The National Atmospheric Deposition Program
Ammonia Monitoring Network (NADP/AMoN)

National Atmospheric Deposition Program
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Outline of Presentation

• Introduction to the National Atmospheric Deposition Program (NADP)
• Passive Air Sampling
• Ammonia Monitoring Network (AMoN) Methodology
• AMoN Data Quality Objectives
• Evaluation of AMoN Data Quality Indicators
Mission of the National Atmospheric Deposition Program (NADP)

• Provide data on the exposure of managed and natural ecosystems and cultural resources to acidic compounds, nutrients, mercury, and base cations in precipitation.

• Remain one of the nation’s premier cooperative research support programs, serving science and education and supporting communication and informed decisions on air quality issues affecting ecosystems and human health.
National Atmospheric Deposition Program (NADP) Stations

NTN – National Trends Network (acidic precipitation), since 1978; 265 sites
MDN – Mercury Deposition Network (mercury in precipitation), since 1995; 120 sites
AIRMoN – Atmospheric Integrated Research Monitoring Network (acidic precipitation events), since 1992; 6 sites
AMNet – Ambient Mercury Network (gaseous mercury), since 2009; 24 sites
AMoN – Ammonia Monitoring Network (gaseous ammonia), since 2007; 93 sites

Not Shown: Argentina (NTN) Taiwan (AMNet)
Motivation

Ammonium ion wet deposition, 1985

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu
Motivation
Ammonium ion wet deposition, 2013

See animated sequence at http://nadp.isws.illinois.edu/data/animaps.aspx

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu
Fraction of Total Reduced Nitrogen as Dry Deposition
(modeled estimates)
Current AMoN Site Locations

- 94 active sites
- 6 inactive sites

Not shown:
Bettles, Alaska (AK06)
Radiello Passive-Diffusive Samplers (PDS)

- Phosphoric acid absorbing surface
- Gas-permeable membrane
- No electricity
- No moving parts
- Suitable for spatially-dense network (economical)
AMoN Laboratory Methodology

• **Sample Preparation**
  – Samples prepared and extracted in dedicated clean-air bench

• **Analysis**
  – Flow injection analysis (FIA) colorimetry for ammonium ion
AMoN Quality Assurance

- **Laboratory Blanks** – Source water, reagent, and extraction blanks with each set analyzed
- **Travel Blanks** – Shipped randomly to 25% of sites with every two week deployment
- **Triplicates** – Deployed randomly at 5% of sites and always at Bondville (rural Champaign, IL); select sites pay supplement to have triplicates for all deployments
- **Reference Comparison** – Denuders and continuous monitor at Bondville, IL
- **External Audit** – Visits to sites when feasible; annual update of site information and photos.
1 μg/m³ = ~1.4 ppb (25°C)
Median (2007 – 2015) = 0.8 μg/m³ = 1.1 ppb

N = 67
(meeting 75% completeness)
Ammonia Concentration Time Series
Cañón ceta, Randall County, Texas
# AMoN Data Quality Objectives (DQOs)

## Proposed

<table>
<thead>
<tr>
<th>Data Quality Indicator</th>
<th>Data Quality Objective</th>
<th>Method of Evaluation</th>
<th>Frequency of Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparability</td>
<td>Slope = ± 20%</td>
<td>Reference Method (denuder)</td>
<td>Reference station (Bondville, IL)</td>
</tr>
<tr>
<td>Precision</td>
<td>COV = ± 20%</td>
<td>Randomized Triplicates</td>
<td>Every deployment (5% of samples)</td>
</tr>
<tr>
<td>Bias</td>
<td>Concentration ≤ 0.2 mg/L (as extract)</td>
<td>Randomized Travel Blanks</td>
<td>Every deployment (25% of samples)</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>≥ 90% of concentrations ≥ median travel blank</td>
<td>Randomized Travel Blanks</td>
<td>Annually</td>
</tr>
</tbody>
</table>
Radiello Measurement Comparison

A comparison was made between ALPHA, Ogawa and Radiello PDS.

Radiello chosen for precision, reproducibility, comparison to denuders, and cost efficiency.

