Air Quality Modeling of Ammonia: A Regional Modeling Perspective

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Ammonia
End Points of Concern

• PM$_{2.5}$ aerosols
  – inorganic fraction – majority fraction
• Watershed nutrient loading and N deposition to lakes and streams
• Coastal estuary nutrient loading
• Coastal ocean nutrient loading
Context of Future Conditions

A Post-Sulfate World
Context of Future Conditions (cont.)

A Modest NO$_x$/Nitric Acid World
Examining Regional Eulerian (grid-model) Approaches to Air Quality Modeling of Ammonia

Includes relevant chemistry & physics, with grid sizes ranging from local 2-4km up to regional at 32-36km grids; 20-24 vertical layers up to top of free troposphere

Atmospheric Diffusion Equation

\[ \frac{\partial c_i}{\partial t} = -\nabla (u c_i) + \nabla (K \nabla c_i) + R_i + S_i + Clouds \]
Modeling System Components That Should be Considered

- Chemical and physical conversions to aerosols
  - Inorganic partitioning / internal processing
- Emissions of NH$_3$
  - Input uncertainty / internal system balance
- Balancing the budget
  - Where does ammonia go? Whole system
- Elements of the budget
  - Mixing
  - Transport
  - Deposition
- Coming up with loads
Chemical and Physical Conversion to Aerosols
Conversion of Inorganics to Aerosols

**PRIMARY EMISSIONS**

- VOC
- CO
- NO
- SO$_2$
- NH$_3$
- NO$_2$
- HNO$_3$
- H$_2$SO$_4$
- O$_3$
- Gas Phase
- Fine Particles

**Gas Phase**

- O$_3$
- OH
- O$_2$
- RO$_2$
- NO$_3$
- PM$_{fine}$
- Fe
- H$_2$O$_2$

**Fine Particles**

- NO$_3$
- PM$_{fine}$
- SO$_4$
- PM$_{fine}$
Chemical conversion to aerosols
Equilibrium modeling of partitioning
Atlanta, summer 1999, 5-minute averages
Majority as NH$_4^+$

Model

Measurements
Chemical conversion to aerosols
Equilibrium modeling of partitioning
Clinton NC, annual 1999, 12-hour averages
Majority as NH₃
Appraisal of Equilibrium Modeling

• On the whole, the representation of the physics and chemistry processes seems fairly well in hand at the higher concentration levels or higher partitioning fractions. There is more difficulty at the lower levels or lower fractions.
  – The faster modules designed for the air quality models are not as accurate as the slower, most accurate stand-alone modules.
  – We may be missing elements or pathways that drive the partitioning such as base cations.

• The partitioning is somewhat sensitive to getting the sulfate right, but is even more sensitive to having the correct NH\textsubscript{X} levels (NH\textsubscript{3} emissions).
  – So getting levels of NH\textsubscript{X} correct is very important. (We will see this more clearly with inverse modeling results).
Other Parts of the Inorganic System and Their Influences

- Sulfate production
- Total Nitrate production
- Coarse Particle Effects
SO$_4$ - 24-Hr mean – IMPROVE - 32 km Domain – Base Case

Model (SO$_4$, ug/m$^3$)-east
Model (SO$_4$, ug/m$^3$)-west
$\text{SO}_4^= \text{ Model vs. CASTNet (Monthly Ave’s)}$

**SO$_4$ AIR CONCENTRATION (UG/M$^3$)**
CMAQ vs. CASTNET
JUNE 1995

**Legend**
- 50% INTERVAL
- RUNNING MEDIAN SMOOTH LINE

**Summer**

**Winter**
Atlanta

$SO_4^- = \text{Relationship with NH}_4^+$

August 1999 Hourly Observations

Hourly Observations

NH4 (ug/m3)

SO4 (ug/m3)

NH4Ave

SO4Ave

Time (EST, 1999)
CMAQ HNO₃ and NO₃⁻ Bias and Improvements with June 2003 vs. June 2002 CMAQ Atlanta Data, August 1999
CMAQ HNO$_3$ Bias Can Throw Off NH$_4^+$ Predictions
Overall Partitioning Appraisal

• The model’s process and multi-pollutant functioning appears to be fairly reasonable in the big-picture, large-scale sense. But it is very hard to get the time and space details right.
  – This is expected to have an impact on representation of local deposition at a high time resolution.

• Large-scale, longer time-scale picture (seasonal/annual) may be fairly reasonable.

