# Proceedings

## **NADP Fall Meeting and Scientific Symposium**

## Climate Change Impacts on Air Quality

October 23-27, 2023

Madison, WI

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National Atmospheric Deposition



e-agenda(html)

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## **Meeting Information and Acknowledgements**

## Locations

October 23-24, 2023 Fall Meeting will be held at the UW-Madison Pyle Center (702 Langdon St, Madison, WI) October 25-26, 2023 Scientific Symposium will be held at the Fluno Center (601 University Ave, Madison, WI)

## **UW-Madison Land Acknowledgement**

The University of Wisconsin–Madison occupies ancestral Ho-Chunk land, a place their nation has called Teejop (day-JOPE) since time immemorial.

In an 1832 treaty, the Ho-Chunk were forced to cede this territory.

Decades of ethnic cleansing followed when both the federal and state government repeatedly, but unsuccessfully, sought to forcibly remove the Ho-Chunk from Wisconsin.

This history of colonization informs our shared future of collaboration and innovation.

Today, UW–Madison respects the inherent sovereignty of the Ho-Chunk Nation, along with the eleven other First Nations of Wisconsin.

## Acknowledgements

The NADP Program Office would like to thank the following people for their support of and contributions to the 2023 Fall Meeting and Scientific Symposium:

Dr. Michael Bell, Scientific Symposium Chair Holly Bender, Sierra Club, Keynote Speaker NADP Executive Committee

In addition, we thank everyone who submitted abstracts and for sharing their research. The use of NADP data by researchers and policymakers is what has made NADP successful for the past 45+ years and will continue to do so for many years to come.

## Message from the NADP Scientific Symposium Chair

As a "plant guy", one of my favorite parts of the NADP calendar is looking in the backgrounds to see what vegetation communities exist at a site. My introduction to NADP came in 2004 in the lava fields of Craters of the Moon National Monument where I assisted in collecting data from ID03. Coming from southern California I was familiar with air pollution but didn't expect it to be an issue in the remote blue skies of Idaho. The next year, I became the site operator at CA67 at Joshua Tree National Park where I learned that air pollution from Los Angeles was not only blowing into the desert, but also causing shifts in the plant communities within the park. It's now been 20 years since I collected that first bucket and have dedicated my career to understanding the relationship between atmospheric deposition and ecosystem response.



Since joining the NPS Air Resources Division almost 9 years ago, I have had the opportunity to visit many more NADP sites and explore the impacts to plants, soils, waters, and the creatures within. With the growing threat of climate change, emerging pollutants such as microplastics and PFAS, and the shifts in nitrogen emissions towards agricultural sources, the NADP monitoring networks have never been more important to help protect our local ecosystems. The long-term data that we collect, analyze, and distribute is crucial to identifying how precipitation patterns are shifting across the country and how this changes what and how much we collect in our samplers. Additionally, each site—whether clean/dirty or sensitive/resilient-contributes to our maps and models that are helping us fortify the networks under the strain of budget

cuts and new pollution sources. While the world changes around us, I am forever grateful to the site operators who stay consistent and are out in the field every Tuesday collecting bags and making the rest of our work possible. Not a day goes by that I use NADP data that I don't think of my drive out to Blackrock and the surrounding ecosystem that my little bucket helped protect. Thank you all for the work you do to support NADP and your contribution to cleaning our air.

I chose the theme "Climate Change Impacts on Air Quality" for the symposium, because after a year of record-breaking temperatures, flooding in cities around the world, and smoke-filled air from Canadian wildfires I believe that it is imperative for us to be intentional about integrating expected climate changes into our models, monitoring strategies, and ecosystem effects studies. Understanding the overlapping impacts and future deposition hotspots will help us continue to be a leader in identifying sources and impacts of air pollution into the future. I am excited about the lineup of talks that we have at the symposium and am grateful to all the researchers for taking the time to share their work with us this week.

Mike Bell, National Park Service

Vice-Chair of the Executive Committee

## Agenda

## **Climate Change Impacts on Air Quality**

## Note all times are in CDT

## **Technical and Science Committee Meetings**

## Monday, October 23, 2023

8:00 AM – 9:00 AM	New to NADP Orientation – Welcome session for students and first time attendees to NADP Fall Meeting
9:00 AM – 10:00 AM	Joint Session (Part 1) Room 209
10:30 AM – 12:30 PM	Aeroallergen Science Monitoring Committee (AMSC) Meeting Room 232
	Critical Loads of Atmospheric Deposition (CLAD) Meeting Room 209
12:30 PM-2:00 PM	Lunch (On your own)
2:00 PM – 5:00 PM	CLAD Working Groups Room 209
2:00 PM – 5:30 PM	Network Operations Subcommittee (NOS) Meeting Room 232
Tuesday, October 24, 20	23
8:00 AM – 9:00 AM	Education and Outreach Subcommittee (EOS) Meeting Room 209
8:30 AM – 12:00 PM	Total Deposition Science Committee (TDep) Meeting Room 232
9:00 AM – 12:00 PM	Mercury in the Environment and Links to Deposition (MELD) Meeting Room 209
12:00 PM – 1:30 PM	Lunch (On your own)
1:30 PM – 3:15 PM	Joint Session (Part 2) Room 209



3:30 PM -6:00 PM **Executive Committee Meeting** Room 232

## **Scientific Symposium**

## Wednesday, October 25, 2023

8:00 AM – 8:15 AM	Welcome and logistics; Room Howard Auditorium
	Opening of Symposium, Michael Bell, National Park Service Welcome, Jamie Schauer, Director Wisconsin State Laboratory of Hygiene
8:15 AM – 8:45 AM	Annual State of the NADP Address, David Gay, Coordinator
8:45 AM – 9:40 AM	Keynote Address: From Air Modeling to Advocacy: How Data-Informed Campaigning Achieves Climate and Clean Air Wins. Holly Bender, Chief Energy Officer, Sierra Club
9:40 AM – 10:00 AM	Break

## Session 1: Ecological effects of deposition and climate change

Co-Chairs: Nifer Wilkening (US FWS)

10:00 AM – 10:20 AM	Emmi Felker-Quinn (NPS) - Ozone Effects on Tree Growth and Survival in the United States
10:20 AM – 10:40 AM (Virtual)	Rob Smith (Washington State University) - Air quality improvements to offset climate warming effects
10:40 AM – 11:00 AM	Jennifer L. Wilkening (U.S. FWS) - Monitoring Air Quality Impacts with Students
11:00 AM – 11:20 AM	Beck Dalton (U.S. EPA) - Soil microbial community response to nitrogen addition experiments under climate change: a meta-analysis
11:20 PM – 11:40 AM	Todd McDonnell (E&S Environmental) - <i>Effects of Climate Change and Atmospheric</i> <i>Nitrogen Deposition on Forest Understory Vegetation Communities in U.S. National</i> <i>Parks</i>
11:40 AM – 12:00 PM	Linda Pardo (USDA Forest Service) - <i>Moderated discussion with session presenters on critical loads, climate, and conservation</i>
12:00 PM – 1:30 PM	Lunch Break (on your own)

## Session 2: Emerging measurements and effects of aeroallergens and wildfire smoke

Chairs: Selma Isil (WSP USA)

1:30 PM – 1:50 PM	Terri Williams (WSLH) - Atmospheric Pollen Measurements in Ambient Air
1:50 PM – 2:10 PM	Katherine Benedict (Los Alamos National Laboratory) - Characterization of bioaerosol emissions from prescribed fires and laboratory burns
2:10 PM – 2:30 PM	Ross Edwards (University of Wisconsin-Madison) Impact of 2023 Wildfire Smoke on Black Carbon in Great Lake Waters
2:30 PM – 2:50 PM	Christopher Lawrence (University of Albany) - Impacts of Transported Wildfire Smoke on the Whiteface Mountain Aqueous Chemical System
2:50 PM – 3:10 PM	Break

## Session 3: Deposition and effects of mercury, toxics, and hazardous air pollutants - Part 1

Chair: David Schmeltz (US EPA) and Collin Eagles-Smith (USGS)

3:10 PM – 3:30 PM (Virtual)	Ting Wing (UMass Lowell) - Atmosphere-surface exchange of gaseous elemental mercury (GEM) in a salt marsh estuary in Massachusetts, USA
3:30 PM – 3:50 PM	Eric Roy (UMass Lowell, MIT) - Use of atmospheric concentration and passive sampler measurements for assessing gaseous elemental mercury exchange at two unpolluted forest sites
3:50 PM – 4:10 PM (Virtual)	Isabella Garrioch (Umeå University) - Understanding Mercury Gaseous Fluxes at Marcell and the SPRUCE experiment Grand Rapids, Minnesota
4:10 PM – 4:30 PM (Virtual)	Guey-Rong Sheu (National Central University) - Climatic regulation of atmospheric mercury concentrations at the Lulin Atmospheric Background Station (LABS) in Taiwan
4:30 PM – 4:50 PM (Virtual)	Peter Weiss-Penzias (UC Santa Cruz) - Investigating the effect of precipitation on airborne reactive mercury washout at Storm Peak Laboratory, Colorado and at sixteen co-located sites in the Atmospheric Mercury (AMNet) and Mercury Deposition (MDN) Networks
4:50 PM – 5:10 PM (Virtual)	Ashley Smith (USGS) - Measuring atmospheric deposition of PFAS in throughfall in an urban environment, Bronx, NY

6:30 PM – 8:30 PM Poster Session – Alumni Lounge, Pyle Center Chair: Michael D. Bell (National Park Service)

## Thursday October 26, 2023

## Session 4: Advances in measurements of atmospheric pollution - Part 1

Chair: Bret Schichtel (NPS) and Winston Luke (NOAA)

8:00 AM – 8:20 AM (Virtual)	Umesh Chandra Kulshrestha (Jawaharlal Nehru University New Delhi) - Measurements of Precipitation Acidity and Reactive Nitrogen Species in South Asia under UKRI-GCRF South Asian Nitrogen Hub
8:20 AM – 8:40 AM (Virtual)	Anshu Sharma (Jawaharlal Nehru University) - Deposition of Reactive Nitrogen Species Through Snow in Western Himalayan Region of India
8:40 AM – 9:00 AM	John T. Walker (U.S. EPA) - Long-term measurements of atmospheric reactive nitrogen at a suburban forest site in the southeastern US
9:00 AM – 9:20 AM (Virtual)	Nate Topie (WSP USA Environment & Infrastructure, Inc.) - <i>Water Soluble Organic</i> <i>Nitrogen Characterization Study</i>
9:20 AM – 9:40 AM	Adam M. Deitsch (NOAA/University at Albany) - A Comparison of Persistent Pollutant Concentrations in Cloud and Rainwater Collected in the Adirondack Mountains
9:40 AM – 10:00 AM	Archana Tripathy (SUNY Albany) - Organic Acids in Cloud Water, Aerosols, and Cloud Droplet Residuals at the Summit of Whiteface Mountain 2018-2023

10:00 AM – 10:20 AM Break

## Session 5: Modeling atmospheric concentrations and deposition

10:20 AM – 10:40 AM	B.H. Baek (George Mason University) - Ammonia Emissions Enhancements with Deep Neural Network CTM and Remote-sensing Observations
10:40 AM – 11:00 AM	Lillian Naimie (Colorado State University) - Contributions of Ammonia Dry Deposition to Excess Nitrogen Deposition in Rocky Mountain National Park
11:00 AM – 11:20 AM	Colleen Baublitz (U.S. EPA) - Inferential modeling of dry deposition fluxes across the Ammonia Monitoring Network (AMoN)
11:20 AM – 11:40 AM	Bret Schichtel (NPS) - US Spatial Patterns of Ammonia Dry Deposition Velocities derived from CMAQ and CAMx Chemical Transport Models

## Session 5: Modeling atmospheric concentrations and deposition (continued)

- 11:40 AM 12:00 PM Krish Vijayaraghavan (Ramboll) PFAS Atmospheric Deposition Modeling
- 12:00 PM 1:30 PM Lunch Break (on your own)

## Session 6: Deposition and effects of mercury, toxics, and hazardous air pollutants - Part 2

Chair: David Schmeltz (US EPA) and Collin Eagles-Smith (USGS)

1:30 PM – 1:50 PM	Ryan Lepak (U.S. EPA ORD GLTED) - Drivers of mercury contamination, methylmercury formation and mercury sources within lake sediments across the contiguous United States
1:50 PM – 2:10 PM	Grace Armstrong (U.S. Geological Survey, University of Wisconsin-Madison) - Mercury in the Great Lakes: How Ecosystem Pressures Influence Mercury Cycling
2:10 PM – 2:30 PM	Vivien Taylor (Dartmouth College) - Environmental drivers of mercury bioaccumulation in the deep and shallow basins of Lake Champlain
2:30 PM – 2:50 PM	Hannah R. Miller (University of Colorado Boulder) - Mercury cycling in high elevation wetlands of the western U.S.: storage, transformations, and transport
2:50 PM – 3:10 PM	Christopher Kotalik (USGS) - Mercury Stable Isotopes in Dragonflies Reveal Habitat and Geographic Drivers of Mercury Entry into Aquatic Food Webs
3:10 PM – 3:30 PM	Break

## Session 7: Advances in measurements of atmospheric pollution – Part 2

Chair: Bret Schichtel (NPS) and Winston Luke (NOAA)

3:30 PM – 3:50 PM	Dane Blanchard (Trent University) - Atmospheric deposition of chromophoric dissolved organic matter throughout the Athabasca Oil Sands Region, Alberta, Canada.
3:50 PM – 4:10 PM	Michael McHale (USGS) - A new method for trend detection in precipitation chemistry: Weighted Regression for Time Precipitation and Season
4:10 PM – 4:30 PM	Rodolfo Sosa Echeverría (Universidad Nacional Autónoma de México) - After more than 20 years evaluating wet atmospheric deposition in Mexico, main findings and challenges
4:30 PM – 4:50 PM (Virtual)	Anam M. Khan (University of Wisconsin-Madison) - <i>Monitoring the stomatal</i> component of tropospheric ozone dry deposition over an agricultural field in central Illinois

## Session 7: Advances in measurements of atmospheric pollution – Part 2 (continued)

4:50 PM – 5:10 PM	Jian Feng (Environment and Climate Change Canada) - <i>Causes of springtime-</i> maximum and long-term trends of ground-level ozone in the eastern United States and Canada for 1990-2019
5:10 PM – 5:30 PM (Virtual)	Mae Gustin (University of Nevada-Reno) - What is the utility of measuring gaseous HgII dry deposition using Aerohead samplers?
5:30 PM	Symposium Closing Remarks

## From Air Modeling to Advocacy: How Data-Informed Campaigning Achieves Climate and Clean Air Wins

## Holly Bender Chief Energy Officer, Sierra Club Wednesday October 25, 2023 8:45 AM

As Chief Energy Officer, Holly brings more than 15 years of experience building winning strategic campaigns to address the climate crisis, including 12 years working on and helping to lead the Sierra Club's Beyond Coal Campaign, which Politico described as the most extensive and effective campaign in the history of the Sierra Club and the environmental movement. Holly leads a team of Campaign Directors, Analysts, and Campaign Strategists who are responsible for developing the Sierra Club's climate strategy through to the transformation of our energy systems away from fossil fuels to clean energy.



