Issues in Ammonia and Nitric Acid Measurements: Experiences in the Midwest

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Overview

• Why ammonia?
• Network sites and equipment
• What have we done with the data?
  – How good is it?
  – What does it tell us about PM?
Why ammonia (and nitric acid)?

- NAAQS? No
- Toxic? Not at ambient concns.
  - TLV=50 ppm, typical ambient = <1-3 ppb
- Nuisance? Yes, at sources (animal feeding, manure spreading)
- Urban pollutant? Don’t really know
- Direct environmental effects? Principal basic gas in atmosphere; deposition results in acidification
- Chemically reactive? Yes
Reactions of ammonia

- \( \text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3 \) (ammonium nitrate)
- \( \text{H}_2\text{SO}_4 + 2 \text{NH}_3 \rightarrow (\text{NH}_4)\text{SO}_4 \) (ammonium sulfate)
- Ammonium nitrate and sulfate are two of the top three constituents of PM2.5
- Ammonia reacts preferentially with sulfate so ammonium nitrate is formed only after all sulfate is fully neutralized
- Ammonium nitrate is formed preferentially at low temperatures and high humidity (winter, nighttime)
- Decreasing sulfate can theoretically cause ammonium nitrate concentrations to increase
Why focus on the Midwest?
1. Ammonia Emissions Density
Why focus on the Midwest?

2. Ammonia/Nitrate link

Ensemble trajectory analysis shows high PM nitrate associated with high-ammonia, agricultural Midwest
Overview

• Despite importance of ammonia in atmospheric chemistry, no national studies or routine monitoring of ambient (non-source-influenced) concentrations has been done
• To fill data gap, MRPO and CENRAP began rural monitoring in Oct. 2003
• Beginning network--10 sites: 9 rural, 1 urban
• Current network – 12 sites, 8 rural, 3 urban
• All rural sites are IMPROVE sites except Pleasant Green, MO
• Denuder/filterpack sampling
  – Phosphoric acid coated denuder for NH3
  – Sodium carbonate coated denuder for HNO3 and SO2
  – Teflon filter followed by nylon filter (for nitrate dissociation)
  – Two sites (Pleasant Green MO, Lake Sugema IA) use automated R&P samplers (different denuder/inlet configurations)
• 1/6 day sampling
• Two continuous samplers, Pranalytica and IC, at Bondville for QA
• Both NH3 and HNO3 very difficult to measure, due to reactivity, ‘stickiness’, low ambient concentrations, significant inlet losses
LADCO-CENRAP NH3 Network

Red=urban sites
Blue=rural sites
Custom-built URG sampler
URG System

R&P System
Temporal variation in NH3

Log scale
Temporal variation in HNO3

Log scale

HNO3

0.001
0.01
0.1
1
10
100

O N D J F M A M J J A S O
C O E A E A P A U U U E C
T V C N B R R Y N L G P T
0 0 0 0 0 0 0 0 0 0 0 0
3 3 3 4 4 4 4 4 4 4 4 4
Spatial variation in NH3
Spatial variation in HNO3
QA Comparisons at Bondville

• Species comparisons
  – Collocated URG and R&P, March 2004-Feb 2005
  – Collocated URGs, Sep. 2004 – Feb. 05
  – Collocated R&Ps, Jan-Feb. 05

• Cyclone Effects

• Denuder Breakthrough

• Ammonium Losses from Filters
Cyclone Effects

NH3 (ppb)

SO2 (ppb)

HNO3 (ppb)

URG without cyclone

R&P (Impactor)
SO2 Breakthrough, ppb

- Denuder 1 for acid gases
- Denuder 2 for NH3
- Denuder 3 for NH3 breakthrough
Ammonium Losses from Filters

Concentration in ug/m³

$0.0816 + 1.1896 \times x$

1:1 line
How good are the network data?

