after collection but were refrigerated at 4 C throughout the analysis process. Set **C** samples were neither filtered nor refrigerated, and Set **D** samples were not filtered but were kept refrigerated throughout the analysis process. A 0.2 micrometer Nuclepore syringe filter was used on each sample prepared for filtration.

FIA analyses were performed at set time intervals (usually at 0,1,2,5,and 10 days-volume permitting) to observe any changes in the nutrient levels of the rain samples. On average, about 15% of the NH₄ and all of the PO₄ concentration was lost over time in Set **C**. Sets **A**, **B** and **D** NH₄ concentrations remained about the same, with fluctuations both up and down over the analysis period reflecting some correspondence to the pH, sample volume, and concentration of PO₄ present. Greater variability was observed in the stability of the PO₄ values. Sample Set **B** offers the most promising option of stabilizing the samples' nutrient species through biota removal. Graphical plots and charts will be used to show the comparisons between these preservation options.

MERCURY DEPOSITION NETWORK: LABORATORY AND FIELD QUALITY ASSURANCE MEASUREMENTS

Robert C. Brunette, Paul E. Laskowski and Eric M. Prestbo
Frontier Geosciences, 414 Pontius Avenue North, Suite B
Seattle, Washington USA, bobb@frontier.wa.com

One advantage of a national network, such as the Mercury Deposition Network (MDN), is the ability to fully develop a comprehensive quality assurance program. We will present the ongoing and new efforts to evaluate the quality of the data generated by the MDN Mercury Analytical Laboratory (HAL). First, two MDN samplers have been co-located at site WA18 in Seattle since March of 1998. With these two co-located samplers, a measurement of precision for a number of variables has been completed. These include temperature, bottle volume catch, total Hg and Methyl Hg. Second, during the last year, a new glassware design and larger sampling bottle has been implemented in the network. To show equivalency to the older equipment, physical and chemical tests were conducted and will be reported. Third, the collection of MDN samples by field technicians is an active area of the quality assurance program. Finally, other routine measurements of MDN laboratory quality assurance will be shown.

**WORLDWIDE PRECIPITATION CHEMISTRY COLLECTION:
CURRENT STATUS AND FUTURE DIRECTION**

Tim Coleman

WMO/GAW Quality Assurance/Science Activity Center for the Americas
Atmospheric Sciences Research Center, SUNY Albany
251 Fuller Road, Albany, NY 12203
tlc@asrc.cestm.albany.edu

This poster session will outline the current process of quality assuring precipitation chemistry data collected for the World Meteorological Organization's Global Atmosphere Watch (WMO/GAW) program. It will focus on some of the challenges faced in producing a long term worldwide quality assured data set, including data acquisition, site distribution and site activity. Trends in laboratory analysis performance will be displayed from the annual intercomparison survey of precipitation chemistry laboratories and how performance data can be linked to site data as an acceptance criterion. In the future, every effort must be made to encourage wider participation. These future plans include providing standardized manuals, and simplifying the data submittal process.

THYMOL PRESERVATION IN DAILY PRECIPITATION SAMPLES OR MORE MOLS WITH THYMOL

Brigita Demir, Jane Rotherth, Lori Henry, and Van C. Bowersox,
Illinois State Water Survey, Champaign, Illinois

Orthophosphate and organic acids in precipitation samples are not generally stable, changing concentration over time. In addition, ammonium and nitrate in some samples change if not preserved. Various methods have been used to preserve all of these parameters. Using a biocide to preserve samples has long been considered the best method for preservation. Several different biocides have been used. This study looks at the use of thymol as a preservative for precipitation samples. The daily samples were collected at the Walker Branch Station, Oak Ridge, TN AIRMoN site (TN00). 0.8 g thymol was added to precipitation collection buckets which were placed on an Aerochem Metrics collector that opened and closed at the same time as the standard AIRMoN collector. All samples collected, therefore, are identical to the standard AIRMoN samples except for the addition of the thymol. The refrigerated AIRMoN samples and the samples with thymol as the preservative were sent to the Illinois State Water Survey and analyzed for pH, conductivity, NH_4^+ , PO_4^{3-} , Cl^- , NO_3^- , and SO_4^{2-} . The changes necessary in the methodology and the biases and interferences found in the measurements because of the thymol are reported. Analytical concentrations of the thymol-preserved samples versus the refrigerated samples are given.