Holly grew up in Vermont, and spent her childhood hiking, canoeing, and exploring in the woods behind her house. A toxic

chemical spill left her childhood home with dangerous levels of indoor air pollution, and at age eight, Holly knew she wanted to become a lawyer working with other families impacted by pollution. Holly became an attorney, and after internships working on environmental justice and air pollution, Holly started at the Sierra Club in the Environmental Law Program managing the organization's litigation approval docket on issues ranging from endangered species protection to regulating toxic chemicals in consumer products. Over 15 years, Holly has held positions as a regional and national campaign leader with a focus on building teams and driving winning strategies that have a meaningful impact on people's lives.

Holly lives in Madison, Wisconsin with her husband Dave (a fellow clean energy lawyer) and their two daughters Hazel and Margot.

## **2023 NADP Site Operator Awards**

## **30 Year Awards**

Site Code	Operator Name	Site Name	Funding Agency	Networks	Start
ME98	Bill Gawley	Acadia National Park-McFarland Hill	National Park Service	MDN, NTN	1993
PA15	Robert Ziegler	Penn State	National Oceanic and Atmospheric Administration	NTN	1993

## 25 Year Awards

Site Code	Operator Name	Site Name	Funding Agency	Networks	Start
GA99	Charles Welsh	Chula	U.S. Geological Survey	NTN	1998
MT96	Linda Weeks Connor	Poplar River	Fort Peck Tribes	NTN	1998
NM08	Linda Madron	Mayhill	U.S. Geological Survey	NTN	1998
PR20	John E. Bithorn	El Verde	USDA-Forest Service/U.S. Geological Survey	MDN, NTN, AMoN	1998

## 20 Year Awards

Site Code	Operator Name	Site Name	Funding Agency	Networks	Start
MI51	Denise Dickson	Unionville	WSP USA-U.S. Environmental Protection Agency	NTN, AMoN	2003
WY00	John Korfmacher	Snowy Range	USDA-Forest Service	NTN	2003
WY95	John Korfmacher	Brooklyn Lake	USDA-Forest Service/WSP USA- U.S. Environmental Protection Agency	NTN, AMoN	2003



## **15 Year Awards**

Site Code	Operator Name	Site Name	Funding Agency	Networks	Start
MI48	Jim Patton	Seney National Wildlife Refuge- Headquarters	U.S. Fish and Wildlife Service	MDN, NTN, MLN	2008
ND08	Janna Robinson	Icelandic State Park	U.S. Geological Survey	NTN	2008
NY06	Sergio Fleishaker	Bronx	New York State Energy Research and Development Authority (NYSERDA)/New York State Department of Environmental Conservation	MDN, NTN	2013

## **10 Year Awards**

Site Code	Operator Name	Site Name	Funding Agency	Networks	Start
CO21	Steven Alton	Manitou	USDA-Forest Service	NTN	2013
CO96	Bob Brantlinger	Molas Pass	USDA-Forest Service	MDN, NTN	2013
IN21	Michael A. Dalgleish	Clifty Falls State Park	Lake Michigan Air Directors Consortium (LADCO)	MDN, MLN	2013
ME94	Martin Dana	Indian Township	Passamaquoady Tribe	NTN	2013
NC35	Deborah Kennedy	Clinton Crops Research Station	North Carolina State University	NTN	2013

## **5 Year Awards**

Site Code	Operator Name	Site Name	Funding Agency	Networks	Start
AK97	Paul Gabriel	Katmai National Park - King Salmon	National Park Service	NTN	2018
CO98	Tim Weinmann	Rocky Mountain National Park-Loch Vale	U.S. Geological Survey-Ft. Collins/National Park Service	NTN, AMoN	2018
CO99	Andrew Spear	Mesa Verde National Park-Chapin Mesa	U.S. Geological Survey	MDN, NTN	2018
KS31	Amanda Kuhl	Konza Prairie	Kansas State University/WSP USA-U.S. Environmental Protection Agency	NTN, AMoN	2018
MD99	Phillip Stratton	Beltsville	Maryland Department of Natural Resources/National Oceanic and Atmospheric Administration	MDN, NTN, AMoN, MLN	2018
ME00	James Gramlich	Caribou	Maine Department of Environmental Protection	MDN, NTN	2018
NC26	Patricia Perry	Candor	North Carolina Department of Environmental Quality	AMON	2018
NC35	Mark Barnes	Clinton Crops Research Station	WSP USA-U.S. Environmental Protection Agency	AMON	2018
NY10	Dr Courtney Wigdahl-Perry	Chautauqua	U.S. Geological Survey	NTN	2018
NY20	James Mills	Huntington Wildlife	New York State Energy Research and Development Authority (NYSERDA)	MDN, NTN, AMoN, AMNet, MLN	2018
NY99	Kate Terlizzi	West Point	U.S. Geological Survey	NTN	2018
SC05	Jerry Tupacz	Cape Romain National Wildlife Refuge	U.S. Fish and Wildlife Service	MDN, NTN, AMoN, MLN	2018
UT98	Dale Roundy	Green River	U.S. Geological Survey	NTN	2018
VA99	Danny Wright	Natural Bridge Station	USDA-Forest Service	NTN	2018
WI01	Nathan Kilger	Odanah	The Bad River Band of Lake Superior Chippewa Tribe	AMoN, MLN	2018

## Abstracts

Session 1: Ecological effects of deposition and climate change



#### **Ozone Effects on Tree Growth and Survival in the United States**

## **<u>Emmi Felker-Quinn</u>**<sup>1\*</sup>, Kris Novak<sup>2</sup>, Jeffrey Herrick<sup>2</sup>, Kemen Austen<sup>3</sup>, Marwa Salem<sup>3</sup>, Jennifer Phelan<sup>3</sup>, and Chris Clark<sup>2</sup>

The effects of deposition upon particular tree species can determine the resilience of forests in the face of other anthropogenic stressors like climate change. Critical loads determined by Horn et al (2018) have allowed NPS to describe the effects of nitrogen and sulfur deposition upon tree growth and tree survival for widespread and abundant tree species. We have followed the approach of Horn et al, testing and comparing multiple models for tree growth and survival using the USFS Forest Inventory and Analysis data. However, we have expanded the models to include a more flexible range of responses to N and S deposition as well as tree response to ozone exposure. We have also relaxed the minimum number of individuals that allow a species to be included in the analysis: Horn et al used at least 2000 individuals, and this analysis uses a minimum of 500 individuals per species. As a result, the analysis tests 399 tree species for air pollution effects in the context of climate and competition controls on growth and survival. This presentation will focus on ozone effects.

153 tree species have some relationship of growth to air pollution, and more than half (83 species) have an ozone term in their winning model for tree growth. 142 tree species have some relationship of 10-year survival rate to air pollution, and about a quarter (38 species) have an ozone term in their winning model for tree survival. Species whose ozone sensitivity has been well-documented by other research, including redwood, ponderosa pine, and quaking aspen, have ozone sensitive models for growth or survival, while black cherry does not. All eight of the Western US's most abundant tree species have a winning model for tree growth or survival which includes an ozone term. This presentation will detail model selection decisions and present ozone critical levels for tree growth and tree survival.

<sup>1</sup>National Park Service

- <sup>2</sup> U.S. Environmental Protection Agency
- <sup>3</sup> RTI International

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#### Air quality improvements to offset climate warming effects

## Robert J. Smith<sup>1,2\*</sup> and Linda H. Geiser<sup>2</sup>

Shifting climate and pollution regimes often result in vegetation shifts most pronounced among sensitive bioindicators. For lichen communities systematically surveyed at 8000+ sites nationwide, we calculated lichen community "airscores" based on species' collective deposition tolerances at each site. Regression surfaces revealed that lichen site scores increased nonlinearly with both deposition and climate warming. We applied various policy scenarios to the regression surfaces. From this, we estimated that modest air-quality improvements (lowered reactive-N deposition of just 0.2-2.0 kg N ha-1 y-1) could help offset the community-level effects of climate warming expected in the next century. Creative solutions to maintain deposition below critical loads would help sustain the unique contributions of lichen communities to forest ecosystem functioning and climate resilience at landscape scale.

<sup>1</sup> Office of Strategy, Planning and Analysis, Washington State University
<sup>2</sup> USDA Forest Service, Air Resource Management Program

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## Unveiling environmental shifts: Investigating potential climate change effects on air and water quality in the National Wildlife Refuge System

## Jennifer L Wilkening<sup>1\*</sup>, Catherine Collins<sup>1</sup>, Tim Allen<sup>1</sup>, Chad Abel, Tara Gracer, Dominic Libera<sup>1</sup>, Jaron Ming

Climate change has the potential to alter air quality patterns, since many of the drivers (e.g., emission, transport, dilution, deposition) are influenced by weather variables such as temperature, humidity, and wind speed and direction. The duration and frequency of extreme events like heat waves is projected to increase, and this may directly result in higher concentrations of air pollution in many regions. Air quality may be worsened by various indirect climate change effects, such as more particulate matter from larger and more frequent fires, increased emissions due to increased energy consumption, and larger amounts of airborne pollens and molds. Likewise, water quality may be affected by climate change. Higher water temperatures and increased drought frequency and severity may exacerbate water pollution in some areas while increased precipitation and flooding may improve it in other regions. The ability of fish and wildlife to tolerate climate change effects such as elevated air and water temperatures may be impaired with co-exposure to increased pollutants, but specific responses are largely unknown for many species. Native plant species may be more susceptible to the effects of air pollution and increases may cause heightened growth of non-desirable invasive species.

Here we examine how climate change may affect trust resources managed by the National Wildlife Refuge System (NWRS). The NWRS is the largest network of lands and waters (856 million acres) conserved specifically for fish, wildlife, and their habitats. NWRS areas (i.e., refuges) can be found in every U.S. state and many territories, providing a continental scale system of conservation. First, we selected several refuges located in geographically diverse areas characterized by different climate change effects (i.e., increased drought vs increased flooding) to serve as case studies. Next, we utilized the Climate Toolbox (climatetoolbox.org) to visualize projected changes in multiple temperature and precipitation metrics for each refuge. We selected the refuge boundary as the geographical area of interest and used 20 CMIP5 climate models and 2 emission scenarios (RCP 4.5 and 8.5) downscaled to a ~4 km resolution. Then, we explored how projected changes may influence air and water quality condition for fish, wildlife, and their habitats for each case study refuge. We evaluated the Air Conditions and Trends database to give an historical perspective for various pollutants. Utilizing these tools, we are able to provide results and a blueprint for refuge managers to incorporate air and water quality considerations into conservation planning efforts.

<sup>1</sup>U.S. Fish and Wildlife Service

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#### Soil microbial community response to nitrogen addition experiments under climate change: a meta-analysis

#### Rebecca M. Dalton<sup>1</sup> and Tara L. Greaver<sup>1</sup>

Atmospheric nitrogen (N) deposition from fossil fuel combustion, land-use change, and fertilizer application has been linked to significant changes in ecosystems. Anthropogenic N addition to terrestrial ecosystems has led to modifications in soil nutrient cycling processes and shifts in soil microbial community structure. Nitrogen deposition and climate change impact ecosystems simultaneously; therefore, understanding how climate mediates microbial community response to N deposition is necessary for informing critical load thresholds important for management and policy decisions. First, we synthesized recently published meta-analyses to determine whether microbial communities naturally occurring in more extreme climatic conditions (e.g., low precipitation, high temperature) were more sensitive to N deposition than communities under milder environmental conditions. We then searched the literature for studies which manipulated N deposition and at least one climate factor (e.g., increased temperature, reduced/supplemental precipitation, or elevated CO2) to determine whether experimental manipulations of climate provide consistent results with observational approaches. We used a multivariate, hierarchical Bayesian meta-analysis approach to examine whether microbial abundances and diversity responses to N deposition were modified under changes in temperature, precipitation, or elevated CO2.

