Is there need to collect routine ammonia/ammonium measurements in ambient air monitoring networks?

Perspectives of a Data Analyst from a Small State Air Pollution Regulatory program
Is there need to collect routine ammonia/ammonium measurements in ambient air monitoring networks?

State Air Program Perspectives

- Data Analyst: Yes, They’re key unmeasured species.
- Modeler: and we need continuous data for all species.
- Monitor: but we’re already measuring NH4, OK?
- QA Skeptic: Current data quality is poor or Uncertain.
- Measurement Wiz: Possible, but labor/cost-Intensive.
- Boss: Monitoring already eats > 60% of my budget! What will you give up to add NH4 & NH3?
NH₃ & NH₄⁺ are critical aerosol and precursor components which are not currently measured (or not measured well) in routine monitoring networks. They Should be!

Direct relevance to current regulatory programs for PM 2.5 and Regional Haze – and especially for future control plans.

If / When / Where there’s just enough NH₃ to fully neutralize SO₄, then SO₂ reductions may yield 2 moles of NH₄NO₃ for each mole of (NH₄)₂SO₄ reduced – resulting in a 50% increase in PM₂.₅ mass and associated health & visibility effects.
**STN** (urban) network measures NH4 on Nylon filters with HNO3 denuder, **IMPROVE** (rural) measures NH4 on Nylon filters at some Southeastern sites with HNO3 & NH3 denuders (with support from NPS & VISTAS).
Regional Haze Regulatory Metrics are based on “Reconstructed Extinction” (Measurements + Assumptions)

<table>
<thead>
<tr>
<th></th>
<th>Measure Major Species</th>
<th>( \text{SO}_4^{2-} )</th>
<th>( \text{NO}_3^- )</th>
<th>EC</th>
<th>OC</th>
<th>Crustal Elements</th>
<th>PM(<em>{10} ) &amp; PM(</em>{2.5} ) Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Assume Unmeasured Species</td>
<td>((\text{NH}_4)_2\text{SO}_4) (1.375 \times \text{SO}_4^{2-})</td>
<td>(\text{NH}_4\text{NO}_3) (1.29 \times \text{NO}_3^-)</td>
<td>1 x EC</td>
<td>C + O + H 1.4 x OC</td>
<td>Soil Oxides Formula</td>
<td>Coarse Mass PM(<em>{10} ) - PM(</em>{2.5} )</td>
</tr>
<tr>
<td>3</td>
<td>X by Dry Extinction Efficiencies</td>
<td>3 m(^2)/g</td>
<td>3 m(^2)/g</td>
<td>10 m(^2)/g</td>
<td>4 m(^2)/g</td>
<td>1 m(^2)/g</td>
<td>0.6 m(^2)/g</td>
</tr>
<tr>
<td>4</td>
<td>X by f(RH) Hygroscopic Growth</td>
<td>about 2 to 4</td>
<td>about 2 to 4</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>Sum &amp; Sort into Best 20% &amp; Worst 20%</td>
<td>(12 \pm 4 \times \text{SO}_4^{2-})</td>
<td>(12 \pm 4 \times \text{NO}_3^-)</td>
<td>10 x EC</td>
<td>6 x OC</td>
<td>3 x Crustal Elements</td>
<td>0.6 x Coarse Mass</td>
</tr>
</tbody>
</table>

Ammonium is Assumed, Not Measured. So what could possibly go wrong?
Without knowing Ambient Ammonium Concentrations,