CHASSAHOWITZKA NATIONAL WILDLIFE REFUGE - STATUS AND TRENDS

L.K. Dixon and E.D. Estevez
Mote Marine Laboratory
1600 Thompson Parkway
Sarasota, FL 34236
lkdixon@mote.org

Chassahowitzka National Wildlife Refuge, west-central Florida, is a large, shallow (<2 m) mosaic of saltmarsh, seagrass beds, and algal assemblages growing on an extensive karstified limestone shelf. Nitrogen loadings to the Refuge from both groundwater discharge and atmospheric deposition appear to be similar in magnitude and both are increasing. Since 1996, the U.S. Fish and Wildlife Service has sponsored work to establish baseline conditions of submerged aquatic vegetation and water quality and to identify indicators of trophic status.

Algal and/or seagrass cover was nearly continuous with moderate densities. Changes in species abundances and density have been noted during the study. The water column was well mixed and trophic state indices were low, indicating "Good" water quality overall. The northern region apparently received a higher nutrient loading than the southern region. Algal growth was nitrogen limited in the coastal region and groundwater nitrate contributed by the Chassahowitzka Springs was removed from the water column before discharge to the coastal region.

**COMPARISON OF CHEMICAL LOADING TO THE COLORADO ROCKY MOUNTAIN
SNOWPACK WITH ANNUAL WET DEPOSITION DATA COLLECTED BY THE
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM**

K. Heuer
National Park Service
P.O. Box 25287, Denver, CO 80225
kristi_heuer@nps.gov

K. Tonnessen
National Park Service
P.O. Box 25287, Denver, CO 80225
kathy_tonnessen@nps.gov

G. Ingersoll
USGS-WRD, MS 415, DFC
Denver, CO 80225
gpingers@usgs.gov.

The National Park Service and the U.S. Geological Survey have cooperatively monitored snowpacks along the Continental Divide in the Rocky Mountains from 1993-1998, measuring total chemical loads at maximum accumulation. At 62 snow survey sites, adjacent to SnoTel sites, we dug snowpits in late March-early April to estimate the chemical concentrations of major anions, cations, trace metals, and sulfur isotopes. The objective of this work is to amass long-term data on the distribution of pollutants to snowpacks to allow us to set critical loads for nitrogen and sulfur. These are the chemicals that can cause changes in surface water chemistry of high-elevation lakes, streams and ponds in sensitive watersheds. NADP sites in the Rocky Mountains provide us with weekly chemical loading estimates during all seasons of the year. Our comparison of the NADP and snow survey data at a number of high elevation sites in the Colorado Rockies has shown that winter frontal storms deposit larger amounts of chemicals in snow on the western slope. During the spring and summer seasons, upslope meteorological conditions result in more loading of nitrogen and sulfur to eastern slope locations. We have also been able to identify interannual patterns of chemical deposition related to total rain and snowfall.

**CURRENT STATUS OF THE TESTING AND EVALUATION OF ALTERNATIVE RAIN GAGES
FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM**

Laura L. Hult (Oak Ridge Associated Universities)
and John Gordon (USGS)
USGS-WRD
Denver Federal Center
Box 25046, MS 401
Denver, CO 80225

Continuing research and development within the rain gage industry has resulted in a variety of precipitation-measuring schemes, including vibrating wire technology, simulated tipping-buckets, and high-resolution weighing-type gages. Four of these recently developed precipitation gages -- the Belfort 3200, Eti NOAA II, Geonor Model T-200, and the Ott PLUVIO -- are currently being tested against the Belfort 5-780 and the National Weather Service 8" stick gage to identify potential replacements for the Belfort 5-780 rain gages presently in use by the National Atmospheric Deposition Program. Testing at the Hydrologic Instrumentation Facility (HIF) in Bay St. Louis, Miss. is being done in two phases. Phase I testing involves weekly indoor application of artificial rainfall to compare accuracy-versus-range for all gages in this study. Long-term performance of all study gages will be compared during 3 months of Phase II study at the HIF, where gages will be monitored weekly in a single outdoor environment. Phase III testing of all study gages under snow and ice conditions is planned, but contingent on funding. Phase I data, testing procedures and equipment will be presented along with Phase II testing procedures and site selection.