We extracted ~3600 data points on microbial abundance and diversity indices from 65 studies published between 1990 and 2022. In a preliminary analysis, we found that across all studies, experimental N addition resulted in an increase in overall archaeal and fungal abundance, while bacterial abundance decreased under N addition. These shifts in abundance resulted in an increase in fungi to bacteria (F:B) ratio under N deposition. In contrast, previous meta-analyses have reported greater negative effects of N addition on fungal abundances relative to bacterial abundances, consequently leading to a negative effect on F:B ratio. Secondly, we found that on average, climate manipulations slightly influenced microbial community response to N deposition. For example, communities experiencing both an increase in temperature and N addition were less likely to exhibit significant changes in bacterial abundance, fungal abundance, and subsequently F:B ratio than communities receiving supplemental N alone. Interestingly, supplemental precipitation led to a slight increase in both fungal and bacterial abundances relative to controls, but when supplemental precipitation was combined with N deposition, the microbial community composition was similar to control communities. We will continue examining the relative effects of climate, length of experiment, and ecosystem characteristics (temperature, precipitation) on microbial community response to N deposition.

- <sup>1</sup>Environmental Protection Agency
- \* Corresponding author: dalton.rebecca@epa.gov

Disclaimer: The views expressed in this abstract are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

## Effects of Climate Change and Atmospheric Nitrogen Deposition on Forest Understory Vegetation Communities in U.S. National Parks

Todd McDonnell<sup>1\*</sup>, Michael D. Bell<sup>2</sup>, and Emmi Felker-Quinn<sup>2</sup>

Emissions of greenhouse gases, ammonium (NH4), nitrate (NO3), and other nitrogen (N)-containing pollutants can result in elevated N deposition and climate change, which can lead to adverse effects on biodiversity. The National Park Service (NPS) is legislatively mandated to protect park resources from adverse impacts caused by air pollution and sustain unimpaired conditions for future generations. More than 1,500 statistical models for estimating the probability of plant species occurrence according to environmental drivers such as N deposition and air temperature have been developed and used for site-level applications in eastern U.S. forests (US-PROPS; McDonnell et al. 2020). Based on a case study at Great Smoky Mountains National Park (McDonnell et al. 2022), this expansive set of vegetation response models has been used to characterize critical loads of N deposition and climate change effects on understory vegetation across eight NPS units: Acadia NP, Glacier NP, Grand Teton NP, Joshua Tree NP, Rocky Mountain NP, Sleeping Bear Dunes National Lakeshore, Theodore Roosevelt NP, and Yosemite NP. Critical loads of atmospheric N deposition were less than 5 kg N/ha/yr for the vast majority of vegetation species and map classes represented by these eight NPS units. Protection of the most sensitive species within vegetation classes typically requires N deposition to be lower than 2.5 kg N/ha/yr. Projected increases in air temperature were shown to have predominantly negative effects on the vegetation communities considered, particularly for mountainous NPS units. Results indicate that with increasing temperatures it will not be possible to reduce N deposition to levels that maintain current community composition and function, though reductions in atmospheric N deposition and greenhouse gas emissions would be expected to contribute to preservation of existing biodiversity within U.S. national parks. Analyses are underway to evaluate critical loads and vegetation response across a larger set (n = 164) of National Parks.

<sup>1</sup>E&S Environmental <sup>2</sup>National Park Service

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## Linda H. Pardo<sup>1\*</sup>

Linda Pardo will moderate a discussion with the presenters of the "Ecological effects of deposition and climate change" session to connect the various research projects together and link current research to the overlapping effects of climate change. This discussion will integrate prepared questions and those from the audience to try to capture the needs of the community when identifying future analyses and data products.

<sup>1</sup>USDA Forest Service, Burlington, VT

\* Corresponding author: linda.pardo@usda.gov



Session 2: Emerging measurements and effects of aeroallergens and wildfire smoke



#### **Atmospheric Pollen Measurements in Ambient Air**

## Terri Williams<sup>1\*</sup> and Eric Uram<sup>1</sup>

A recent NADP study sought to evaluate the potential for producing reasonable and consistent measurements of pollen concentrations using NADP collected samples. This included identifying the quantity of pollen types present in the samples and evaluating the correlation between pollen measurements from traditional sampling methods, NADP samples, and real-time continuous automated monitoring data. This study acquired data from traditional pollen measurements from the NAB, ambient air and wet-deposition samples collected by NADP, and real-time automated monitors co-located at 3 NADP National Trends Network (NTN) sites located in NC, WI and UT from March 1 – October 31, 2021. WI was unique in the use of a high-volume ambient air sampler installed near an NAB reporting location for collecting total suspended particulate (PM) samples for pollen analysis. Pollen identification and counting for the PM samples was done by the Environmental Health Division at the WI State Laboratory of Hygiene. This presentation will look closely at this method and provide a description and discussion regarding the novel sampling and analysis techniques used for this comparison.

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## Characterization of bioaerosol emissions from prescribed fires and laboratory burns

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Wildfires emit a variety of gasses and particles into the atmosphere. Recent work has shown elevated bioaerosols associated with smoke plumes from biomass fires. Bioaerosols or aerosols composed of biogenic material (e.g. bacteria, fungi, pollen) are not well characterized in the atmosphere and the impact of their emissions from biomass fires remains unclear. Specifically, the impact of viable or live bioaerosol emissions may have unexplored downwind impacts on as they are transported downwind and deposited to other ecosystems. Deposition in terrestrial ecosystems may impact ecosystem services related to plant/soil health and greenhouse gas emissions. To begin to address this gap, in a laboratory setting, we performed controlled burns in a tube furnace using grass, leaf, and evergreen fuels at two temperatures (500C and 1000C) to understand the effect of smoldering and flaming temperatures on the amount and properties of bioaerosol particles emitted. We also sampled emissions from a prescribed fire in the Konza Prairie Grasslands. Bioaerosol particles were measured using Wideband Integrated Bioaerosol Sensor-NEO (WIBS-NEO, DMT). WIBS uses fluorescence excitations (280 and 370 nm) to detect (310-400 nm and 420-650 nm) bioaerosols which are then classified according to fluorescence behavior, size, and a shape parameter. Our preliminary analyses suggest that smoldering and flaming temperatures contribute to emitting different abundances, types, and shapes of bioaerosol particles. Additionally, the emitted bioaerosols from our various fuels have different properties. We will compare the properties of bioaerosol from our laboratory burns to emissions from prescribed fires and to background or non-fire impacted air masses.

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#### Impact of 2023 Wildfire Smoke on Black Carbon in Great Lake Waters

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From March to September 2023, historic Canadian wildfires repeatedly produced continental-scale smoke plumes impacting air quality over large regions of North America, including the Great Lakes. Wildfire smoke deposited on the surface waters of the Great Lakes is a potential source of refractory black carbon (rBC) and numerous gaseous and particulate pollutants, nutrients, and heavy metals. rBC nanoparticles are emitted by the incomplete combustion of biomass burning and fossil fuel, particularly wildfires in forested areas. These particles are a significant component of fine particulate matter (less than 2.5 microns in diameter, PM2.5) and are known to have human health effects and climate impacts. Once deposited to lake surfaces, the large surface areas of rBC particles may sorb heavy metals and organic contaminants, altering their fate and bioavailability. To investigate the impact of smoke deposition on the Great Lakes surface waters, we collected and analyzed paired epilimnetic and benthic water samples for rBC. Nearly 80 samples were collected in August 2023 from the US EPA's RV Lake Guardian and analyzed for rBC by single particle intracavity-induced incandescence. The forthcoming results of the rBC analysis will be presented and discussed.

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## Impacts of Transported Wildfire Smoke on the Whiteface Mountain Aqueous Chemical System

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Wildfire smoke is a rapidly expanding topic in the fields of atmospheric chemistry, air quality, and climate science. Smoke can lead to significant deterioration of air quality, interact with solar radiation, and impact the formation of clouds and rain. Additionally, wildfire smoke can add large quantities of organic carbon, nitrogen, sulfur, and dust, rapidly changing the chemical composition of the local atmosphere. This smoke can also travel 1000s of kilometers, impacting the air quality of environments far removed from the source. Whiteface Mountain (WFM) in the High Peaks Region of the Adirondack Mountains in upstate New York has been monitoring the chemical composition of cloud water since 1994. This site serves as a useful rural location to measure background air quality and monitor the transport of pollutants from far away locations. The original goal of the site was to investigate the controlling factors of acid rain and to monitor the progress of the Clean Air Act Amendments (CAAA) of the 1990s. As the concentrations of  $SO_4^{2-}$  and  $NO_3^{-}$  have decreased due to CAAA, total organic carbon (TOC) may be increasing in WFM cloud water and is becoming a more dominant component of the chemical system. The causes behind this increase remain unclear, but there is evidence that wildfire smoke can lead to enhancements of cloud water TOC. This work will investigate the role of wildfire smoke on the chemical composition of WFM cloud water, with an emphasis on TOC, select organic acids, and nitrogen. Known biomass burning chemical tracers like potassium and carbon monoxide will be used to help identify smoke influenced cloud samples. HYSPLIT trajectory analysis will be conducted to discover source locations of various wildfires. Statistical techniques will be used to compare wildfire vs non-wildfire cloud water samples to determine the impacts of wildfire smoke on cloud chemical composition and to see if they contribute significantly to the overall increasing TOC trend. Finally, the implications of potentially increasing wildfire influence due to anthropogenic climate change will be discussed.

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**Session 3:** Deposition and effects of mercury, toxics, and hazardous air pollutants – Part 1



## Atmosphere-surface exchange of gaseous elemental mercury (GEM) in a salt marsh estuary in Massachusetts, USA

## Ting Wang<sup>1</sup>, Inke Forbrich<sup>2,3</sup>, Jun Zhou<sup>1</sup>, Mikaela Martiros<sup>2</sup>, Daniel Obrist<sup>1,4\*</sup>

Terrestrial ecosystems serve as important global atmospheric Hg sinks, driven by plant-uptake of atmospheric gaseous elemental mercury (GEM), but the importance of GEM deposition or emission in estuarine ecosystems is largely unknown. The goal of this study is to measure the annual atmosphere-surface exchange of GEM in a densely vegetated salt marsh estuary in Massachusetts, USA, using a tower-based micrometeorological flux approach.

Our current measurement record spans 258 days from May 3rd of 2021 to January 16th of 2022, during which a catastrophic tower failure occurred due to a major winter storm. It also covers 412 days from July 15th, when the tower and measurements were re-installed, to August 31st of 2023. We measured highly variable GEM exchange fluxes ranging from -446.5 ng m-2 hr-1 (i.e., deposition to the ecosystem) to 426.9 ng m-2 hr-1 (i.e., emissions to the atmosphere), which is typical of such GEM flux records due to challenge to measure very small GEM fluxes against a large atmospheric GEM background. On average, the marsh experienced a net GEM emission flux of 1.7 ng m-2 hr-1, which is this agrees with previously reported GEM evasion from aquatic ecosystems attributed to transpiration losses by aquatic macrophytes, but this contrasts with previously reported GEM deposition in two nearby forest ecosystems (e.g., 13.4 µg m-2 yr-1 and 25.1 µg m-2 yr-1, respectively). In addition, GEM exchange was not dominated by typical growing-season GEM deposition and showed poor correlation to corresponding CO2 exchanges, suggesting a reduced role of plant uptake of GEM compared to forest ecosystems. In fact, active growing season periods showed variable GEM exchanges, such as GEM deposition during the early season in 2021 but emission in 2023, as well as GEM emissions during late seasons in 2021 but emission in 2023. These findings suggest high variability of GEM exchange processes.

Furthermore, GEM fluxes exhibited diel patterns, with smaller and less variability during the night and more enhancement and variability during the day. The ongoing work aims to identify the dominant drivers impact GEM exchanges in this salt marsh during the daytime, including vegetated surfaces, temperature, solar radiation, humidity, and other factors. We also aim to elucidate reasons for highly variable GEM fluxes, ultimately enabling us to construct a comprehensive annual mass balance of Hg sources.

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## Use of atmospheric concentration and passive sampler measurements for assessing gaseous elemental mercury exchange at two unpolluted forest sites

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Mercury is a neurotoxic pollutant present in the atmosphere primarily as gaseous elemental mercury (GEM). Terrestrial ecosystems serve as important receptors for GEM, which can be transferred to aquatic ecosystems and form highly toxic methylmercury. Despite recent advances in observational methods, direct measurements of GEM exchange above global ecosystems are currently limited due to complex and costly measurement systems.

Here we present an evaluation of the use of atmospheric GEM concentrations measured by active and passive techniques to assess underlying ecosystem GEM exchanges at two rural temperate forests (Harvard Forest in Massachusetts, USA and Howland Forest in Maine, USA). We find strong temporal alignments between springtime atmospheric GEM concentration declines and ecosystem GEM deposition at both forests, which followed patterns of CO2 and suggests that ambient air GEM concentration monitoring provides a proxy measurement to assess forest GEM sinks. In fall, we observe atmospheric GEM concentration increases and reversal of forest GEM fluxes to emissions, but with poor temporal alignments. Diel GEM concentration variability did not correspond to diel patterns of ecosystem GEM fluxes, which is driven by boundary layer dynamics with different atmospheric mixing depths during daytime and nocturnal regimes. Passive samplers (PASs) deployed to measure vertical GEM gradients across six heights throughout one of the forest canopies showed excellent agreements with active measurements in detecting seasonal concentration patterns at all deployment heights. We also find qualitative agreements between the direction of active and PAS derived gradients, but concentration differences were too small and variable for quantitative comparison of methods. We show that time-averaged GEM concentration gradient measurements are always biased towards stable nighttime periods, while ecosystem GEM fluxes are dominated by daytime exchanges, which highlights a profound limitation for the use of temporally integrated measurements such as PAS to quantify forest GEM exchanges.

We conclude that GEM concentration measurements both via active and passive sampling can serve as proxies to assess underlying ecosystem GEM sinks and sources, but that the use of passive samplers to quantify GEM exchange via gradient measurements is limited due their strong nighttime biases.

