Reactive Nitrogen Monitoring
Some definitions

• $\text{NO}_y \equiv \text{NO} + \text{NO}_2 + \text{NO}_3 + 2\times\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{HONO} + \text{HO}_2\text{NO}_2 + \text{RONO}_2$ (organic nitrates such as PAN and alkyl nitrates) + RONO (organic nitrites) + NO$_3^-$ (particulate nitrate).

• The ecology community defines “Total Reactive Nitrogen” to include N$_2$O which is not reactive in the sense considered here, thus we define “Total Chemically Reactive Nitrogen” to exclude N$_2$O and N$_2$. 
NEEDS

• Ecosystem health
  – Total deposition estimates (wet and dry) of all sulfur and reactive nitrogen species –
  – Critical loads

• Attribution of each species to its emission source (control measures)

• Other effects of these species (visibility, health………)
Issues

• Deposition is not measured but estimated from limited wind measurements.
• Some key species are not measured
• Accuracy with which some species are measured
• Time scale of measurement
  – 1 week
  – Need shorter sampling time increment for credible source apportionment (preferable hourly but not >24 hr.)
Species of interest

• Dry Species (Current)
  – $\text{SO}_2/\text{SO}_4$
  – $\text{HNO}_3/\text{NO}_3$
  – $\text{NH}_4$

• Dry Species (Missing)
  – $\text{NH}_3$
  – Reduced organic gases (Aliphatic amines ….)
  – $\text{NO}_x$ (NO and NO$_2$)
  – Oxidized organic gases (PAN - alkyl nitrates ….)
  – Reduced and oxidized organic nitrogen containing particulates.
Accuracy/Uncertainty

- \( \text{SO}_2/\text{SO}_4 \) measured reasonable well for both wet and dry
- Nitrogen is problematic across the board
  - Cut point is ill defined (coarse vs fine)
  - \( \text{HNO}_3/\text{NO}_3 \) split has large error
  - \( \text{NH}_4 \) error (underestimated) may be on order of 20-50%
A typical dry deposition budget?

**Total Deposition Budget (Spring)**

- wet ON: 20%
- wet no3: 4%
- wet nh4: 10%
- hno3: 9%
- nh3: 1%
- nox: 3%
- ON Gas: 26%

**GAS CONCENTRATION BUDGET**

- NOx: 7%
- NO3: 1%
- NH4: 5%
- HNO3: 26%
- ON Gas: 27%
- NH3: 34%
Modified IMPROVE

Sum of Reduced Nitrogen Species ($\text{NH}_3 + \text{NH}_4^+$)

- IMP3 Tot Red Nit = 5.43
- URG Tot Red Nit = 4.73

Concentration ($\mu g/m^3$)

Day of Year

August | September | October
Urban Comparison of 3 NH₃
Outline

• Motivation
• CASTNET Overview
• Sampling Setups of the Major Networks
• Proposed Sampling Trains for CASTNET and the Chemical Speciation Network
• Features of SASS Denuder Prototype 1
• SASS Testing: Experimental Design
• Results: Blanks, Collection Efficiency, Total Load Capacity
• Conclusions: Prototype 1
• Features of SASS Denuder Prototype 2
• Results: Blanks and Collection Efficiency
• Conclusions: Prototype 2
Developing and Testing Prototype Compact Denuders for Ambient Air Sampling Applications

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Dry gas and particle ON

• Can get estimates of oxidized ON both in gas and particle phase using catalytic converters and NO\textsubscript{x} boxes on a near real time basis
Trace Gas Samplers (off the shelf and custom)
Online N measurements: Two 3 Channel Instruments

**NO\textsubscript{y}** analyzer

1. NO\textsubscript{y} (inlet moly 285C)
2. NO\textsubscript{y}' (denuded inlet)
3. NO\textsubscript{y}'' (filtered inlet)

**NH\textsubscript{3}** analyzer

1. ‘Total’ Gas Phase Nitrogen (moly 815C)
2. ‘Traditional’ NO\textsubscript{x} (moly 315C)
3. NO