THE CHANGING PRECIPITATION CHEMISTRY PICTURE AND HYPOXIA IN THE GULF OF MEXICO - CONTEMPORARY APPLICATIONS OF NADP DATA

Robert Larson, Roger Claybrooke, Gary Stensland, and Van Bowersox
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820
blarson at sws.uiuc.edu

For 20 years, NADP has been measuring the concentrations of acids, nutrients, base cations, and salt in precipitation at nonurban U.S. sites. NADP data have been used to scope out the area receiving acid rain and to examine the countervailing effects of sulfate and nitrate versus ammonium and calcium in shaping the acid rain picture. Two questions being asked today are:

- Are recent changes in pollutant concentrations in precipitation consistent with emissions changes?
- Are the nutrients deposited by precipitation important in causing excess nutrients in rivers and estuarine waters?

We address the first question by showing the spatial distributions of 5-year average concentrations and displaying changes in these distributions over three time periods, 1985-89, 1990-94, and 1995-1997. Sulfate, nitrate, ammonium, and calcium maps are shown. Sulfur dioxide and nitrogen oxide emissions in these three time periods are also displayed. The largest reductions in sulfate concentrations in precipitation generally occurred in the northeastern United States, where the largest reductions in sulfur dioxide emissions also occurred. The changing pictures of each of these ions suggests how emissions patterns are evolving in the United States.

We address the second question by comparing the atmospheric deposition of nutrients from nitrate and ammonium with other nitrogen fluxes in the Mississippi River watershed. A zone of hypoxic water (dissolved oxygen <2mg/L) covering several thousand square miles of bottom water forms in the northern Gulf of Mexico during the warm season. Fish and shrimp cannot live in this hypoxic water. Nutrients borne by the waters of the Mississippi River stimulate the growth of algae in Gulf surface water. Oxygen is removed from the water column, leading to hypoxic conditions, when these algae descend and decay. This problem, hypoxia in the Gulf of Mexico, is currently the subject of a national assessment. Waste treatment facilities and manure and fertilizer applications are sources of nutrients in the Mississippi River Basin. Atmospheric deposition of nutrients, though smaller, is a significant source of nutrients that should not be ignored.

**A COMPARISON OF ELEVATIONALLY DIFFERENT, PAIRED NADP SITES
ON THE FRONT RANGE, COLORADO**

Mark Losleben, University of Colorado, Mountain Research Station

Nick Pepinn, University of Durham, UK

Bret Peterson, Meghan Pedden, Thomas Davinroy, Univ. of Colorado

Data from two NADP sites, located west of Boulder, CO, at 8300 feet and 11,500 feet elevation, are examined for temporal and chemical trends over their common time period, January 1986 to present.

The lower site, CO94, Sugarloaf is closer to the Denver urban corridor, and thus receives urban influenced air masses before the higher site, CO02, Niwot. The intuitive expectation is that Sugarloaf should have lower pH and higher conductivity compared to Niwot, and this may indeed be the case for the early portion of the record. Data suggest that this relationship may not be true at present.

To explore this possible change, this report presents a temporal comparison of the precipitation chemistry, as well as a look at possible changes in circulation patterns during this period, by developing circulation indices at several elevations.

**PROJECTED IMPACTS OF ACID DEPOSITION FOLLOWING PHASE I OF THE
1990 CLEAN AIR ACT AMENDMENTS**

Paul E. Miller
Maryland Department of Natural Resources
580 Taylor Avenue, C-2
Annapolis, MD 21401
pmiller@dnr.state.md.us

Mark T. Southerland, Nancy E. Roth, and Emily C. Rzemien
Versar, Inc.
9200 Rumsey Road
Columbia, MD 21045
rothnan@versar.com

James A. Lynch
Pennsylvania State University
311 Forest Resources Laboratory
University Park, PA 16802-4703
jal@psu.edu

Reductions in acid deposition have the potential to improve the condition of Maryland surface waters, particularly in small streams most susceptible to acidification. To evaluate changes in stream chemistry associated with implementation of the 1990 Clean Air Act Amendments Title IV, Phase I (CAAA), wet deposition patterns determined from a regional wet deposition model were compared to critical load estimates and results from the 1995-97 Maryland Biological Stream Survey (MBSS). Critical loads were estimated from modeled source/receptor relationships at 73 streams in the state using resident fish species as indicator organisms. The results of this analysis suggest that critical loads continue to be exceeded in some areas of the state despite reductions in sulfate deposition. Above average precipitation amounts in 1996 contributed to sulfate deposition in excess of critical loads in a number of sensitive areas. Fish communities in affected areas exhibited low species richness and abundance; in cases with extremely low pH, fish were absent. Although Phase I results are encouraging, it is unlikely that complete implementation of Title IV will eliminate the acidification problems in some Maryland streams.