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#### Understanding Mercury Gaseous Fluxes at Marcell and the SPRUCE experiment Grand Rapids, Minnesota

#### Isabella Garrioch<sup>1\*</sup>, Kevin Behrens, Ed Nater, and Randall Kolka

Mercury (Hg) is a contaminant that is found in every ecosystem and deposition of Hg into waterways is a growing global concern. Another growing global concern is anthropogenic climate change, which is predicted to increase global average temperatures by more than 2°C by 2100. Hg is present as gaseous forms or particle-bound in the atmosphere, where a large percentage comes from human-related emissions. In this study, we examine the atmospheric Hg concentrations from a northern peatland to determine the fluxes based on climate conditions at the Spruce and Peatland Responses Under a Changing Environment (SPRUCE) experiment. Ten large experimental enclosures with include five sets of paired plots with temperatures ranging from ambient (+0.0°C) to 2.25°C, 4.5°C, 6.75°C, and 9.0°C above ambient, and with and without elevated carbon dioxide. Using the passive Hg air samplers, we assessed the effect of ecosystem warming on Hg gaseous fluxes. Multiple linear regressions were carried out to compare calculated mercury gas fluxes with mean air temperature at 2 m, and soil temperature at 10 and 20 cm depths. Our results show that there is a significant correlation with warming leading to increased gaseous Hg. Air temperature appeared to have the most effect on mercury flux rate compared to soil temperatures at 10 and 20 cm. Gas flux rates increased up to 7 ng/m2/hr when comparing warmed plots. Combined, our results indicate that climate warming has the potential to greatly increase net Hg gaseous fluxes from northern peatlands.

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## Climatic regulation of atmospheric mercury concentrations at the Lulin Atmospheric Background Station (LABS) in Taiwan

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Atmospheric mercury (Hg) cycling is sensitive to climate-driven changes, but links with various teleconnections are not well studied due to the scarcity of long-term monitoring dataset. Concentrations of atmospheric mercury Hg have been monitored since April 2006 at the Lulin Atmospheric Background Station (LABS; 120.87°E, 23.47°N, 2862 m a.s.l.), a high mountain forest site in central Taiwan, and the monitoring is still ongoing. Multiscale temporal variations of gaseous elemental Hg (GEM) concentrations at LABS in 2007-2019 were studied and distinguished by the application of the Hilbert-Huang transformation (HHT). Diurnal, monthly, annual, and inter-annual GEM cycles were identified. Daily GEM variability at the LABS is controlled by the local upslope movement of boundary layer air, whereas seasonal variability is driven by regional air mass origins and transport paths. The amplitude of the GEM concentration inter-annual variability (IAV) is greater than that for diurnal and seasonal variability, highlighting the importance of GEM IAV and the associated driving factors. The IAV cycles for the SOI were similar in frequency to the GEM IAV cycles but negatively correlated, revealing the dependency of GEM IAV on large-scale climatology variations (e.g., ENSO). Large-scale atmospheric circulation likely plays an important role in modulating GEM IAV. Furthermore, the relationship between ENSO and GEM is sensitive to extreme events (e.g., 2015–2016 El Niño), resulting in perturbation of the long-term trend and atmospheric Hg cycling. Future climate change will likely increase the number of extreme El Niño events and, hence, could alter atmospheric Hg cycling and influence the effectiveness evaluation of the Minamata Convention on Mercury. Further research on this topic using only the March GEM data is still underway and the results will be presented in the meeting.

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## Investigating the effect of precipitation on airborne reactive mercury washout at Storm Peak Laboratory, Colorado and at sixteen co-located sites in the Atmospheric Mercury (AMNet) and Mercury Deposition (MDN) Networks

## Peter Weiss-Penzias<sup>1\*</sup>, Mae Gustin<sup>2</sup>, Seth Lyman<sup>3</sup>, and Lynne Gratz<sup>4</sup>

Airborne oxidized mercury (Hg) species, termed reactive Hg (RM) have high solubility in precipitation compared with gaseous elemental Hg (GEM) and are believed to control Hg concentrations in precipitation ([Hg]aq). However, a direct link between RM in air and [Hg]aq has not been established due to the different timescales of the measurements and the complexity of the relationship. In this study we focused on RM and GEM measurements from a dual-channel Tekran 2537 system, which quantifies RM without a KCl denuder, at Storm Peak Laboratory (SPL) in the Rocky Mountains of Colorado, USA. These hourly measurements spanned March-October of 2021 and were compared with hourly meteorological and chemical data, weekly [Hg]aq at the MDN site CO97, and 24-h back trajectories, to assess the extent of RM removal in precipitation events and what is the role of meteorology and transport. Our results showed that RM concentrations were lower on average by 37 pg m-3 during precipitation compared to dry periods. In comparison, the magnitude of the average diel cycle of RM was only 22 pg m-3. While these results suggest washout of RM is significant, we observe that RM concentrations did not approach zero like PM10 did during multiday rain events suggesting that a less soluble RM fraction remains airborne. GEM concentrations during precipitation events increased by an average 89 pg m-3, possibly due to surface emissions or conversion of RM to GEM in clouds. We then analyzed RM and GEM during hourly precipitation at 16 co-located AMNet and MDN sites with multiyear airborne and aqueous concentrations data. Across all sites there was an average loss of RM of 5.9 pg m-3 and an average increase in GEM of 56.2 pg m-3 during precipitation. The RM loss is a factor of 6 smaller than that seen at SPL which may be because of a low bias in the KCl denuder used in AMNet. Like at SPL we observed only weak correlations between RM and [Hg]aq at each of the 16 sites suggesting a limited connection between sources/processes important for hourly RM and weekly [Hg]aq.

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#### Measuring atmospheric deposition of PFAS in throughfall in an urban environment, Bronx, NY

<u>Ashley Smith-Krudener</u><sup>1\*</sup>, Douglas Burns<sup>1</sup>, Irene Fisher<sup>1</sup>, Kaitlyn Cunningham<sup>1</sup>, Martin Shafer<sup>2</sup>, Emily Sellers<sup>2</sup>, and Jared Kunick<sup>2</sup>

Per- and polyfluoroalkyl substances (PFAS) are a widely used and persistent class of anthropogenic chemical compounds which are emitted to the atmosphere from numerous sources. Once airborne they may be transported long distances through the atmosphere before removal by wet and dry deposition. Contamination of aquatic and terrestrial environments by PFAS is of great concern for human and ecosystem health, however, documentation of the magnitude and flux of atmospheric PFAS contamination, especially in urban areas, remains sparse. In coordination with the National Atmospheric Deposition Program (NADP), the U.S Geological Survey (USGS) has collected throughfall samples since April 2023 at the Thain Family Forest in the New York Botanical Gardens, Bronx, NY to quantify atmospheric PFAS deposition under a tree canopy within an urban environment. Recent (2019) discrete sampling of the nearby Bronx River by the USGS documented the presence of PFAS and indicated that the stream maybe influenced by atmospheric deposition of PFAS. Several studies have quantified PFAS concentrations and deposition in precipitation, but little data are available on the role of the tree canopy in PFAS deposition. Sample collection in the current study is designed to parallel collection and PFAS analysis of open-air precipitation samples at an adjacent site (NY06) at the New York Botanical Gardens. Seven throughfall collectors are deployed at the Thain Family Forest study site, for weekly collection throughout the growing season (April to November 2023). Both pooled samples and individual collectors on selected dates are analyzed for 34 PFAS compounds, dissolved organic carbon, and major ions by the Wisconsin State Laboratory of Hygiene (WSLH). In fall months, litter-fall with be collected and analyzed for mercury and PFAS. Data from this monitoring study will be compared to that of open-air precipitation at the NY06 site to quantify the effect of the tree canopy on PFAS deposition to the forest floor. Results will also advance our understanding of depositional trends and spatial variability of PFAS deposition fluxes in an urban environment. Results to date will be presented.

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**Poster Session** 



#### Multi-year comparison of performance for wet-deposition sample analysis laboratories in the Northern Hemisphere

## Gregory A. Wetherbee<sup>1\*</sup>, Martin, RoseAnn<sup>2</sup>, Burns, Douglas<sup>3</sup>

The United States Geological Survey (USGS) has operated the Precipitation Chemistry Quality Assurance Project (PCQA) for nearly 44 years to quantify the variability and bias of National Atmospheric Deposition Program (NADP - US) data. The PCQA also evaluates the performance of monitoring-network laboratories in Canada, Europe, Japan, Mexico, Southeast Asia, and US, for precipitation-sample analysis for major ions, ammonium, pH, and total mercury. Predominant Northern Hemisphere precipitation monitoring networks participate in the PCQA interlaboratory-comparison programs, which informs the comparability of the data for global studies. Results for each participating laboratory are released on the web in USGS ScienceBase data releases (https://www.sciencebase.gov/catalog/item/5b0dbb48e4b0c39c934b081c ), and the data are statistically interpreted in published reports every two years (https://doi.org/10.3133/sir20205084).

Multi-year control charts are presented to indicate the comparability of the data provided by each of the monitoring networks over the past two decades. Long-term trends in variability and bias and inflections within the control chart time series indicate changes in the laboratories such as facility locations and conditions, instrument upgrades, supplies, and methods. Therefore, the results can be used to distinguish between laboratory effects and actual changes in atmospheric deposition.

Currently the PCQA compares variability and bias in laboratory sample analyses, but the sampling/collection components of international networks are largely not compared except between the NADP and the Canadian Air and Precipitation Monitoring Network (CAPMON), which operate two co-located sampling sites in Quebec and Pennsylvania. A more robust comparison of field sampling procedures would need to be done using co-located sites in more international networks to fully characterize differences in deposition data for global studies.

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## Assessment of the ALPHA<sup>®</sup> Passive Ammonia Sampler for use in the National Atmospheric Deposition Program's (NADP) Ammonia Monitoring Network (AMoN)

## Abby Carr<sup>1</sup>, Katie Blaydes<sup>1</sup>, and David Gay<sup>1</sup>

Since 2010, the NADP has been measuring ambient ammonia utilizing passive sampler technology. The NADP AMON network (Ammonia Monitoring Network) collects 2-week integrated samples from nearly 100 locations across the US and Canada. In a comparison study completed in 2008 it was determined that three different ammonia passive sampling devices: Adapted Low-Cost Passive High Absorption (ALPHA<sup>®</sup>), Radiello<sup>®</sup>, and Ogawa were comparable in terms of accuracy and precision (Puchalski et al., 2011). Despite their higher purchase cost, the Radiello<sup>®</sup> samplers were chosen for the NADP AMON due to the seemingly less labor intensive preparation procedures outlined in the available literature. However, after more than a decade of use, it is now firmly established that a time-consuming and rigorous cleaning protocol of the samplers is required to achieve NADP's data quality objectives. The laborious cleaning is further necessitated by the clogging prone nature of the Radiello<sup>®</sup> diffusive bodies. In addition, breakages of the diffusive body are commonly observed both in the field and the laboratory. Taken together, these factors result in high operational costs for a Radiello<sup>®</sup> based ammonia monitoring network.

In this study we revisit the ALPHA<sup>®</sup> sampler and critically evaluate them for ease of preparation and cost-saving measures for the NADP AMON. Recent work by Martin et al. (2019) has documented the superior absolute performance of this sampler. The 1<sup>st</sup> phase of this evaluation was achieved by co-locating the Radiello<sup>®</sup> and ALPHA<sup>®</sup> samplers in a laboratory setting and comparing the cleaning, extraction, and sample analysis processes. If the ALPHA<sup>®</sup> samplers prove to be a viable option, providing comparable or better performance to the Radiello's<sup>®</sup>, at a reduced cost, their use will have positive implications for the sustainability of the network.

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# CLAD Critical Load Summary Reports provide a risk assessment of ecosystem harm from air pollution in Class I areas that help guide decision-making and future research

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The NADP-CLAD science committee has been compiling information on how ecosystems respond to nitrogen (N) and sulfur (S) deposition since 2006, but faced challenges in effectively influencing policy without a standard data summaries to assess ecosystem health. Recent research has developed national- and regional-scale critical load (CL) datasets that provide increased spatial resolution and species-specific responses for when and where ecosystem components are harmed by deposited nitrogen air pollution. In an effort to make the data more accessible to decision-makers, CLAD has developed a standardized methodology for each CL and developed a CL Summary Report incorporating all of the available CL data within protected Class I areas. CL exceedances (e.g. deposition > CL), and thus harm to the ecosystem components, are evaluated using NADP-TDep modeled Total N deposition to determine current risk and trends since 2000.

This analysis summarizes data from seven ecosystem components with CLs of N (alpine, aquatic, epiphytic macrolichen, herbaceous community, herbaceous species, tree species, and soil mycorrhizal) and four ecosystem components with CLs of S (aquatic, epiphytic macrolichen, herbaceous species, tree species) within Class I federal lands. While total N deposition has decreased across the country in the last 30 years due to a host of economics and air pollution regulations, our analysis shows that at least one CL is exceeded in 147 of the 150 Class I areas. There is currently an average of 6 CLs of N per Class I area with only 15 units having data for all 8 possible CLs, and 3.5 CLs of S with 29 units having data for all 5 possible CLs. The distribution of available CLs and their exceedances is being used to communicate sensitivity to air pollution with other stakeholders, provide consistent interpretation of results for managers, and integration of the data into future policy decisions. This synthesis highlights how academic research can effectively be combined with inter-governmental agency collaboration to guide active management and pollution reduction efforts needed to minimize harm to sensitive resources.