**DIRECT**

**BY DIFFERENCE**

1. Total
2. HNO\textsubscript{3}
3. pNO\textsubscript{3}+HNO\textsubscript{3}

1. ‘NH\textsubscript{3}’
2. ‘NO\textsubscript{2}’
Winter Overnight NO\textsubscript{y} Event

- Dominated by NO\textsubscript{y} plus smaller contributions of NH\textsubscript{3} and particulate NO\textsubscript{3}\textsuperscript{−}
- Low NO\textsubscript{i}: not a locally driven event
Questions

• Are current procedures for estimating dry deposition meaningful? (high time resolution met data combined with 1 wk average concentrations measurements)

• What needs to be measured that isn’t currently being measured?

• Is split between various species important
  – SO\textsubscript{2}/SO\textsubscript{4}, HNO\textsubscript{3}/NO\textsubscript{3}, NH\textsubscript{3}/NH\textsubscript{4}, etc or is total sulfur, or total gas/particle phase reactive nitrogen adequate?
    • For ecosystem response may not be so important?
    • For attribution and model assessment it is critical!

• Can defensible critical loads be set without a knowledge of total nitrogen?

• What sampling frequency/duration is acceptable – both in time and space?
Some Possible Changes

- Eliminate met monitoring if it isn’t being used for other purposes.
- At a minimum add an impregnated filter to the existing filter pack to measure NH$_3$.
- Replace current filter pack with similar filter pack (including NH$_3$) that operates automatically for time intervals of
  - Everyday or
  - Every third day.
- Add NH$_3$ and HNO$_3$ to the IMPROVE system.
- Measure total ON gas/particles at some sites.
  - Speciate ON at some basic level
Notes: Average 2007 and 2008 annual NO$_2$ from SCIAMACHY satellite. The factor on colorbar is 1.0E+14 molecules per cm$^2$. The resolution of the data is 0.125 deg x 0.125 deg. Each pixel contain the median of monthly data.
Notes: The ratio of average NO2 for year 2008 to the year 2007 (i.e. $\frac{NO_2_{-year2008}}{NO_2_{-year2008}}$) annual NO2 from SCIAMACHY satellite. The low NO2 concentration data ($NO_2 < 10^{15}$) are not considered here. The resolution of the data is 0.125 x 0.125. Each pixel is derived from the median of 2007 and 2007 months data.
Climate Change

- Effects of Climate Change
- Radiation Balance
- Carbon Feedbacks
- Greenhouse Gas Contributors
- What Can Be Done?

- Rising Oceans
- Changing Precipitation Patterns
- Dying Coral Reefs
- Melting Permafrost
- Changing Ecosystems
- Melting Glaciers
Radiation Balance

- Solar radiation 100
  - Scattered into space by the atmosphere 6
  - Scattered into space by clouds 20
  - Reflected into space by earth's surface 4
  - Absorbed by the earth 51
- Absorbed by atmosphere and clouds 19
  - Combined solar heating of ground and longwave radiation emitted by the earth 147
  - Longwave radiation scattered back into space from the earth 6
  - Longwave radiation scattered back into space from the atmosphere and clouds 64
  - Longwave radiation reflected back to earth 96
  - Longwave radiation emitted by the earth 96
Other Recommendations from EPA NOX/SOX review

- We recommend monitoring a suite of reactive nitrogen species the sum of which is “Total Chemically Reactive Nitrogen” defined as the sum of all oxidized species except N₂O and the sum of ammonia and ammonium.

- Total Chemically Reactive Nitrogen = NOy + NHx

- **Species Method** NOy (total oxidized nitrogen) Reduction to NO followed by chemiluminescence NO₃⁻ (particulate nitrate) Denuder/filter sampling followed by ion chromatography HNO₃ (nitric acid vapor) Filter/denuder and followed by ion chromatography. NH₃ (ammonia) Filter/denuder followed by colorimetry or ion chromatography NH₄⁺ (ammonium) Denuder/filter followed by colorimetry or ion chromatography
**WHAT WE REALLY NEED TO MEASURE**