Biweekly Sampler Variation

standard deviation of concentration

Radiello | ALPHA | OGAWA | RADIELLO

0.0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0

Radiello, ALPHa, Ogawa
Comparison to Other Methods

Bondville (Champaign County, IL)
Accuracy and Comparability

Triplicate denuders and passives deployed at Bondville, IL

Bondville – IL11 Historical NH3 Concentrations

DQO +/- 20%
Comparability

Radiello = 0.93 * denuder – 0.012

$R^2 = 0.9$

DQO: ± 20%

January 2010 – January 2014
## Precision of Triplicates in 2014

<table>
<thead>
<tr>
<th>Year</th>
<th>Precision</th>
<th>No. of triplicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008</td>
<td>6.9%</td>
<td>357</td>
</tr>
<tr>
<td>2009</td>
<td>6.5%</td>
<td>518</td>
</tr>
<tr>
<td>2010</td>
<td>5.3%</td>
<td>522</td>
</tr>
<tr>
<td>2011</td>
<td>9.0%</td>
<td>81</td>
</tr>
<tr>
<td>2012</td>
<td>5.8%</td>
<td>90</td>
</tr>
<tr>
<td>2013</td>
<td>4.1%</td>
<td>146</td>
</tr>
<tr>
<td>2014</td>
<td>4.6%</td>
<td>168</td>
</tr>
<tr>
<td>2015</td>
<td>4.5%</td>
<td>60</td>
</tr>
<tr>
<td><strong>Overall</strong></td>
<td><strong>5.5%</strong></td>
<td><strong>1942</strong></td>
</tr>
</tbody>
</table>

### Denuder Precision (Bondville)

<table>
<thead>
<tr>
<th>Year</th>
<th>Precision</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>15%</td>
<td>17</td>
</tr>
<tr>
<td>2011</td>
<td>6%</td>
<td>11</td>
</tr>
<tr>
<td>2012</td>
<td>5%</td>
<td>26</td>
</tr>
<tr>
<td>2013</td>
<td>17%</td>
<td>24</td>
</tr>
<tr>
<td>2014</td>
<td>8%</td>
<td>25</td>
</tr>
<tr>
<td>2015</td>
<td>7%</td>
<td>11</td>
</tr>
<tr>
<td><strong>Overall</strong></td>
<td><strong>9%</strong></td>
<td><strong>114</strong></td>
</tr>
</tbody>
</table>

**DQO: ± 20%**

*Label indicates number of deployed samples*
Precision

Absolute Relative Percent Difference

DQO: ± 20%
Bias

AMoN Concentrations

DQO: ≥ 90% of data above median travel blank

Travel blank flag: 0.4 μg/m³
Lab MDL: 0.02 μg/m³
73% of concentration values are ≥ 95\textsuperscript{th} percentile of travel blanks

AMoN Concentrations
Sensitivity

Percent of AMoN Samples Above Median Travel Blanks

DQO: ≥ 90% of data above median travel blank

Number of Deployments
N = 60 499 531 524 1075 1446 1658 1714 788
N = 59 494 523 523 1075 1446 498 432 181

Number of Travel Blanks
Sensitivity

Percent of samples < 2 x Mean Travel Blank, 2014

AMoN Samples Below 2x Mean Travel Blank (%)

- ≤ 10%
- 10% - 20%
- 20% - 30%
- 30% - 40%
- 40% - 50%
- 50% - 60%
- 50% - 70%
- > 70%
Spatial Representativeness

Week 5/5/14 to 5/12/14 (1st ALL Deployment)
Ammonia Concentration, µg/m³

Week 6/2/14 to 6/9/14 (2nd ALL Deployment)
Ammonia Concentration, µg/m³
Spatial Variability Studies
Bondville, IL

- Evaluate data usability as inputs for modeled estimates of deposition
- Samples deployed for 2 weeks, once every 6 weeks
Spatial Variability Study
Ft. Collins, CO

- Evaluate data usability as inputs for modeled estimates of deposition
- Samples deployed for 2 weeks, once every 6 weeks
Coweeta, NC
Flux Study

- Southern Appalachia Nitrogen Deposition Study (SANDS)
- Quantify seasonal and annual total deposition fluxes of nitrogen
  - CASTNET filterpack
  - Passive Monitors (NH$_3$, SO$_2$, HNO$_3$)
  - Continuous Analyzer (MARGA 2-S and fast response NOy analyzer)
Publications Using AMoN Data

• Examining the transport of NH$_3$ emissions across landscapes using nitrogen isotope ratios (Felix et. al., 2014)
• CALPUFF and CAFOs: Air pollution modeling and environmental justice analysis in the NC hog industry (Ogneva-Himmelberger et. al., 2015)
• Ammonia losses and nitrogen partitioning at a southern High Plains open lot dairy (Todd et. al., 2015)
• A statistical comparison of active and passive ammonia measurements collected at Clean Air Status and Trends Network (CASTNET) sites (Puchalski et. al., 2015)
• The increasing importance of deposition of reduced nitrogen in the United States (Li et. al., in progress)
Please join us at our next NADP meeting.

http://acidrain2015.org
For more information, see http://nadp.isws.illinois.edu/amon or email clehmann@illinois.edu

Ammonia Monitoring Network (AMoN)

The AMoN is the only network providing a consistent, long-term record of ammonia gas concentrations across the United States.

Ammonia (NH₃) is a gas readily released into the air from a variety of biological sources, as well as from industrial and combustion processes. It is the most prevalent base gas in the atmosphere. While NH₃ has many beneficial uses, it can detrimentally affect the quality of the environment through acidification and eutrophication of