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#### Mercury Deposition in the Great Lakes Region

#### Angela F. Dickens<sup>1\*</sup> and Zachariah Adelman<sup>1</sup>

The atmosphere is a crucial reservoir for mercury cycling that receives primary and secondary emissions and redistributes mercury via transport and deposition. This presentation examines the amounts and trends in wet and dry (litterfall) deposition of mercury in the Great Lakes region, along with the limited records of mercury concentrations in the atmosphere in this region. These records derive from data collected as part of the National Atmospheric Deposition Program (NADP). While trends in atmospheric concentrations of mercury are difficult to discern based on the limited data available, there are clear patterns in the spatial distribution and trends in both wet and litterfall dry deposition of mercury in the Great Lakes region. Both wet and litterfall deposition are highest in the southern areas near the Ohio River Valley and lowest in the far northern parts of the region. However, these regional differences have decreased over time. Wet deposition of mercury is slightly increasing in the northern part of the region, likely due to increased precipitation, but strongly decreasing in the south, likely in response to decreased mercury emissions. Trends in litterfall deposition are unclear in the north but decreasing in the southern part of the region, and additional work is needed to better characterize dry deposition within the Great Lakes regions. This work supports the findings of other studies that local and regional emissions sources contribute to mercury deposition in this region, likely in combination with global sources.

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# NOx Source Apportionment and Oxidation Chemistry in a Coastal Urban Airshed Using Stable Isotope Techniques: An Approach to Intermittent Sources

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 $NO_x$  (NO + NO<sub>2</sub>) emissions decrease urban air quality, and its subsequent deposition can be a significant source of excess nitrogen loading to coastal waters. Photochemical reactions between volatile organic compounds and NO<sub>x</sub> in the atmosphere create ozone ( $O_3$ ). Previous studies suggest coastal urban airsheds tend to have a NO<sub>x</sub> limited ozone regime, so an increase in NO<sub>x</sub> would lead to an increase in  $O_3$ . The first step to NO<sub>x</sub> emission mitigation and thus ozone reductions in these regions is to quantify the contributions of NO<sub>x</sub> sources. These sources have unique nitrogen isotopic compositions  $(\delta^{15}$ N-NO<sub>x</sub>) or "source signatures", which allow the use of isotope mixing models to aid in determining emission source contribution. The corresponding oxygen isotopic composition ( $\delta^{18}$ O-NO<sub>2</sub>) of NO<sub>2</sub> can be used to estimate the NO oxidation chemistry after emission from the sources. To investigate NO<sub>x</sub> dynamics in a representative coastal urban air shed, NO<sub>x</sub> and NO<sub>2</sub> were passively sampled at four NO<sub>x</sub> and ozone monitoring stations of the City of Corpus Christi, Texas each month for one year and the nitrogen and oxygen isotopic composition ( $\delta^{15}N$ ,  $\delta^{18}O$ ) of each sample was measured. The  $\delta^{15}N$ -NO<sub>x</sub> and  $\delta^{18}$ O-NO<sub>2</sub> values were applied to a Bayesian type mixing model to determine point (natural gas combustion) and nonpoint (biogenic soils, vehicles, biomass burning, and lightning) NO<sub>x</sub> sources in the air shed and determine NO oxidation chemistry (i.e. peroxy radical vs ozone pathway). Often, studies using this Bayesian mixing model include biomass burning and lighting as sources however, these are not continuous sources, and biomass burning and lightning events do not always produce enough NO<sub>x</sub> to be considered significant. We present an alternative to this "blanket" source approach by coupling HYSPLIT airmass back trajectories with lightning and fire remote sensing products to determine the significance of intermittent sources before including in a mixing model. Preliminary results suggest that biomass burning would be significant in the Corpus Christi airshed during the burning season in Mexico (February-May), and lightning events would be significant during the rainy season (May-October). Results will provide a greater understanding of  $NO_x$  and ozone dynamics in coastal urban airsheds and will directly aid in the modification of the City of Corpus Christi ozone action plan. Results will also enhance the understanding of atmospheric oxidative chemistry, information that is vital to constrain chemical transport models. Effective source apportionments will be extremely useful for creating air quality regulations and ozone mitigation.

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#### A Comprehensive Examination of National Aquatic Critical Loads of Acidity Across the U.S.

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In the 1980s, emissions of sulfur dioxide (SO<sub>2</sub>) and nitrogen oxide (NOx) in the eastern U.S. had far reaching impacts on aquatic life through acidification of sensitive waterbodies. Since 1990 emissions of sulfur and nitrogen compounds into the air mainly in this region have decreased by some 90 percent due to a host of factors, including the 1990 Clean Air Act Amendments. Today SO₂ and NO<sub>x</sub> emissions from the power sector are less than 0.9 and 0.75 million tons, respectively. As a result, total sulfur deposition is below 3 Kg S/ha/yr across most of the U.S. However, total nitrogen is still relatively high with values above 8 Kg N/ha/yr across much of the east and 2-3 Kg N/ha/yr in the west. The decrease has led to marked declines in acid deposition to our soils and waterbodies, allowing for recovery of acidified streams and lakes. Here we provide a comprehensive examination of national aquatic critical loads across the U.S. to look at the current state of surface water acidification and recovery. We examined aquatic critical loads from the National Critical Load Database (NCLDv3.2) and exceedances (e.g. deposition > critical load) using NADP and TDEP deposition since 1990 and an ANC threshold of 20 and 50 µeq/L for waterbodies in western and eastern U.S., respectively. Uncertainty of the critical load was factored into the exceedances and determined using a Montecarlo analysis for those critical loads with sufficient data. On average, the value of uncertainty was 7.68 meq/m2/yr or equivalent 1.3 kg S/ha/yr. About half of the waterbodies examined exceeded their critical load in 1989-1991. Today, most of the U.S. has percent exceedances below 5% where total sulfur and nitrogen deposition levels are below 3 kg S/ha/yr and 8 kg N/ha/yr, except for sensitive surface waters along the Appalachian Mountains spline. These sensitive surface waters would likely need to see additional reduction in sulfur and nitrogen deposition of 1 to 2 kg/ha/yr to drop below their critical load.

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# Developing background condition nitrogen critical loads and ozone critical levels for U.S. tree species using nonanthropogenic background concentrations

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Atmospheric nitrogen deposition and ambient ozone exposure can cause numerous impacts to terrestrial ecosystems. The impacts of nitrogen can include increased growth of tree species, but there can be undesirable consequences from excess nitrogen, leading to terrestrial eutrophication and changes in forest community composition. Exposure to elevated ozone concentrations can also result in decreased biomass and increased mortality of tree species. Critical loads (deposition) and levels (air concentrations) are calculated based on the determination of the threshold at which detrimental impacts begin to occur. Calculation of such a threshold requires a reference condition against which the decline is evaluated. Historically in the U.S., these have been determined as a decline in function from the level of deposition or air concentration exposure at which the response function (i.e., tree growth or survival) is maximized. However, the selection of this condition as the critical load or level in dose-response relationships can potentially include positive impacts that are experienced due to anthropogenic influences, such as enhanced carbon sequestration and forest nitrogen uptake due to excessive nitrogen deposition. Internationally, metrics such as Phytotoxic  $O_3$  Dose above a threshold flux of Y (POD<sub>Y</sub>) establish ozone critical levels using background ozone concentrations (e.g., 10 ppb) as a reference condition. There is a need to assess the impact of the selection of the reference condition on critical load and level determinations given the outcomes and management goals that rely on these calculations. Here, we expand upon our previous machine learning modeling of tree species' doseresponse relationships to evaluate how the selection of background nitrogen deposition and ozone concentration levels in the U.S., as a background condition critical load or level, alters results when compared to results using the maximum function as a reference point. Atmospheric nitrogen deposition and ozone concentrations were modeled using the Comprehensive Air quality Model with extensions (CAMx), with and without anthropogenic influences, to strictly evaluate tree growth and survival probability under natural conditions. Our work demonstrates that the choice of the reference condition for critical loads and levels can have substantial and important implications for policymaking and resource management.

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# Predicting the effects of ozone on growth of large aspen trees from response functions developed from seedlings grown in field chambers

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Tropospheric ozone is one of the most pervasive and harmful air pollutants known to affect natural and agricultural ecosystems in the United States (U.S.). In the U.S., the Environmental Protection Agency (US EPA) and other government agencies are concerned with protecting plants and ecosystems from harmful ozone exposures. Controlled exposure experiments conducted in field chambers have been used to establish tree growth response relationships to ozone exposure for more than 16 species of trees. Given the nature of field chambers, small seedlings were used. One of the most consequential questions about those studies is the validity of the predictions they support when applied to trees grown for longer period in less controlled environments. The goal of our study was to test the accuracy of the predicted biomass of trees growing in a long-term open-air experiment, when the prediction is based on seedlings grown in field chambers. We used an ozone exposure-response empirical model for quaking aspen (Populus tremuloides) parameterized from several field chamber studies to predict the biomass of quaking aspen trees grown in an Aspen-FACE "free-air" ozone exposure experiment over 11 years. We acquired the individual tree growth data and hourly ozone exposure from the ambient and elevated ozone plots from the Aspen-FACE experiment in Rhinelander, WI. We computed exposure and biomass using matched metrics for both study types. Over the 11 years of the Aspen-FACE experiment, a simple empirical exposureresponse model parameterized using the filed chamber data on seedlings predicted the ambient-to-elevated exposure biomass loss due to ozone in the open-air long-term environment. The effect of ozone in early years of the Aspen-FACE experiment turned out to be an important determinant of the effect of ozone on exposed trees in the later years. In conclusion, our study suggests that ozone exposure response relationships developed in chambers on seedlings are very useful for making inferences about effects on larger trees. These results imply that researchers can use these relationships with more confidence when estimating risks to ozone pollution across the U.S.

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

#### Establishment of the National Atmospheric Deposition Program for Mexico

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In Mexico, the atmospheric deposition has been assessed adequately for more than twenty years, and the main research findings have shown the need to incorporate a program based on the National Atmospheric Deposition Program (NADP) Quality Assurance / Quality Control (QA/QC) protocols.

It is important to standardize both the sampling and the physicochemical analysis of wet atmospheric deposition across all measurements and across North America, so the objective of this research is to establish the national atmospheric deposition program for Mexico.

The relevance of addressing the problem of acid rain in Mexico is discussed, due to the environmental impacts it causes. The importance of a coordinated action between government, industry, and civil society to reduce pollutant emissions and protect the environment in the long term is highlighted.

Studies performed in the MCMA and in the Gulf of Mexico region have shown the presence of the acidic atmospheric deposition.

Based on the NADP Networks review, it was decided to emphasize the study of the chemical composition of rainfall by proposing the National Trends Network considering as a starting point the REDDA ("Red de Depósito Atmosférico") sampling stations that are currently in operation at MCMA, and new sites are proposed to expand the monitoring coverage for the evaluation of the wet atmospheric deposition in Mexico.

Collaboration with NADP, which has been ongoing for more than ten years, will be fundamental to understand the mechanisms of formation and transport of acid rain precursors in MCMA and others strategic located sites in our country.

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## Assessment of PFAS Deposition via Precipitation at Selected Locations in the Eastern U.S.

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The atmospheric cycling of PFAS compounds is a major factor contributing to their widespread environmental distribution, moving these persistent chemicals over long distances and depositing them in a variety of ecosystems. Many PFAS compounds, due to their strong carbon-fluorine bonds exhibit high stability and resistance to environmental breakdown, leading to their persistence and accumulation in ecosystems and human populations.

The research summarized in this presentation derives from a larger on-going study of PFAS in precipitation, supported by the US EPA-ORD, and performed by researchers at the Wisconsin State Laboratory of Hygiene working with precipitation samples from the National Atmospheric Deposition Program (NADP). The study involves analyzing weekly precipitation samples from NADP's National Trends Network (NTN) for PFAS concentrations. The data/conclusions presented here are from six NTN sites covering the first 16 months of the larger on-going study (Fall 2020 through December 2021). Also presented will be a review of the extensive field and laboratory quality assurance (QA) data from that study period, including a summary of the co-location outcomes at NC30, NC96 and NC97.

We used LC/MS/MS methods to quantify the levels of 34 PFAS compounds, representing several major chemical classes of PFAS, including, perfluoroalkyl carboxylates, perfluoroalkylsulfonates, n-fluorotelomer sulfonates, perfluoroalkylsulfonamides, and GEN-X related compounds. The predominant class of PFAS observed across all samples was perfluoroalkyl carboxylic acids. We calculated both average deposition flux and concentration of each PFAS species at the study sites. The deposition fluxes of many PFAS species are < 0.1 ng/m2/day. However, notable among the detected compounds is PFBA, with the highest fluxes & levels (1-2 ng/m²/day and 0.4-0.7 ng/L), followed by PFHxA and PFHpA, exhibiting fluxes of 0.4-0.8 ng/m²/day and concentrations of 0.1-0.3 ng/L. The sum of concentrations of all PFAS usually exhibits lower values around January and July, with notable increases around May and October. These months record the highest summed concentrations of around 5 ng/L at all four major sites.

This presentation will provide an in-depth analysis of the seasonal and geographic trends in PFAS concentrations and deposition from the study sites and in doing so the study has significant implications for understanding the distribution and impact of PFAS compounds across the Eastern US, and contribute to the growing body of knowledge concerning the environmental prevalence of these compounds.

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#### **Defining Spatial Representation of CASTNET Ozone Monitoring Sites**

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The Environmental Protection Agency made addressing health and environmental issues within overburdened communities a top priority. To better understand the impact of air pollution on rural overburdened communities, we developed a unique methodology to estimate the representative monitoring airshed around each CASTNET site. The methodology was based on assessing the statistical similarities of measured ozone concentrations at each CASTNET site with nearby sites. Thresholds for Pearson correlations (Pearson) and relative percent differences were established to define the representative boundary of each site, with the median radii of influence ranging between 125 and 159 km depending on the threshold set for each criterion. This methodology produced representative regions for approximately half of the 81 CASTNET sites. The boundaries were overlayed with an Environmental Justice screening tool to identify nearby overburdened communities. In this paper we summarize the method for defining the representative boundary and the populations (demographic and socioeconomic burdens) for communities benefiting from air quality data provided by the CASTNET program.