**MAJOR ION AND TRACE ELEMENT BUDGETS FOR A FORESTED WATERSHED IN
WESTERN MARYLAND**

John Sherwell
Power Plant Research Program
Maryland Department of Natural Resources
Tawes Building B-3
Annapolis, MD 21401
jsherwell@dnr.state.md.us

Mark Castro
Appalachian Laboratory
University of Maryland Center for Environmental Science
Frostburg, MD 21532

This study reports on the movement of major ions in a completely forested watershed that receives some of the highest atmospheric deposition rates in North America. Wet deposition was measured daily and throughfall inputs and stream water outputs on a weekly basis for the period June 1996 through May 1997. Sulfate was the dominant anion in wet deposition, throughfall and stream water. Hydrogen was the dominant cation in wet deposition, while potassium was dominant in throughfall and calcium in stream water. Input-output budgets suggest that the watershed is a net source of SO_4^{2-} , Na^+ , Ca^{2+} and Mg^{2+} , and a sink for H^+ , K^+ , NH_4^+ and NO_3^- . Results from an on-going measurement program that includes a suite of heavy metals will also be presented.

PREDICTION OF AMBIENT PM_{2.5} CONCENTRATIONS IN MARYLAND

John Sherwell
Power Plant Research Program
Maryland Department of Natural Resources
Tawes Building, B-3
Annapolis, Md 21401
Jsherwell@dnr.state.md.us

Kenneth Walsh and Richard Gardner
Science Applications International Corporation
615 Oberlin Rd., Suite 300
Raleigh, NC 27601

On July 18, 1997 the US EPA promulgated a Final Rule on the National Ambient Air Quality Standards (NAAQS) for Particulate Matter that added two standards to address particulate matter with an aerodynamic diameter of less than 2.5 microns. The State of Maryland currently has no Federal Reference Method data on particulate matter less than 2.5 microns (PM_{2.5}) but does have annual ambient data for particulate matter smaller than 10 microns (PM₁₀) at 24 sites. This study reports on an prediction, based on this PM₁₀ data, of annual average and seasonal high PM_{2.5} concentrations at the PM₁₀ monitor sites for the period 1992 to 1996. The method uses annual and seasonal ZIP code-level primary PM emission inventories and the speciated PM_{2.5} data from four nearby monitors in the IMPROVE network (located in National Parks and wilderness areas). All the seasonal high concentrations are predicted to be less than the 24-hour PM_{2.5} NAAQS of 65 $\mu\text{g}/\text{m}^3$. The projections indicate that twelve monitor sites might exceed the three-year annual average PM_{2.5} NAAQS of 15 $\mu\text{g}/\text{m}^3$.

SOME HISTORICAL ASPECTS OF THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

Gary J. Stensland and Sarah C. Milton
Illinois State Water Survey
2204 Griffith Drive, Champaign, IL 61820

1998 marks the 20th year of operation for the National Atmospheric Deposition Program (NADP.) Over the years the program has gone through several changes and improvements. It has grown from a small network of just 22 sites, to its current size of 198 active sites in the U.S., Canada, Puerto Rico, and the U.S. Virgin Islands. Improvements have been made in sampling methods at the sites, quality assurance programs, and the facilities at the Central Analytical Laboratory (CAL.) The dramatic changes in computer technology over the last 20 years have had a tremendous impact on the way data are managed by the CAL and the Coordination Office, and on the availability of data to users.

The greatest achievement of the program, however, is how *little* it has changed. Equipment used at the sites today is the same equipment used when the program started, siting criteria have remained the same, and sample analysis procedures at the CAL are virtually unchanged. This poster highlights the stability of the NADP by focusing on the few major changes in the program, the longevity of the sites, and the longevity of site operators. Other topics include the growth of the network through the addition of new sites, the locations of past NADP meetings, and past committee chairmen. The poster will also give an overview of the topics that have stirred up the most discussion and controversy at NADP meetings, such as, the use of field pH data, the use of contour maps to present data, what to do about sites that do not follow all siting rules, and whether the NADP should continue to collect dry deposition samples.