<table>
<thead>
<tr>
<th></th>
<th>WET</th>
<th>GAS</th>
<th>PARTICLE</th>
<th>Temporal scale (gas/particle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_2/\text{SO}_4^{2-}$</td>
<td>*****</td>
<td>****</td>
<td>*****</td>
<td>Min/hr/day/week</td>
</tr>
<tr>
<td>$\text{NO}_2/\text{HNO}_3^-/\text{NO}_3^-$</td>
<td>****</td>
<td>****(***CASTNET)</td>
<td>****(***CASTNET)</td>
<td>Min/hr/day/week</td>
</tr>
<tr>
<td>$\text{NH}_3/\text{NH}_4^-$</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>Min/hr/day/week</td>
</tr>
<tr>
<td>Total ON</td>
<td>***</td>
<td>*</td>
<td>*</td>
<td>Integrated sample/event based</td>
</tr>
<tr>
<td>$\text{ON}_r$ (markers)</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>?</td>
</tr>
<tr>
<td>$\text{ON}_o$ (markers)</td>
<td>*</td>
<td>***</td>
<td>***</td>
<td>Min/hr/day/week (gas/part) Event for markers</td>
</tr>
<tr>
<td>$\text{ON}_b$ (markers)</td>
<td>*</td>
<td>**</td>
<td>*</td>
<td>Integrated samples</td>
</tr>
</tbody>
</table>

***** Measure with high degree of accuracy  
**** Measure with reasonable accuracy  
*** Measure with low accuracy  
** Research monitoring  
* Currently cannot do

Note: measurements should be event based for wet deposition and gases and particles measured at least on a 24 hr schedule.
Next Steps

- Establish/examine need for ON measurements at x number of sites?
- Develop denuders to do NH$_3$, NH$_4$, and HNO$_3$/NO$_3$ split (within 6 months – year)
- Test filter based measurements for gas/particle phase oxidized ON measurements (1+ years)
- Develop marker technology/methodology for apportioning ON in wet deposition (2+ years ?)
- Do the same for reduced gas/particles (time ?)
- Implementation schedule (Funding??)
Nitrogen Monitoring

• Wet ON at a number of regionally representative sites
• Develop method for apportioning wet ON to reduced, oxidized, biological
• NHx at a number of regionally representative sites
• NOy at a number regionally representative sites
• How to measure total reduced ON gas and/or particle phase?
• Supplemental measurements in ROMO – east/west – additional species – temporally representative
Wet DON

• Can measure TON
• Can’t directly measure reduced, oxidized, or biological ON – important to make these distinctions from an apportionment perspective because sources are distinctive
• Can use receptor type models to apportion DON if one has reliable chemical markers
  – Measure reduced OC markers such as amines and urea for reduced DOC
  – Measure oxidized OC markers such as alkyl nitrates, nitrophenols, and other nitroaromatic
  – Measure biological markers such as amino acids and peptides
  – Apply simple regression models or more sophisticated models such as PMF and UNMIX.
How important is AON?

- 51 studies in North America have DON at 38±19% of TON (Wet)
- As much as 30% of particulate OC is nitrogen containing
- Gas % of TON?
What isn’t measured?

• $\text{NH}_3$

• Organic nitrogen either in wet or dry (gas and particle phase) or its reduced, oxidized or biological forms
  – $\text{NO}_2$, peroxyacetyl nitrate (PAN) and related alkyl nitrates
  – Aliphatic amines
  – Proteins, amino acids, etc
## Tabular summary

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
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<tbody>
<tr>
<td>NOy (total oxidized nitrogen)</td>
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<tr>
<td>NO$_3^-$ (particulate nitrate)</td>
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</tr>
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<td>HNO$_3$ (nitric acid vapor)</td>
<td>Filter/denuder and followed by ion chromatography.</td>
</tr>
<tr>
<td>NH$_3$ (ammonia)</td>
<td>Filter/denuder followed by colorimetry or ion chromatography</td>
</tr>
<tr>
<td>NH$_4^+$ (ammonium)</td>
<td>Denuder/filter followed by colorimetry or ion chromatography</td>
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</tbody>
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**WHAT’S MISSING: ORGANIC NITROGEN**