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# Historic Depositional Fluxes of PFAS as Documented in Lake Sediment and Soil Cores from Southern Wisconsin

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Contamination of aquatic and terrestrial environments by PFAS is of great concern for human and ecosystem health. An increasing body of evidence documents the important role of atmospheric cycling to PFAS dissemination, with a myriad (many uncharacterized) of sources emitting PFAS to the atmosphere where they may be transported long distances through the atmosphere before removal by wet and dry deposition. However, although recent studies have provided important new information on wet deposition of PFAS, regional and global wet and dry depositional fluxes of PFAS are still very poorly quantified.

Numerous studies going back now more than 50 years have documented that lake sediment cores and soil cores under appropriate environmental and physical settings, contain an accurate record of the depositional history of many environmental contaminants. And if the lakes are limited to seepage lakes (those with minimal watershed runoff and fluvial inputs), that the record obtained will primarily represent atmospheric deposition. Furthermore, if the sediment cores are finely sectioned, dated, and sediment focused corrected, you can estimate the annual deposition fluxes from current times back to when the contaminant was first introduced into the environment.

In this study two seepage lakes in Southern Wisconsin (Devils Lake and Hope Lake) were cored in Winter 2023, while icecovered. The recovered sediment cores were sectioned in the field at 1-2cm intervals (20 – 30 sections per core), and then immediately frozen. The lower core sections should represent sediment deposited well before PFAS were introduced into commerce. In addition, multiple soil cores (each capturing three separate 20cm depth horizons of soil) were collected from historically undisturbed natural meadows in Devils Lake State Park and the University of Wisconsin-Madison Arboretum. In the laboratory the sediment core sections were processed for water content, density, loss-on-ignition, PFAS (34 compounds of various classes) and radiochemical dating (210Pb and 137Cs). Soil cores were processed similarly but were not dated. Results to date will be presented.

The sediment/soil effort was performed in parallel with a full year of weekly measurements of the PFAS depositional flux via precipitation (wet-deposition) and weekly to semi-weekly measurements of air concentrations of PFAS (from which dry deposition fluxes can be calculated) at both Devils Lake State Park and in Madison WI. We will estimate the total annual wet+dry deposition of PFAS and compare those data with the recent and historic depositional fluxes as recorded in the lake sediment and soil cores.

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# Results of the workshop Measurement of Atmospheric Mercury: Assessment of new measurement and calibration methods and development of a path forward

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In October 2023, the above listed workshop was convened on the campus of the University of Nevada-Reno. The workshop focused on bringing together scientists that measure atmospheric mercury to discuss the benefits and limitations of current measurement and calibration methods, as well as suggest needs for new measurement systems. These measurements are critical to addressing question regarding mitigation of human and ecosystem impacts due to atmospheric Hg - the primary pathway for Hg input into ecosystems. Workshop participants identified specific gaps in data and instrumentation, suggested development of new air sampling systems and improvements to existing methods, discussed how method results fit within our understanding of atmospheric chemistry, and determined locations where new data need to be collected. This presentation will introduce the participants of the workshop and report the major results/outcome of the meeting.

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# Aeroallergen Monitoring by the NAB: A Review of the Past and a Look into the Future

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The National Allergy Bureau<sup>™</sup> (NAB<sup>™</sup>) is a section of the American Academy of Allergy Asthma and Immunology (AAAAI). The NAB operates an Aeroallergen Monitoring Network across the Continental USA collecting, archiving, and reporting on current pollen and fungal spore levels. Recently, the Organization published a position paper in the Journal of Allergy and Clinical Immunology with this same title. The paper examined the current methods for sampling, training of analysts, and the near future of automated air sampling.

Automation shows potential for invigorating the Aeroallergen Monitoring Network which has declined in size in recent years as station operators have retired. At this time, however, automated samplers do not present a viable alternative. While much progress has been made to develop a fully automated system none has passed the rigorous tests of demonstrating reliable performance at affordable costs. This presentation will summarize these recent findings and conclusions.

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Session 4: Advances in measurements of atmospheric pollution – Part 1



# Measurements of Precipitation Acidity and Reactive Nitrogen Species in South Asia under UKRI-GCRF South Asian Nitrogen Hub

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The chemical composition of precipitation provides very important information about air quality and sources of pollution. In recent decades, fossil fuel emissions, fertilizer production and application have affected the atmospheric composition by adding NH3 And NOx in air. This has also altered the N cycle. This study reports wet deposition of reactive nitrogen species and the acidity of rain water at a number of sites in south Asia. The study is a part of UKRI GCRF South Asian Nitrogen Hub project. The selected sites included DTG, Peradeniya (Sri Lanka), MAP (Maldives), KU, Dhulikhel (Nepal), BSMRAU, Dhaka (Bangladesh) and BRRI, Rangpur (Bangladesh), SC, Kanglung (Bhutan) and NCSCM, Chennai (India). The samples of rain water were collected during 2022-23 using a manual wet collector. In order to maintain quality control in sampling, a uniform protocol was followed through out the network. A small amount of thymol was added to the storage bottle for controlling microbial degradation of samples during storage before chemical analysis. These samples were analysed for major anions and cations, pH and electrical conductivity (EC). Preliminary data analysis showed that there was a large spatial variation in all the parameters. KU had pH of rain water at higher side while BSMRAU, BRRI, MAP, DTG and NCSCM showed relatively lower pH. Almost 81% samples had pH below 5.6 at BRRI followed by 63% at DTG, 61% at BSMRAU, 30% at MAP, 27% at RC, 27% at NCSCM and 10% at KU. Similarly, NH4+ and NO3- which are considered as soil nutrients showed a huge spatial variation indicating varying sources and their local and long-range source influence in south Asia. Variation was recorded in accordance with the density of humans, vehicles and industries in the area. Automobiles and industries are the major sources of NOx. NH4+-N was higher than NO3--N at most of the sites which can be attributed to the agricultural activities and sanitation sources of NH3. Below cloud scavenging effect was noticed greater for the sites away from the sea. The wet deposition budget of NO3- and NH4+ will be discussed during the meeting.

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# Deposition of Reactive Nitrogen Species Through Snow in Western Himalayan Region of India

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Recent reports reveal that the levels of atmospheric reactive nitrogen (Nr) species are increasing globally due to increase in fossil fuel combustion for energy security and agriculture productivity. The consequences of such rise of Nr species are linked with climate change, human health and ecosystems. The wet deposition of Nr species can have significant effects on vegetation, soils, water bodies and buildings. In spite of its high importance, the atmospheric deposition of reactive nitrogen species through snowfall is not extensively reported in the Himalayan region of India. Hence, the present study was carried out to understand wet deposition with special emphasis on the estimation of fluxes of dissolved inorganic nitrogen (DIN) species (NH4+ and NO3-) and the dissolved organic nitrogen (DON) in snowmelt samples at three different land use sites-i). Leh (urban), ii). Beerwah (sub-urban) and iii). Nirmand (rural) in the western Himalayan region. The study was carried out during winter season (2016 – 2019). The DIN (NH4 + + NO3-) concentration was recorded as high as 75.39  $\mu$ mol l–1 at rural site and relatively low (38.23  $\mu$ mol l–1) at the urban site. The DON was higher at sub urban site and lower at the urban site. Wet deposition fluxes of atmospheric total nitrogen (TN) followed the order- Nirmand>Beerwah> Leh. NH4+-N contributed major fraction of TN at all the sites. This study is important to understand the factors affecting wet deposition and related local vs distant sources in the Himalayan region.

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#### Long-term measurements of atmospheric reactive nitrogen at a suburban forest site in the southeastern US

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The Duke Forest Blackwood Division is situated within the urban to rural gradient to the northwest of Chapel Hill, NC. Atmospheric chemistry at this site is influenced by anthropogenic urban emissions from the Raleigh-Durham-Chapel Hill metropolitan area (population 2.1 million) and biogenic and agricultural emissions from the surrounding rural areas typical of the North Carolina Piedmont. Since the 1990s, several intensive studies have been conducted at Duke Forest to better understand atmosphere-biosphere exchange of reactive nitrogen and carbon. More recently, Duke Forest has added time integrated air (CASTNET, NADP/AMON) and precipitation (NADP/NTN) measurements of reactive nitrogen. In addition to CASTNET filter pack (HNO<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) and AMON (NH<sub>3</sub>) measurements, continuous hourly measurements of total reactive nitrogen (TN<sub>r</sub>), total oxidized nitrogen (NO<sub>y</sub>), HNO<sub>3</sub>, NO<sub>2</sub>, and NO have been measured above the forest canopy since 2017 using a chemiluminescence/converter method referred to as Nitrotrain. This presentation summarizes the full suite of reactive nitrogen measurements conducted at Duke Forest over the past seven years, highlighting seasonal and annual patterns. The relative importance of individual species and groups of compounds to the atmospheric reactive nitrogen pool is explored, with emphasis on better characterization of the role of oxidized versus reduced nitrogen compounds. Differences between time integrated and continuous measurement methods are also discussed.

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# Water Soluble Organic Nitrogen Characterization Study

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Organic forms of nitrogen (N) are an important component of atmospheric deposition to terrestrial and aquatic ecosystems, which are not routinely measured. As summarized by Jickells et al. (2013), global datasets of precipitation chemistry indicate that water soluble organic nitrogen (WSON) contributes ~25% of the total N in wet deposition, on average. In the U.S, various studies show that annual averages of WSON range from <5% to ~30%. Generally, measurements of WSON in precipitation and aerosol are limited in North America due to a lack of routine monitoring, precluding development of a complete picture of the spatial and temporal patterns of the contribution of WSON to WSTN in wet and dry deposition at regional to continental scales.

The Clean Air Status and Trends Network (CASTNET) is a long-term environmental monitoring network of approximately 100 stations that measure changes in ambient air quality and assesses atmospheric deposition over broad geographic regions of the U.S. (https://www.epa.gov/castnet). The Environmental Protection Agency (EPA) coordinates the operation of the network in cooperation with numerous federal, tribal, state, and local partners. CASTNET sites measure weekly average concentrations of particulate sulfate (SO42-), particulate nitrate (NO3-), particulate ammonium (NH4+), sulfur dioxide (SO2), nitric acid (HNO3), chloride (Cl-) and the base cations (Na+, K+, Mg2+and Ca2+) using a 3-stage filter pack.

A pilot study was conducted in 2020 to investigate the feasibility of quantifying WSTN and WSON on CASTNET Teflon filters, including assessment of potential effects from storage and handling. Bulk WSON in PM is calculated by measuring the concentration of WSTN and then subtracting the concentrations of the measured inorganic components (NH4+, NO2-, and NO3-). Currently, a 27 site one-year study is being conducted from November 2022 to November 2023 to assess seasonal and spatial patterns as well as to estimate the contribution and correlation of WSON to the total nitrogen deposition budget. Preliminary interpretation of data has been performed, and seasonality as well as impacts from extreme events such as forest fires can be identified. Averaged across all the sites, preliminary data shows that WSON is around 10-15% of total N, with increases in late-spring and summer months, although results can differ at individual sites.

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#### A Comparison of Persistent Pollutant Concentrations in Cloud and Rainwater Collected in the Adirondack Mountains

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Persistent pollutants, such as per- and polyfluoroalkyl substances (PFAS), have been found in almost all sample media including natural and public water supplies, humans, animals, crops, soils, and the atmosphere. As PFAS are known to lead to negative health impacts, understanding the mechanisms that lead to exposure through atmospheric transport, chemical processing, and deposition is of great importance. The National Atmospheric Deposition Program's (NADP) PFAS pilot wet deposition study is a great example of the benefits that can be gained from the infrastructure and samples provided by an existing network of monitoring sites. Here we present initial results from a study comparing PFAS concentrations in precipitation from the wet deposition (WD) samples collected at the base of Whiteface Mountain (WFM) (NADP National Trends Network site: NY98) with that of cloud water (CW) samples collected at the WFM summit by the University at Albany Atmospheric Sciences Research Center. In this study, PFAS concentrations from 50 NY98 samples (September 2020 – January 2022) are compared to 30 CW samples out of 193 archived samples from 2018-2021 CW seasons (June -September). These CW samples were selected to represent the variations of air mass trajectories that WFM encounters, established through cluster analysis of HYSPLIT back-trajectories for CW collection periods 2014-2021 (during which time 804 CW samples were collected). Cloud water and WD samples were analyzed for a wide range of PFAS compounds (including PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFOS, HFPO-DA, and several sulfonamides), and total summation of PFAS concentration measured in more than 50% of the CW samples exceeded 4ppt. There was also a higher relative concentration of carboxylate PFAS in CW than WD samples, which brings forth more unknowns about the chemical transformations of PFAS from point sources to sinks, and reinforces the need for a network of high-altitude, remote sampling sites to couple with surface networks.

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#### Organic Acids in Cloud Water, Aerosols, and Cloud Droplet Residuals at the Summit of Whiteface Mountain 2018-2023

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The organic compounds in the atmosphere play a significant role in atmospheric chemistry, and clouds can play an important role in the formation and transformation of organic compounds. Di-carboxylic organic anions like oxalate are considered a tracer of aqueous processing. In this talk, we report summertime measurements of 3 major organic acids (formic acid, acetic acid, oxalic acid), along with inorganic anions (sulfate, chloride, nitrate) in cloud water and aerosol samples collected at the summit of Whiteface Mountain (WFM) in the Adirondack Mountains in northern New York State in 2021-2023. We also assess the contribution of these organic acids to the measured water-soluble organic carbon (WSOC) concentrations. Previous studies have evaluated the relationship between oxalate:WSOC ratio and ozone concentrations, to infer the surrounding forest ecosystem. In this talk, we show observations that substantially expand upon the relationship between oxalate:WSOC ratio and ozone concentrations, allowing us to compare very different environments across the globe, and compare the cloud water and aerosol phases. We also report oxalate:sulfate ratios for our dataset, which other researchers have proposed as an important aqueous processing indicator because the ions' production rates are enhanced by either liquid water content (sulfate ion) or droplet surface area (oxalate ion). The range of oxalate:sulfate ratios observed in our dataset are compared to field campaigns in other regions, and the impact of wildfire smoke is discussed.

