Ammonia: Measurement role in National Ambient Air Networks

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Topics

- Role of NH3 in air quality management
- Overview of NH3/related measurements in routine networks
- Measurement issues
- National Monitoring Strategy and associated recommendations
NH3...effects

• Deposition
  - watershed eutrophication
  - Acidification/neutralization
• Global climate radiation budget (aerosol)
• National Air program standards
  - PM10
  - PM2.5
Further progress under the Clean Air Act is complex, burdensome and uncertain.

Note: Dotted lines indicate a range of possible dates.

1 Further action on ozone would be considered based on the 2007 assessment.
2 The SIP-submittal and attainment dates are keyed off the date of designation; for example, if PM or ozone are designated in 2004, the first attainment date is 2009.

EPA is required to update the new source performance standards (NSPS) for boilers and turbines every 8 years.

In developing the timeline of current CAA requirements, it was necessary for EPA to make assumptions about rulemakings that have not been completed or, in some cases, not even started. EPA’s rulemakings will be conducted through the usual notice-and-comment process, and the conclusions may vary from these assumptions.
Complex system

- **Measurements**
  - Stability/volatility
    - Ammonium nitrate, association with nitric acid (sticky)
      - Real exposure indoors?...given volatility?
    - Consequently, NH₄, NH₃g, HNO₃g all present challenges

- **Uncertain emission estimates**
  - Diversity of area sources
  - Many agricultural based

- **Modeling confounded by heterogeneous processes**
  and above (i.e., ability to diagnose)
NH3 is not a “central” player in atmospheric chemistry; however, various inter-pollutant interactions impact pollutant/component specific strategies?
Organic
Carbon
Ozone
Sulfate
Nitrate

Consequently,

| Impacts on major aerosol components due to precursor reductions...confusing! |
|---|---|---|
| Reductions of | NOx | SOx | VOC/CO |
| ? | ? | ? | ? |
| Nitrate | ? | ? | ? |
| Sulfate | ? | ? | ? |
| Ozone | ? | ? | ? |
| Organic Carbon | ? | ? | ? |
Is NH3 limiting .....in formation of ammoniumnitrate?

• Or, where and when are NOx controls most effective in reducing p- NO3?
Limiting Reactant: Ammonia or Nitric Acid (courtesy, Pandis, CMU)?

Ammonium Nitrate ($\mu g m^{-3}$)

A: Ammonia limited
B: Nitric acid limited
The Sulfuric Acid/Ammonia System
2001...courtesy, Pandis, CMU

2 Ammonia:1 Sulfate

<table>
<thead>
<tr>
<th>Total Available Ammonia (µg m⁻³)</th>
<th>Concentration (µg m⁻³)</th>
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<tbody>
<tr>
<td>0</td>
<td>Ammonia</td>
</tr>
<tr>
<td>1</td>
<td>Ammonium</td>
</tr>
<tr>
<td>2</td>
<td>Sulfate</td>
</tr>
<tr>
<td>3</td>
<td>Bisulfate</td>
</tr>
<tr>
<td>3.6</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

- Ammonia
- Ammonium
- Sulfate
- Bisulfate
- Sulfuric acid
Model Sensitivity Runs

- When/where are Nox controls most effective?
- Impact on nitrates associated with SO2 and VOC reductions
CMAQ Ammonia Sensitivity Runs- 50% NH3 Reduction- January

CMAQ Jan Avg Nitrate

Basecase Nitrate

CMAQ Jan Avg Nitrate- 50% NH3 Red.

Nitrate with 50% Ammonia Reduction
50% NOx Reduction - January
Effect on Sulfate and Nitrate

Jan Avg Sulfate Change - 50% NOx Cut

Jan Avg Nitrate Change - 50% NOx Cut

January 1, 1996 1:00:00
Min = -0.0 at (51,8), Max = 1.2 at (99,42)

January 1, 1996 1:00:00
Min = -5.2 at (13,44), Max = 0.8 at (19,33)
50% NOx Reduction - Reduced NH3 base (50% NH3 reduction) - January effect on Sulfate and Nitrate

Jan Avg Sulfate Change - 50% NOx Cut (from reduced NH3 base)

Jan Avg Nitrate Change - 50% NOx Cut (from reduced NH3 base)
50% SO2 Reduction - July
Effect on Sulfate and Nitrate

July Avg Sulfate Change - 50% SO2 Cut

July Avg Nitrate Change - 50% SO2 Cut
50% SO2 Reduction - January
Effect on Sulfate and Nitrate

Jan Avg Sulfate Change - 50% SO2 Cut

Jan Avg Nitrate Change - 50% SO2 Cut

Seasonal Average IMPROVE Nitrate

Seasonal Average Particulate Nitrate- IMPROVE and CASTNET Visibility Network*

*CASTNET Visibility network data is for 8 sites- fall only
Where are the measurements?