• Relative changes should be reasonable.
Emissions of NH$_3$

There are at least 5 components to emissions input uncertainties

- Absolute levels
  - combine discussion with seasonal
- Seasonal variation in levels
- Diurnal variation in emissions
- Spatial issues
- Source issues (e.g. missing)
Developing Seasonal NH$_3$ Emission Estimates with Inverse Modeling

Alice Gilliland, Robin Dennis, Shawn Roselle, and Tom Pierce

Gilliland, Dennis, Roselle, and Pierce, Seasonal NH$_3$ emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method, JGR-Atmospheres 108, No. D15, 4477 (2003)
### 1990 National Emissions Inventory (NEI):
Annual U.S. Ammonia Emissions (thousand short tons)

<table>
<thead>
<tr>
<th>Category</th>
<th>Emissions</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Livestock</td>
<td>3307</td>
<td>76%</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>420</td>
<td>10%</td>
</tr>
<tr>
<td>On-road vehicles</td>
<td>192</td>
<td>4%</td>
</tr>
<tr>
<td>Chemical and Allied Product Manufacturing</td>
<td>183</td>
<td>4%</td>
</tr>
<tr>
<td>Other (Industrial Processes, Off-road vehicles)</td>
<td>229</td>
<td>5%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>4,331</strong></td>
<td></td>
</tr>
</tbody>
</table>

Community Multiscale Air Quality (CMAQ) Model

• Regional scale domain
  – 36km horizontal grids
  – 21 vertical layers
  – Eastern US

• RADM2 chemical mechanism
  – Aerosol v.2

• Emissions
  – 1990 USEPA National Emissions Inventory
  – Mobile 5b
  – BEIS2

For inverse application, entire domain is treated as 1 source region \( m \).
Inverse Methodology
(aka “adaptive iterative Kalman Filter”, optimal estimation via cost function min.)

\[ \chi_{\text{post}} (m) = \chi_{\text{prior}} (m) + G(m \times n) \left( \chi_{\text{obs}} (n) - \chi_{\text{model}} (n) \right) \]

\[
G = S_a K^T \left( KS_a K^T + S_\Sigma \right)^{-1} = \left( K^T S_\Sigma^{-1} K + S_a^{-1} \right)^{-1} K^T S_\Sigma^{-1}
\]

\[
K = \frac{\partial f}{\partial E};
\]

\[
y = \chi_{t+1} - \chi_t = f(\chi_t, \kappa_{t-1}, M_t, w_t)
\]
[NH$_4^+$] wet concentrations used in inverse modeling
- 15% bias
  [Butler and Likens, 1998; Gilliland et al., 2002]

Also...
- EMEFS [NH$_x$]
- CASTNET [NO$_3$], [NH$_4$], and [SO$_4$]
If $\Delta E \neq 0$, adjust emissions globally.
January 1990

Before: RMSE = 0.52 mg/l, R = 0.65, N = 78
After: RMSE = 0.25 mg/l, R = 0.67, N = 78
Before: RMSE = 2.79 mg/l, R = 0.64, N = 53
After: RMSE = 0.67 mg/l, R = 0.64, N = 53
January 1990

Before: RMSE = 4.81 mg/l, R = 0.77, N = 43
After: RMSE = 0.79 mg/l, R = 0.89, N = 43
SUMMARY of SEASONAL ADJUSTMENTS
(S_Σ based on 4% relative uncertainty * Obs)
Estimates of wet $[\text{NH}_4^+]$ based on range of emission adjustments stemming from different treatments of uncertainty:
Ammonia Inverse Appraisal

• After applying the inverse adjustment we get good agreement with the partitioning. This is essential.

• The inverse results in a significant improvement of model predictions.

• The internal balance achieved is important. The inverse suggests the emissions are a bit too high, but we must take model errors into account. The agreement is actually quite good (difference of 25%).
Diurnal Patterns

Atlanta Supersite 1999
Each hour sorted by time of day

Time (EST, 8/13-8/31 1999)

NH₃ (ppb)

GASNHPJ
Model
Spatial Issues

• We are missing some emissions across space or the emission factors are incorrect for certain categories.

• This makes it impossible for the model to “get it right.”
Ammonium ion concentration, 2001

Sites not pictured:
- AK01 0.03 mg/L
- AK03 0.02 mg/L
- HI89 0.01 mg/L
- VI01 0.03 mg/L

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu
Annual Area Source Ammonia Emissions

1999
32km domain

Min = 0 at (1,1), Max = 17684 at (150,54)
LOG10 Annual Area Source Ammonia Emissions

1999
32km domain

Min= 0 at (1.1), Max= 4 at (150,54)
Ammonia Emissions Appraisal

- There are still fairly large uncertainties in ammonia emissions.
  - These uncertainties are not the same across space.

- There seem to be some missing categories of NH$_3$ emissions.

- It is very hard to dissect the uncertainties, in part, because the data are so sparse. We need help.

- Inverse modeling can provide a big help to provide a top-down assessment of the ammonia emissions and uncertainties. But, it has its limitations.

- It is important to create an internal consistency in the model. One cannot simply apply emissions estimates blindly in an air quality model.
Balancing the NH$_3$ Budget

Where does the ammonia go?