<table>
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<tr>
<th>Measure Major Species</th>
<th>( \text{SO}_4^{2-} )</th>
<th>( \text{NO}_3^- )</th>
<th>Nitrate sometimes &quot;Missing&quot; (nylon filter clogs) on Dirtiest days, which are often worst Sulfate episodes (but can't &quot;reconstruct&quot;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assume Unmeasured Species</td>
<td>((\text{NH}_4)_2\text{SO}_4) 1.375 ( \times ) ( \text{SO}_4^{2-} )</td>
<td>( \text{NH}_4\text{NO}_3 ) 1.29 ( \times ) ( \text{NO}_3^- )</td>
<td>Sulfate could be ( \text{NH}_4\text{HSO}_4 ) or ( \text{H}_2\text{SO}_4 ) (20 to 40% Error) Nitrate could be ( \text{NaNO}_3 ) from aged sea salt (trivial Error)</td>
</tr>
<tr>
<td>( X ) by Dry Extinction Efficiencies</td>
<td>3 ( \text{m}^2/\text{g} )</td>
<td>3 ( \text{m}^2/\text{g} )</td>
<td>3 ( \text{m}^2/\text{g} ) is reasonable for all accumulation mode Sulfates but Too high for fine tail of coarse mode Nitrates (300% error), Also too high for ( \text{SO}_4^{2-} ) &amp; ( \text{NO}_3^- ) adsorbed to coarse soil particles.</td>
</tr>
<tr>
<td>( X ) by ( f(\text{RH}) ) Hygroscopic Growth</td>
<td>about 2 to 4</td>
<td>about 2 to 4</td>
<td>Acidic Sulfates adsorb more water (partly offsetting Error #1), But at high acidity, water uptake &gt;&gt; mass overestimate. Coarse mode ( \text{NaNO}_3 ) was already larger than efficient size.</td>
</tr>
<tr>
<td>Sum &amp; Sort into Best 20% &amp; Worst 20%</td>
<td>12 ( \pm ) 4 ( \times ) ( \text{SO}_4^{2-} )</td>
<td>12 ( \pm ) 4 ( \times ) ( \text{NO}_3^- )</td>
<td>Sulfate and Nitrate Contributions overestimated on clean days, Sulfate Contributions underestimated on hazy days with acidity.</td>
</tr>
</tbody>
</table>

We’ll occasionally make big mistakes, especially on cleanest & dirtiest days
Nitrate in Big Bend N.P. (BRAVO)

- The sea salt link
  - High particulate nitrate associated with flow from Gulf
  - Not necessarily high when total nitrate (including HNO$_3$(g)) was high

From Jeff Collett, CSU
Nitrate in Big Bend N.P. (BRAVO)

- Found in coarse mode particles
  - Mode size ~4-5 μm
  - Size distribution similar to Na⁺
- PM₂.₅ size cut does not separate fine and coarse modes well

From Jeff Collett, CSU
IMPROVE Ion Study

Aerosol NO$_3^-$, Cl$^-$, SO$_4^{2-}$, Na$^+$, K$^+$, NH$_4^+$, Ca$^{2+}$, Mg$^{2+}$

Gaseous NH$_3$, HNO$_3$

Bondville, IL
February, 2003

San Gregornio, CA
March/April, 2003

Brigantine, NJ
November, 2003

Sequoia NP, CA
February, 2004

Grand Canyon NP, AZ
April/May, 2004

From Jeff Collett, CSU
Sampling and extraction issues

- Does water efficiently extract nitrate from nylon filters?
  - Nitric acid collected on nylon filters not efficiently recovered with water extraction

- What happens to NH₄NO₃ volatilized from nylon filters?
  - HNO₃ trapped? Decrease in water extraction efficiency?
  - NH₃ lost? Bias in measured PM₂.₅ ammonium?

From Jeff Collett, CSU
Bondville test results

- Nylon filter extraction by water looks good

- Up to 18% of NH$_4^+$ lost from nylon filter

From Jeff Collett, CSU
Molar Ratio NH4:SO4 at IMPROVE Sites

Great Smoky Mtns, TN

From Pat Brewer, VISTAS

Shenandoah, VA

From Pat Brewer, VISTAS
Molar Ratio NH4:SO4 at SEARCH Sites
Birmingham, AL

These data suggest local urban sources of NH3 emissions.
From Pat Brewer, VISTAS
Hygroscopic Growth functions for Sulfate compounds and Organics, showing theoretical $f(RH)$ & least squares regression results from GSRM

Adapted from Malm et al. (2000) IMPROVE Report
Recent Comparative Receptor Model and Ensemble Trajectory Analyses

- Poirot et al. (2001)
- Polissar et al. (2001)
- Underhill VT
- Lee et al. (2002)
- Poirot et al. (2002)
- Brigantine NJ
- Chen et al. (2002)
- Ft Mead MD
- Coutant et al. (2003)
  (EPA STN sites)
  - Houston TX
  - Indianapolis IN
  - St Louis MO
  - Bronx NY
  - Charlotte NC
  - Milwaukee WI
  - Birmingham AL
  - Washington D.C.