• Comparison of collocated monitors
• Comparison with IMPROVE
• Comparison with modeled data
Comparison of IMPROVE with LADCO data

Work by Blanchard & Tanenbaum
Comparison of Ambient with Modeled (ISORROPIA) Species

\[
\text{PHNO}_3 = 0.172 + 0.862 \times \text{MNNO}_3; \ R^2 = .502
\]

\[
\text{PNH}_3 = -0.119 + 0.969 \times \text{MNH}_3; \ R^2 = .978
\]

\[
\text{PN}_3 = -0.117 + 1.042 \times \text{MN}_3; \ R^2 = .936
\]

\[
\text{PNH}_4 = 0.185 + 0.931 \times \text{MNH}_4; \ R^2 = .912
\]

From Blanchard & Tanenbaum report
Thermodynamic Models—
ISORROPIA and SCAPE2

- Thermodynamic models predict the partitioning of PM species between gas and particle phases, based on concentration, temperature, and RH
- Using measured NH3, HNO3, NH4, NO3, and SO4, systematically vary concentrations from starting (ambient) conditions and calculate new equilibrium concentrations
- Resulting isopleths tell us how sensitive PM is to changes in precursors
  - SO4 and NO3 – 25, 50, 75, 100% of current
  - NH4 – 50, 100, 150, 200% of current
Predicted PM$_{2.5}$ Concentrations

PM is about equally sensitive to reductions in SO$_4$ and NO$_3$

PM is slightly more sensitive to NH$_3$ reductions than to HNO$_3$
Seasonal PM$_{2.5}$ Concentrations

PM is most responsive to NO3 in the winter; response to sulfate is similar year-round.
Expected reductions in SO4 may lead to PM being less responsive to reductions in ammonia
Geographic extremes

Blue Mounds, MN:
Least sensitive to NH3; farthest north, and highest NH3 site

Athens, OH:
Most sensitive to NH3; farthest east, lowest NH3 site
Sample-by-sample evaluation of gas ratio and excess ammonia
How do ambient results compare with modeling?

**Agricultural (CMU Model) NH3 30% Reduction Annual Average Difference**

**Entire Domain Anthropogenic NOX 30% Reduction Annual Average Difference**
Analysis of hourly data from IC

- Predicted HNO$_3$ vs. Measured HNO$_3$:
  \[ \text{P(HNO}_3\text{(ug/m}^3) = .008 + .967 \times \text{M(HNO}_3\text{(ug/m}^3)), R^2 = .884} \]

- Predicted NH$_3$ vs. Measured NH$_3$:
  \[ \text{P(NH}_3\text{(ug/m}^3) = .681 + 1.023 \times \text{M(NH}_3\text{(ug/m}^3)), R^2 = .981} \]

- Predicted NO$_3$ vs. Measured NO$_3$:
  \[ \text{P(NO}_3\text{(ug/m}^3) = -.008 + .967 \times \text{M(NO}_3\text{(ug/m}^3)), R^2 = .929} \]

- Predicted NH$_4$ vs. Measured NH$_4$:
  \[ \text{P(NH}_4\text{(ug/m}^3) = -.094 + .652 \times \text{M(NH}_4\text{(ug/m}^3)), R^2 = .732} \]
24-hr vs. hourly model results at current NH3
24-hr vs. hourly model results at current SO4
Preliminary Conclusions

• At current conditions, PM mass decreases in response to reductions in sulfate, nitric acid, and ammonia

• At current conditions, particulate nitrate formation limited generally by nitric acid

• At expected future conditions (i.e., lower sulfate), PM mass is more responsive to nitric acid reductions

• Daily and hourly data support same conclusions
Conclusions

• No significant differences between URG and R&P samplers except in HNO3 measurements
• Differences in HNO3 due partly to cyclone losses
• Ammonium losses average 20%
• Denuders highly efficient for SO2 and NH3; HNO3 results were erratic
Applications for NH3 data

- Thermodynamic evaluation across the region; when and where are conditions limited by nitric acid vs. ammonia (Charlie Blanchard)
- PM episode analysis – Feb. ’05 event, role of snow as source/sink
- Model evaluation (Kirk Baker dissertation?)
- Eventually: inventory validation
Seasonal Changes in Diurnal NH₃ Variability

NH₃ Concentration in ppb

Hour of Day

season  Summer  Winter
Seasonal Changes in Diurnal HNO₃ Variability

HNO₃ Concentration in ppb

Hour of Day

season  Summer  Winter
Extremes in Nitrolux Hourly NH₃ Averages

Hourly NH₃ at Bondville

NH₃ ppbv (hourly average)

Hours Elapsed

0 1000 2000 3000 4000 5000 6000

28JUL03 3NOV03 1DEC03 16FEB04 3MAY04
Ammonia Concentrations Aloft, by Route

Red lines = Ground-level median concentrations, summer (top) and winter (bottom)
Spatial Patterns: NADP NH4 and LADCO NH3
Method Intercomparison: IC vs. Denuder

Conc, ppb

01OCT03  01NOV03  01DEC03  01JAN04  01FEB04  01MAR04

Ion Chrom.  Denuder