- Ammonium (Dry)….PM2.5 speciation (including IMPROVE); CASTNET

- Ammonium Wet (NADP)

- NH3….SEARCH/ARIES…..network

- Special studies (PM2.5 Supersites)
Current/Planned
Urban & Rural PM$_{2.5}$ Speciation Networks

- **Trends (54)**
- **Supplemental (~215 sites currently known)**
- **Supersites**
- **Daily Sites**

**IMPROVE**
- **IMPROVE Protocol**
- **Castnet conversion**
- **Deploy in 2002**
- **Deploy in 2003**

01/02
SEARCH Enhanced Air Quality Measurement Network

- Oak Grove (OAK)
- Centreville (CTR)
- Pensacola (PNS)
- Yorkville (YRK)
- Jefferson Street (JST)
- North Birmingham (BHM)
- Gulfport (GFP)
- Outer Landing Field #8 (OLF)

Legend:
- Star: Rural
- Red: Urban
- Blue Star: Suburban
Measurement Issues, NH3

• Integrated methods
  - Absorption, extraction, analysis
    • CASTNET filter pack/denuder system (1 week)
    • Acid denuders in low volume particle samplers (typically 24 hr.)
  - Labor intensive, lack temporal detail

• Semi-continuous methods
  - Cycled difference techniques
  - IC particle/gas methods
  - Optical techniques (FTIR, DOAS)
  - Cost, familiarity, reliability, commercial availability
Measurement Issues, NH4

- **PM2.5 speciation networks**
  - 24 hr. integrated measurement; 1/3 day
  - 54 trends sites; ~200 SIP sites
    - Acid gas denuding; nylon (basic) filter substrate
  - small subset of IMPROVE sites
    - Acid/base gas denuding; nylon (basic) filter substrate...traps NO3 loss...what about NH3 loss?
Recent Example Applications

- St. Louis Supersite (Integrated)
- Search/ARIES...ARA (continuous)

Ammonia Concentration (ppb)

- Park Hills, MO (90 km south of St. Louis)
- East St. Louis, IL (3km east of City of St. Louis, MO, central business district)
Yorkville, GA SEARCH Site (courtesy, ARA..Edgerton)

Lat. 33.95 N
Long. 85.01 W
Elev. 390 m
Instrumentation

- 10 meter met
- Trace gas: $O_3$, CO, $SO_2$, NO, $NO_2$(photolytic), $HNO_3$, NOy
- Filter PM 2.5: FRM Mass, Particle Composition Monitor (PCM) Speciation Monitor
- Filter PM Coarse Mass (Dichot)
- Semi-Continuous PM: Nephelometer, Aethelometer, R&P 5400, Harvard $SO_4$, ARA NO$_3$/NH$_4$, Dried 30°C TEOM
TRN Diagram
TRN NH$_3$ vs Denuder NH$_3$

24 Hour Samples

Continuous NH$_3$ = 1.12 Denuder NH$_3$ - 0.19

R$^2$ = 0.92
HNO₃, NH₃, NH₄NO₃ events
NOy Budget Time-Series
What should we do?

- New National Monitoring Strategy
- NCORE multiple pollutant stations
- Emphasis on more science based measurements, model evaluation, long term program accountability
National Core Network: NCORE

- Goal: Move from loosely tied single-pollutant networks to coordinated, highly leveraged multi-pollutant networks with real-time reporting capability.
Level 2: ~75 Multi-pollutant (MP) Sites, “Core Species” Plus Leveraging From PAMS, Speciation Program, Air Toxics

Level 1: 3-10 Master Sites Comprehensive Measurements, Advance Methods Serving Science and Technology Transfer Needs

Level 3: Single Pollutant Sites (e.g. >500 sites each for O3 and PM2.5) Mapping Support

Minimum “Core” Level 2 Measurements
Continuous N, SO2, CO, PM2.5, PM10, O3; PM2.5 FRM, Meteorology (T, RH, WS, WD)...NH3, HNO3 at subset?