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Session 5: Modeling atmospheric concentrations and deposition



#### Ammonia Emissions Enhancements with Deep Neural Network CTM and Remote-sensing Observations

## **B.H., Baek**<sup>1\*</sup>, Jia Xing<sup>1</sup>, Mark Shepard<sup>2</sup>, Chi-Tsan Wang<sup>1</sup>, and Daniel Tong<sup>3</sup>

Timely accurate estimation of NH3 emissions plays a critical role in forming PM2.5 concentrations in the atmosphere. While the bottom-up method can provide an averaged value, the satellite-based top-down methods can generate near-real-time constraints on emissions; however, the existing numerical models (e.g., chemical transport model, CTM) can be computationally expensive, and its efficiency can be largely limited by efforts in dealing with the complex emission-concentration response. However, the computational burden can be significantly improved with the use of a deep neural network trained with CTM simulations, note as DeepCTM. We apply this novel machine-learning-based method (DeepCTM) using a physically informed variational autoencoder (VAE) emission predictor to infer NH3 emissions from satellite-retrieved surface NH3 concentrations. The VAE emission predictor has successfully implemented in NO2 concentrations with the satellite-retrieved surface NO2 concentrations. The proven interpretability of the VAE emission predictor will be applied using sensitivity analysis by modulating each feature, indicating that NH3 concentration and local meteorology are highly correlated for estimating NH3 emissions. The advantages of the VAE emission predictor in efficiency, flexibility, and accuracy demonstrate its great potential in estimating the latest emissions and evaluating the control effectiveness from observations.

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#### Contributions of Ammonia Dry Deposition to Excess Nitrogen Deposition in Rocky Mountain National Park

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# and Jeffrey L. Collett, Jr.<sup>1</sup>

Rocky Mountain National Park (RMNP) was established to preserve the natural landscape, including montane, subalpine, and alpine ecosystems. Excess reactive nitrogen (N) deposition in RMNP is a historical problem with well documented impacts including changes in soil biogeochemistry, enhanced microbial activity, and increased N in freshwater bodies. The Front Range and the plains to the east are marked by both agricultural and urban emissions of ammonia (NH3) and NOx. Upslope flows driven by the mountain-plains circulation periodically transport these emissions into RMNP. Dry and wet deposition of reduced N are estimated to account for more than half of the N deposited into RMNP, with substantial contributions from Front Range and NE Colorado sources. However, NH3 dry deposition is poorly quantified due to the bidirectional nature of NH3 atmosphere-surface exchange. To better quantify NH3 dry deposition, measurements of NH3 were made at two heights above a RMNP forest canopy and used to parameterize a bidirectional flux model with a suite of additional measurements including atmospheric turbulence, relative humidity, solar radiation, precipitation, surface wetness, soil temperature, soil moisture, and soil and vegetation compositions. Biweekly passive NH3 and meteorological measurements are used, along with the model, to evaluate the importance of NH3 in the annual RMNP nitrogen deposition budget from August 2021 through August 2022. Wet deposition from the National Trends Network and additional gas measurements are used to calculate the importance of other nitrogen deposition pathways and to estimate the NH3 diel pattern. Local meteorological and back trajectory analysis are used to investigate reactive nitrogen transport pathways throughout the study period, including during periods of elevated deposition. A significant fraction of NH3 dry deposition occurred during upslope transport events, indicating impacts on the park from Front Range sources. The importance of upslope transport is consistent with previous work and indicates that mitigation strategies in the Front Range have the potential to effectively reduce N deposition in RMNP. Measurements from our intensive campaign indicate that NH3 dry deposits 10 times faster to forests than grasslands in RMNP. Dry deposition during the summer in RMNP (1.4 kg N ha-1) is approximately equivalent to the 5-year annual average goal of 1.5 kg N ha-1 for wet inorganic nitrogen deposition set in the Nitrogen Deposition Reduction Plan to avoid adverse ecosystem effects.

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#### Inferential modeling of dry deposition fluxes across the Ammonia Monitoring Network (AMoN)

#### Colleen Baublitz<sup>1\*</sup>, John Walker<sup>1</sup>, Zhiyong Wu<sup>2</sup>, Jesse Bash<sup>1</sup>

Ammonia dry deposition is a growing contributor to the U.S. nitrogen budget, but there is not currently a measurement network for tracking variations in this process over space and time. This lack of measurement constraints hinders evaluation of modeled ammonia dry deposition, relevant for projections of ecosystem and air quality impacts. We use concentration measurements from the Ammonia Monitoring Network (AMoN) in combination with the field-scale version of the Surface Tiled Aerosol and Gaseous Exchange (STAGE) model to estimate ammonia dry deposition across AMoN for 2018. We also develop sensitivity simulations to test the influence of individual processes and parameters on the component (stomatal, cuticular and soil) ammonia fluxes. Preliminary results indicate that the largest magnitude of ammonia fluxes occur in the US southwest and midwest on an annual basis and extend eastward in the summer. Among landcover categories sampled by AMoN, deciduous and mixed forests contribute most to the total annual flux via the cuticular pathway. The downward cuticular signal is enhanced by the soil pathway and offset by stomatal fluxes that are generally upward and from croplands. These results are sensitive to the relatively uncertain empirical parameter  $\alpha$ cut, reflecting the role of relative humidity in cuticular deposition, suggesting that measurements targeting this process and parameter could facilitate greater confidence in model estimates of ammonia dry deposition. Soil pH and soil sorption parameters were also influential, especially where soil pH is high. These parameters are often assumed to be invariant or are unspecified in chemical transport models, however, suggesting that better understanding of related soil dynamics could improve model representation of the ammonia depositional lifetime. Additionally, our results indicate that increased spatial coverage of AMoN sites in the western USA would help to improve our understanding of the role of high soil pH in atmospheric ammonia variability related to its dry deposition.

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#### US Spatial Patterns of Ammonia Dry Deposition Velocities derived from CMAQ and CAMx Chemical Transport Models

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Agricultural activities are the largest source of ammonia emissions accounting for about 80% of emissions in the United States, as well as a source of NOx and dust. Together, these emissions contribute to excess nitrogen deposition adversely affecting ecosystems; to particulate matter affecting human health, visibility and climate; to ozone affecting human and plant health; and to dust deposition to snow pack, which can alter the hydrological cycle. In addition, the ammonia emissions partially determine aerosol properties including acidity and hygroscopicity. Many National Parks (NP) are located in rural lands downwind of intensive agricultural activities and suffer from excess levels of nitrogen deposition, haze and ozone. With a few notable exceptions, the contribution of agricultural activities to these NP issues are unknown. To address this information gap, the CAMx and CMAQ chemical transport models (CTMs) are being used to simulate the contributions of agricultural and other source sectors to National Parks and wilderness areas. The modeling is based on emission and meteorological data from the WRAP 2016 modeling platform. Critical to this work is the proper simulation of ammonia emissions and their deposition, of which ammonia dry deposition is an important but poorly understood removal pathway. The two CTMs employ different deposition mechanism and simulate both uni- or bi-direction ammonia fluxes. The seasonal and annual effective ammonia dry deposition velocities were calculated for the conterminous US using the different CTMs and deposition mechanism. It was found that the different mechanism yielded significantly different average spatial patterns and removal rates, which could alter the importance of agricultural contributions to total nitrogen deposition. In this presentation, we will contrast the ammonia deposition velocity spatial patterns and reconciliation of some of the discrepancies.

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#### **PFAS Atmospheric Deposition Modeling**

# Krish Vijayaraghavan<sup>1\*</sup>

The atmospheric deposition of per- and polyfluoroalkyl substances (PFAS) may constitute a significant pathway for human and ecological exposure of PFAS in the environment. This paper will discuss the current data needs, implications and confounding factors for application of air deposition modeling in estimating and interpreting PFAS exposure patterns. Issues addressed include emissions sources, temporal and spatial trends, physical and chemical properties affecting PFAS wet and dry deposition and air concentrations, atmospheric chemical transformation of precursors to PFAS terminal products, the symbiotic relationship between modeling and measurements, the importance of PFAS background deposition, and the appropriate characterization of local versus long-range source contributions.

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**Session 6:** Deposition and effects of mercury, toxics, and hazardous air pollutants – Part 2



# Drivers of mercury contamination, methylmercury formation and mercury sources within lake sediments across the contiguous United States

**Ryan F. Lepak**<sup>1\*</sup>, Sarah E. Janssen<sup>2</sup>, Kelsey Vitense<sup>1</sup>, Benjamin Geyman<sup>3</sup>, Michael T. Tate<sup>2</sup>, Thomas Hollenhorst<sup>1</sup>, Brandon Krumwiede<sup>4</sup>, and David P. Krabbenhoft<sup>2</sup>

Atmospheric deposition is the predominant source of mercury (Hg) to food webs across the United States and is dictated by both international and domestic emissions. This study's objectives are to identify ecosystem drivers of sensitivity to Hg inputs and Hg sources to provide the framework to predict how changes in Hg emissions will impact aquatic ecosystems. This will be accomplished through spatial analyses of existing data, including over 1000 sites measured for speciated Hg concentrations in sediment, and through recent Hg-isotope analyses of a subset of over 400 sites from the USEPA 2012 National Lakes Assessment (NLA). Identifying the spatial drivers for ecosystem sensitivity to Hg inputs and responsiveness throughout the U.S. will rely upon many existing federal datasets sediment chemistry (NLA metadata), atmospheric Hg measurements (e.g., National Atmospheric Deposition Program), emission inventories (National Emissions Inventory), and landscape physical lake characteristics (LakeCat and others). Stemming from a Random Forest model, top predictors of Hg concentrations in sediments were catchment characteristics and the GEOS-Chem modeled Hg deposition. Relatively less predictive ability was found for lake trophic status, productivity, or proximity to urban areas. When evaluating Hg isotope heterogeneity across the U.S., we observed isotope clustering within ecoregions to form regional isoscapes. Largely the isotope heterogeneity was driven by differences in precipitation, erosion, and water residency rather than trophic condition or proximity to urban areas. While this work seeks to understand drivers of Hg contamination and Hg sources, it also marks our only known effort to constrain the range of Hg isotope values that may be measured in lake sediment. In that sense, this study serves as a platform for cross evaluation for studies that are comparatively less spatially robust or for ecosystems that lack the wealth of metadata presented here.

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#### Mercury in the Great Lakes: How Ecosystem Pressures Influence Mercury Cycling

# Sarah E. Janssen<sup>1</sup>, <u>Grace J. Armstrong</u><sup>2\*</sup>, Ryan F. Lepak<sup>3</sup>, and Michael T. Tate<sup>1</sup>

Mercury (Hg) has been recognized as a persistent pollutant in the Great Lakes for over 30 years, but our understanding of Hg cycling is insufficient to predict ecosystem responses to changes in Hg delivery and bioaccumulation. In addition, emerging factors including invasive species, land use alterations, and changes in water delivery due to climate change disconnect biological Hg burdens from trends in atmospheric Hg deposition, making it difficult to assess changes in biological Hg burdens resulting from management actions. Atmospheric deposition is the dominant pathway for Hg delivery across the Great Lakes, however, declines in atmospheric Hg concentrations no longer mirror biological Hg trajectories. Long-term fish monitoring coupled to more recent sediment assessments have aided in defining Hg sources to the lake and concentration trends, but controls on Hg cycling between the lakes can be vastly different. To elucidate lake-specific Hg dynamics we conducted mechanistic studies and monitoring initiatives across Lake Superior, Lake Huron, and Lake Ontario. In Lake Superior we implemented a binational tributary assessment of Hg fluxes to examine the influence of watershed sources to nearshore environments as well as to determine if Hg concentrations have declined over time. For Lake Huron, we shift focus to bioaccumulation at the base of the food web to determine if Hg uptake varies across nearshore to offshore transects and explains inconsistent trends in fish tissue Hg burdens. Lastly, in Lake Ontario we will cover ongoing field work and the experimental design of incubation assays to assess if Hg methylation is impacted by changes in organic carbon loads and wetting/drying cycles in coastal wetlands environments. These studies highlight binational synergistic activities between federal, state, and academic partners which will help build a comprehensive framework on Hg sources and controls dictating biological Hg burdens across the Great Lakes.

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# **V.F.Taylor**<sup>1\*</sup>, C.Y. Chen<sup>1</sup>, A.W. Schroth<sup>2</sup>, K. Stepenuck<sup>2</sup>

Over the past half century, air quality management efforts have led to substantial decreases in mercury emission across the United States. Subsequent declines of mercury concentrations in air and precipitation have been well documented, resulting in lower mercury fluxes in wet deposition. The responsiveness of ecosystems to these decreasing inputs is an on-going point of scientific inquiry and for some matrices, considerable uncertainty exists. Organic surface soils are one such example, with relatively little known about how and on what time scale soils react to changes in mercury deposition. Here, we present an analysis of total mercury in organic soils from the Hubbard Brook Experimental Forest (HBEF), spanning over 20 years. Archived soil samples representing the Oie and Oa horizons in the reference watershed (WS6) were oven-dried, milled, and analyzed via direct mercury analyzer. Trends in total mercury concentration varied over time and among organic soil horizons, with overall mercury concentration decreasing. Trends in soil concentration were compared with tree ring analysis and modeled deposition for the experimental area and found to be in agreement. Calculated changes in the organic soil mercury reservoir for the watershed were compared to modeled inputs to estimate the turnover time for organic soils at HBES. Overall, results suggest that organic soils at HBEF are dynamic and responsive to changes in atmospheric emissions.