- Lee et al. (2003)
- Poirot et al. (200?)
- Toronto CAN

- Coutant et al. (2002)
  (MANE-VU & MWRPO)
  IMPROVE & CASTNET
  - Acadia ME
  - Boundary Waters MN
  - Brigantine NJ
  - Dolly Sods WV
  - Great Smoky Mtns TN
  - James River Face VA
  - Lye Brook VT
  - Mammoth Cave KY
  - Shenandoah VA
  - Washington D.C.
  - Connecticut Hill NY
  - Arendstville PA
  - M.K. Goddard PA
  - Quaker City OH
  - Livonia IN
  - Bondville IL

All of the Above
Available in CATT
Evaluation of Sea Salt Source by Surface Met and Ensemble Back Trajectories confirms that Sea Salt comes from the sea shore, as she should…
Highest fine soil at Brigantine & other Eastern Sites is from Sahara Dust.
But chemical composition of BRIG Salt & Soil sources shows substantial excess SO4 & NO3 associated with these (coarse mode) aerosols.
Most of the NO$_3$ (67%) and SO$_4$ (70%) from Brigantine Unmix results was associated with 2 large secondary sources with strong, opposite seasonal patterns (winter NO$_3$ vs. summer SO$_4$).

Trajectory-based upwind probability fields for high contributions from these sources suggest coal burning contributions for both, but also suggest importance of agricultural NH$_3$ for aerosol nitrates.
Comparative Receptor Modeling of Toronto Speciated Fine Particle Data

Jeff Brook, Env. Canada
Patrick Lee, U. Toronto
R. Poirot, VT DEC &
P. Wishinski, VT DEC
Daily PM$_{2.5}$: Feb, 2000 – Feb., 2001

Mass: by Partisol FRM

Ions: SO$_4$, NO$_3$, NH$_4$, K, Na, Cl, PO$_4$ by IC

Elements: by ICP-AES and ICP-MS

Carbon by TOT (O1, O2, O3, O4, EC)

Organic Acids: by Capillary Electrophoresis

• Sampling Schedule: 9 AM – 9 AM (reduces volatile losses)

• Ions on (NH$_3$ & HNO$_3$-denuded) Teflon with backup Nylon for volatile NO$_3$ (what happens to NH$_4$ from NH$_4$NO$_3$ on nylon?)

• Carbon on quartz by “modified TOT (NIOSH+TOR) and with OP quantified at each thermal stage on subset of samples, with ratios used to disaggregate OP among O1 – O4 (& with no blank subtract?)
Is this “Acid Catalyzed SOA” formation as in Jang et al. (2002)?
OC benefit from NOx/SOx`reductions?
Yields from Teflon bag experiments

(Kamens and Jang)
Contributions of 3 Coal-related sources increase as wind speed increases (red) from the South.

HY-SPLIT trajectory-based upwind probability fields indicate the 3 “coal-related” sources have similar regional origins, consistent with similar model results from other receptor sites.
NH$_4$NO$_3$ shows more Westerly transport influence, consistent with NH$_3$ from US agricultural regions, but Weekday/Weekend pattern also suggests local sources.
Average PM-2.5 Species Concentrations at Washington DC and nearby Shenandoah NP

What is Urban aerosol Nitrate 3 x greater than Rural?
Reasons to measure NH₃ and/or NH₄ in routine monitoring networks

- Evaluation and Improvement of Ammonia Emission Inventories
- Evaluation and Improvement of Photochemical Aerosol Models
- Understanding Indoor vs. Outdoor NH₄NO₃
- Is NH₃ Transported and does NO₃ “Assist”?
- Improved Performance and Evaluation of Aerosol Receptor Models
- Understanding Acid Aerosol Health (direct or indirect) Effects
- Understanding Acid Aerosol Water uptake & associated Visibility Effects
- Understanding Acid Catalyst formation of Secondary Organic Aerosols
- Discerning Contributions and Effects of Fine & Coarse Mode Aerosols
- Understanding Where & When Less SO₄ may result in More NO₃
- Developing and Tracking Efficient Pollutant Control Strategies