**WET DEPOSITION OF TOTAL MERCURY AT MERCURY DEPOSITION NETWORK (MDN)
SITES IN 1996 AND 1997**

Clyde Sweet
Illinois State Water Survey

Eric Prestbo
Bob Brunette
Frontier Geosciences Inc

The Mercury Deposition Network (MDN) is an NADP subnetwork collecting weekly precipitation samples for analysis of total mercury. During 1996 and 1997, the first two years of official MDN operation, 34 sites in the US and Canada were active for at least part of this period. Of these, 14 were collocated with NADP/NTN sites. The samples are collected with an all glass sampling train in a modified Aerochem Metrics sampler using special handling techniques. Analysis is by cold vapor atomic fluorescence spectroscopy at Frontier Geosciences Inc., a laboratory nationally recognized for ultra-trace mercury analysis. For the whole network, the average concentration of total mercury in collected precipitation is about 12 ng/L and the average deposition is about 100 ng/m²/week. Concentration and deposition values vary by about a factor of 3 between the highest and lowest locations. In eastern North America, deposition of total mercury is about twice as high during the summer as it is in the winter. This is due to both higher concentrations of mercury and higher precipitation amounts during the summer months.

COMPARISON OF IONIC CONCENTRATIONS IN RAIN AT THREE GEORGIA LOCATIONS OVER THIRTEEN YEARS

J.T. Walker and J.B. Melin
Department of Plant Pathology
University of Georgia
College of Agricultural and Environmental Sciences
Griffin Campus, Griffin, GA 30223-1797

The ionic constituents of precipitation at the three widely separated NADP sites in Georgia indicate slight differences between volume-weighted concentrations of nine ions over the last thirteen years. Sulfate concentrations were highest at the Georgia Station site (GA41), 64 kilometers south of Atlanta, followed by Belville (GA20), and lowest at Tifton/Chula (GA50/GA99), the southernmost site, 309 kilometers south of Atlanta in the Coastal Plain. Nitrate concentrations were similar at the Georgia Station and Belville locations, but lower at Tifton/Chula. Ammonium and calcium ion concentrations differed little among the three locations. Potassium concentrations were higher at Belville than at the other two locations. Sodium and chloride concentrations were higher at Belville and Tifton/Chula than at the Georgia Station. The pH of rain at the Georgia Station has increased over the period from a low of 4.43 to 4.79, whereas the pH at the Tifton\Chula collection point has changed less (0.17). The pH of rain at Belville ranged from 4.54 to 4.82. The 13-year average rainfall at Georgia Station and Belville was identical, although the annual amounts varied between the two locations. The Tifton/Chula location recorded greater rainfall approximately 50 percent of the time; the 13 year average was only 4 cm greater than that of the Georgia Station and Belville sites. Compiling ionic deposition data provides a scientific basis for understanding any long term environmental changes that could impact the state's agro-forestry industry. The results will be presented graphically.

**ANNUAL SULFUR AND NITROGEN, WET AND DRY DEPOSITION IN
SNOWY RANGE WYOMING**

Karl Zeller,
USDA Forest Service
240 W. Prospect
Ft. Collins, CO 80526

The collocation of three national networked programs NADP, EPA's CASTNET, and the Forest Service's IMPROVE Module A, within a few hundred meters of each other in the Medicine Bow forest of Wyoming has made it possible to assess the total amount of deposition, both wet and dry in this alpine ecosystem. Wet deposition assessed using NADP data accounts for 1 to a little over 3 kg ha⁻¹ for both nitrogen and sulfur, however annual trends for the two species differ. Dry deposition assessed using both CASTNET (a.k.a. NDDN) and IMPROVE demonstrates 1 to 2 kg ha⁻¹ for nitrogen but less than 1 for sulfur. The over all trend of wet plus dry for nitrogen has been downward from 5 kg ha⁻¹ in 1989 to 3.6 kg ha⁻¹ in 1994, while varying between 2 and under 4 kg ha⁻¹ for sulfur. This analysis presents the site, the three programs and the analysis approach. An analysis of the weekly data from two separate Medicine Bow NADP sites, 15 km separation horizontally and 3000 ft vertically demonstrates that winter season data requires careful analysis due to the vagaries of proper collection during high winds and snow fall.