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#### Mercury cycling in high elevation wetlands of the western U.S.: storage, transformations, and transport

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Despite decreasing mercury (Hg) emissions across the United States (U.S.), Hg deposition in the Western U.S. is increasing. Mountain ecosystems are particularly sensitive to increasing Hg inputs because they experience more rapid changes in climate and high rates of atmospheric Hg deposition, as well as having aquatic regions conducive for microbial conversion of inorganic Hg to methylmercury (MeHg). In this study, we examine the role of high elevation wetlands in Hg cycling by investigating Hg storage, transformations, and transport in alpine (~3000m) and subalpine (~2,500 m) environments in the Colorado Rocky Mountains (Fig. 1). Soil total mercury (THg) concentrations were significantly higher in alpine (61.3±25.5 ng/g) and subalpine (114.7±29.7ng/g) wetlands compared to dry soil regions (39.7±11.1ng/g, p<0.01). Concentrations of MeHg were an order of magnitude higher in subalpine (6.4±2.2ng/g) than alpine wetlands (0.6±0.5ng/g, p<0.05), and both subalpine and alpine wetlands had significantly higher concentrations than dry soil regions (0.2±0.1ng/g, p<0.05, Fig. 2). Mercury methylation rates were three orders of magnitude higher in the subalpine wetlands (0.324ng/g/day) than the alpine wetlands (0.013ng/g/day) and dry soil regions (0.006ng/g/day). Sulfate additions increased methylation rates in the subalpine wetlands by approximately 2ng/g/day. This pattern suggests that increased sulfate runoff from the weathering of pyrite in melting rock glaciers, and other ice features, may stimulate MeHg production in alpine ecosystems with continued warming. Stream THg concentrations across all sites were highest in the spring during snowmelt but were significantly higher in the subalpine (4.77±2.46ng/L) compared to the alpine (1.14±0.55ng/L, p<0.01). Stream MeHg concentrations gradually increased throughout the growing season and were an order of magnitude higher in the subalpine (0.71±0.02ng/L) than the alpine (0.006±0.01ng/L, Fig. 2). Methylmercury concentrations in overlying wetland waters within the subalpine wetland were highest during spring snowmelt, and the inlet to the wetland was significantly lower (0.09±0.07ng/L) than the outlet (0.21±0.08ng/L, Fig. 2). This suggests that MeHg is produced within subalpine wetlands and exported downstream. Overall, this study demonstrates that high elevation wetlands play a disproportionate role in storing and transforming atmospherically deposited Hg with implications for downstream ecosystems and local food webs.

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# Mercury Stable Isotopes in Dragonflies Reveal Habitat and Geographic Drivers of Mercury Entry into Aquatic Food Webs

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Atmospheric transport and subsequent deposition of mercury (Hg) is a major concern within protected lands, such as national parks, where it can bioaccumulate to levels that are detrimental to human and wildlife health. Despite this risk, there is limited understanding of the relative importance of different Hg sources and delivery pathways within protected regions. In this research, we used Hg stable isotope measurements in dragonfly biosentinels to elucidate Hg sources and to resolve spatial patterns in Hg delivery and aquatic cycling. Dragonflies were collected across 73 national parks across the US as part of the Dragonfly Mercury Project. We observed differences in  $\delta$ 202Hg between the eastern and the western US, suggesting differences in Hg emission sources and MeHg production at a national scale. Variation in  $\Delta$ 199Hg within dragonfly tissues demonstrated that photochemical Hg degradation across the US was habitat dependent and associated with environmental characteristics such as dissolved organic carbon, nutrients, and vegetation cover. Strong patterns for  $\Delta$ 200Hg emerged in the Western Cordillera ecoregion, which demonstrated the prevalence of wet deposition to arid regions in contrast to mixed dry and wet deposition within canopy-covered regions of the Pacific Northwest. While further exploration of Hg isotopes within dragonfly tissues is needed to constrain variability among sites and to better characterize the underlying drivers for Hg isotope patterns, this work provides the first comprehensive examination of biosentinels to track Hg sources and processes on geographic scales not previously considered.

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Session 7: Advances in measurements of atmospheric pollution – Part 2



# Atmospheric deposition of chromophoric dissolved organic matter throughout the Athabasca Oil Sands Region, Alberta, Canada.

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Atmospheric chromophoric dissolved organic matter (CDOM) consists of a broad range of light-absorbing natural and anthropogenic organic compounds that can impact terrestrial and aquatic ecosystems following deposition. Industrial operations in the Athabasca Oil Sands Region (AOSR), Alberta, Canada, are a substantial source of atmospheric CDOM, including a diversity of aromatic organic pollutants and water-soluble brown carbon aerosols. However, there is limited knowledge on the variability of CDOM deposition throughout the AOSR. In this study, weekly wet-only deposition samples (2021 meteorological year) from three National Atmospheric Deposition Program (NADP) stations and regional snow-pack samples (2020 and 2023) were collected to evaluate the spatial and temporal variation of CDOM deposition surrounding the oil sands (OS) industry. Absorbance and excitation-emission matrix fluorescence spectroscopy techniques were used to characterize CDOM within precipitation samples and identify regional pollutant emissions sources. Key absorbance indices and petrogenic fluorescent compounds (fluorophores) were significantly elevated among near-field NADP and snow-pack sites, and further displayed strong agreement with elemental species typically associated with OS sources. Humic acid-like fluorophores were prominent among precipitation samples during the summer months, possibly due to increased wildfire and road dust emissions, while petrogenic fluorophores were elevated during the winter. These results suggest that spectroscopy is a versatile and cost-effective alternative to detect anthropogenic organic pollutants throughout the AOSR.

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#### A new method for trend detection in precipitation chemistry: Weighted Regression for Time Precipitation and Season

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A new method for trend calculation of precipitation chemistry has been developed based on the weighted regression on time, discharge and season trend tool for rivers and streams. The new tool, weighted regression of time, precipitation, and season (WRTPS), is designed to allow detailed investigation of long-term trends in precipitation chemistry and operates within the R programming environment. The WRTPS model calculates daily precipitation concentration based on weekly values using a weighted multiple linear regression that allows the effect of precipitation amount and season on precipitation concentration to change through time. WRTPS allows for changes in the concentration trend slope and seasonal patterns of concentration through time. The tool also allows us to investigate trends in specific classes of precipitation amount, to examine trends within specific seasons and changes in the precipitation-concentration through time. WRTPS is currently being used to examine trends in mercury (Hg) concentration in precipitation from 17 National Atmospheric Deposition Program Mercury Deposition Network stations.

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#### After more than 20 years evaluating wet atmospheric deposition in Mexico, main findings and challenges

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The evaluation of atmospheric pollution in Mexico dates back to the 1970s, while the first efforts to determine wet atmospheric deposition have been carried out since the 1980s. The evaluation of wet atmospheric deposition based on internationally recognized protocols, such as those of the National Atmospheric Deposition Program (NADP) and the World Meteorological Organization (WMO), has been carried out from 2002 to the present. Of particular note are the research activities carried out in Mexico City Metropolitan Area (MCMA) in collaboration with the Government of Mexico City and the National Autonomous University of Mexico (UNAM), as well as studies in the Gulf of Mexico region, in collaboration with industry and academy.

Some of the main findings of this research for the MCMA include: 1).- Despite the fact that the reduction of sulfur dioxide emissions has been very important, resulting in the improvement of air quality, the sulfate ion continues to be the largest contributor to the acidity of rain; 2.-) The southern zone experiences the highest acidity, combining meteorological aspects, as well as the presence of less neutralizing agents like ammonium and 3.-) The presence of reactive nitrogen has as its greatest component its reduced form compared to the oxidized form, with an average value of 2.5 for the NH4+/NO3- ratio.

For the larger Gulf of Mexico region, main findings include: 1). – Air masses impacting the Mexican coast and the State of Veracruz originate from the Caribbean Sea, crossing the Yucatan Peninsula and then crossing the Gulf of Mexico. 2).- The SO42-/NO3- ratio is higher than 3 on the Mexican coast, largely due to higher sulfur dioxide emissions.

Based on these findings, the following challenges represent opportunities for collaboration among institutions such as NADP, USGS and the USEPA: 1). - Considering the already existing infrastructure in Mexico City, to evaluate air quality and wet atmospheric deposition, complemented with the ammonia ambient air monitoring to gradually establish a reactive nitrogen network. 2).- Establish as soon as possible a program to evaluate the critical loads for nitrogen, sulfur and ozone for ecosystems in Mexico. 3).- Due to the international strategic importance of the Gulf of Mexico, both offshore and on its coasts, expand the capacity of atmospheric deposition and air quality stations on the Mexican coast of the Gulf of Mexico, based on national collaboration with governments and local universities, as well as internationally with NADP and the USEPA, among others.

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#### Monitoring the stomatal component of tropospheric ozone dry deposition over an agricultural field in central Illinois

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Plant physiology directly impacts the tropospheric ozone ( $O_3$ ) budget by the uptake of  $O_3$  through plant stomata, which makes up a significant portion of  $O_3$  dry deposition over vegetated areas. Furthermore, the stomatal uptake of  $O_3$  correlates tightly with  $O_3$  induced losses in net photosynthesis and biomass, emphasizing its importance to plant productivity. The dual significance of stomatal  $O_3$  flux as an indicator of the phytotoxic dose to vegetation and as a tropospheric  $O_3$  loss pathway warrants continued monitoring of  $O_3$  fluxes over agricultural fields and natural ecosystems. While national ambient  $O_3$ monitoring networks have been a valuable source of data to determine harmful levels of  $O_3$  exposure to vegetation,  $O_3$  flux measurements can provide more precise estimates of stomatal uptake because fluxes incorporate information on both ambient concentrations and plant physiology.

Here, we present direct measurements of  $O_3$  fluxes and estimates of the stomatal component of  $O_3$  dry deposition over the growing season in an agricultural field in central Illinois. We monitored  $O_3$  fluxes using the eddy covariance technique with 10 Hz measurements of wind velocity and  $O_3$  concentrations from two instruments based on UV-absorption; one relatively inexpensive to explore the development of cost-effective monitoring systems. We isolated the stomatal component using  $CO_2$  and  $H_2O$  fluxes with an inversion of the Penman-Monteith equation which describes ecosystem latent heat flux and a separate approach based on turbulent transport used to partition  $H_2O$  and  $CO_2$  fluxes into their stomatal and non-stomatal components. We analyze how micrometeorological conditions and crop physiological activity impact diurnal and growing season  $O_3$  dry deposition at this agricultural field. Eddy covariance fluxes of  $O_3$  across tower networks can help monitor the cumulative uptake of  $O_3$  by natural ecosystems and agricultural fields along with providing relevant observations for testing  $O_3$  dry deposition schemes in air quality and chemical transport models.

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# Causes of springtime-maximum and long-term trends of ground-level ozone in the eastern United States and Canada for 1990-2019

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With the implementation of the Clean Air Act Amendments of 1990 in the U.S. and similar measures taken in Canada, anthropogenic emissions of volatile organic compounds (VOCs) and nitrogen oxides (NOx), precursors to form ozone in the troposphere, decreased significantly in both the U.S. and Canada since 1990. In this study, we use novel statistical methods to analyze the long-term measurement data of ground-level ozone from the Clean Air Status Trends Network (CASTNET) and the Canadian Air and Precipitation Monitoring Network (CAPMoN), as well as Canadian National Air Pollution Surveillance (NAPS) program to reveal the quantitative spatial and temporal changes in ground-level ozone concentration in the eastern U.S. and Canada for 1990-2019. Based on the analysis of the CASTNET and CAPMoN data, we also propose a new explanation for the springtime-maximum of ground-level ozone in the eastern U.S. and Canada. The fundamental reason that the monthly mean concentration of ground-level ozone peaks in the spring is that the ozone diurnal decrease rate is much smaller in the spring (e.g., April) than that in the summer (e.g., June) due to a lack of vegetation and tree leaves on the Earth's surface during the springtime. The ozone diurnal decrease rate is defined as the normalized change rate, in unit of hr<sup>-1</sup>, between the monthly means of ozone diurnal value at 18 PM and 7 AM local time. The normalization is done by dividing the change rate with the monthly mean of ozone diurnal value at 18 PM local time. When the larger ozone diurnal decrease rate during the summer due to higher leaf area index (LAI) cannot be compensated for by significantly higher diurnal ozone production in the summer, the monthly mean concentration of ground-level ozone peaks in the spring. The new explanation explores the role of seasonal variations of LAI and the corresponding seasonal changes of ozone dry deposition velocity to the formation of springtime-maximum of ground-level ozone.

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#### What is the utility of measuring gaseous Hg<sup>II</sup> dry deposition using Aerohead samplers?

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The most efficient way to quantify Hg<sup>II</sup> inputs to ecosystems is to measure wet and dry deposition. Wet deposition is determined by measuring Hg concentrations and the volume of precipitation. Dry deposition of Hg<sup>II</sup> is determined through direct measurement and/or by measuring air concentrations and using these in a model. Here, data collected using an Aerohead sampler holding cation exchange membranes are summarized, and the utility of this method for understanding dry deposition and other measurements and processes is discussed. This analysis includes information from publications, and recent data collected at Guadalupe Mountains National Park, Texas, USA, and Amsterdam Island, Southern Indian Ocean. This method primarily measures gaseous Hg<sup>II</sup> and little particulate-bound Hg.

The Aerohead method is useful for looking at large-scale trends in deposition, verifying Hg depletion events, understanding dry deposition velocities for compounds with specific chemistry, and identification of sources of Hg<sup>II</sup>. At numerous locations in the western USA, deposition rates were higher at higher elevations due to long-range transport of atmospheric pollution. When used in tandem with the Reactive Mercury Active System or a dual-channel system, more accurate deposition velocities – that vary as a function of GOM compound chemistry – can be calculated.

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