First show NH$_X$ performance
Then summarize budget calculations
Winter NH\textsubscript{x} Comparisons After Applying Inverse

St. Louis Jan 2002 CMAQ tot-NH\textsubscript{x} Comparison

- 02Release
- NewHeteroRxn
- NoHeteroRxn
- STL-NH\textsubscript{x}

Pittsburgh Jan 2002 CMAQ NH\textsubscript{x} Comparisons

- NewHeteroRxn
- NoHeteroRxn
- SCHPKNH\textsubscript{x}

St. Louis data courtesy Jay Turner (preliminary)
Pittsburgh data courtesy Beth Wittig and Spyros Pandis (preliminary)
Summer NH\textsubscript{x} Comparisons After Applying Inverse

Jefferson St Aug99 NHx Comparison

![Graph showing total NH\textsubscript{x} (ug/m\textsuperscript{3}) over days from 8/13 to 8/31, 1999.](image)
Clinton NH$_x$ Comparison for July 1999
Day-Night Averages
CMAQ 2003 version H3w

Clinton data courtesy John Walker and Wayne Robarge
Gas to Particle Conversion

Free Troposphere

Mixed Layer

Layer 1 Analysis

PBL Analysis

NH3 Emissions

Dry Deposition

Vertical

Horizontal

38m

2 km

Surface

Gas to Particle Conversion

NH3 Emissions

Dry Deposition

Vertical

Horizontal

Gas to Particle Conversion

NH3 Emissions

Dry Deposition
Layer 1 NH3_DDEPk

k=event_avg_nhx_pamass_12km.ncf

June 20, 1996 4:00:00
Min = -15.619 at (54, 28). Max = -0.000 at (72, 19)

Sampson County
Sampson Co. Maximum Cell

Free Troposphere

Mixed Layer 2 km

Surface

38m

Gas to Particle Conversion

0.7%

Vertical

74%

NH3 Emissions

Layer 1

Dry Deposition

3.7%

Horizontal

23%

MAQSIP model calculations in collaboration with Rohit Mathur, Carolina Environmental Program
Sampson Co. Maximum Cell

MAQSIP model calculations in collaboration with Rohit Mathur, Carolina Environmental Program

Free Troposphere

Mixed Layer

NH₃ Emissions

Surface

Layer 1

Gas to Particle Conversion

Dry Deposition

Vertical (NH₃+NH₄)

2 km

15%

Horizontal (NH₃+NH₄)

82%

15%

Gas to Particle Conversion

NH₃ Emissions

PBL

Dry Deposition

3.7%

0.7%

74%

23%

3.7%
Sampson County

Free Troposphere

MAQSIP model calculations in collaboration with Rohit Mathur, Carolina Environmental Program

Surface

Layer 1

NH₃ Emissions

Gas to Particle Conversion

Dry Deposition 38m

Mixed Layer

2 km

Vertical (NH₃+NH₄)

28%

Gas to Particle Conversion

Horizontal

86%

NH₃ Emissions

Dry Deposition

5.6%

Vertical

2%

Layer 1 PBL

28%

NH₃ Emissions

Dry Deposition

5.9%

PBL

28%

Horizontal (NH₃+NH₄)

65%
NH₃ Budget Appraisal

• These results are not what many expect. The ammonia rapidly moves up and away from the surface.

• These results are consistent with David Fowler’s estimate of the dry deposition around a poultry operation, which was 3-5% of the emissions dry-deposited locally.

• These results are also in line with Wayne Robarge’s budget calculations for eastern North Carolina where he estimated that 10-15% of the emissions dry-deposited (equal to the wet deposition)
Ammonia Has a Regional Reach, Therefore
EXTENDED RADM 20KM TOTAL REDUCED NITROGEN DEPOSITION (KG/HA)

16 CELL SCENARIO
NORTH CAROLINA
EXTENDED RADM 20KM TOTAL REDUCED NITROGEN DEPOSITION (KG/HA)

4 CELL SCENARIO
NORTH CAROLINA
EXTENDED RADM 20KM TOTAL REDUCED NITROGEN DEPOSITION (KG/HA)

1 CELL SCENARIO
NORTH CAROLINA

23.8
EXTENDED RADM 20KM TOTAL REDUCED NITROGEN DEPOSITION (KG/HA)
INTEGRATED PERCENT CONTRIBUTION FROM
NORTH CAROLINA (32 CELLS)
EXTENDED RADM 20KM TOTAL REDUCED NITROGEN DEPOSITION (KG/HA)
INTEGRATED PERCENT CONTRIBUTION FROM NORTH CAROLINA (16 CELLS)
EXTENDED RADM 20KM TOTAL REDUCED NITROGEN DEPOSITION (KG/HA)
INTEGRATED PERCENT CONTRIBUTION FROM NORTH CAROLINA (4 CELLS)
EXTENDED RADM 20KM TOTAL REDUCED NITROGEN DEPOSITION (KG/HA)
INTEGRATED PERCENT CONTRIBUTION FROM
NORTH CAROLINA (1 CELL)
PRINCIPAL NITROGEN AIRSHEDS FOR:
CHESAPEAKE BAY

[Map showing principal nitrogen airsheds for Chesapeake Bay with reduced and oxidized areas marked.]
Ammonia Budget Appraisal

• There is (a serious) disagreement about ammonia budgets and where it goes.
  – We need more empirical data and studies to sort this out more definitively.

• Ammonia is both regional and local. Airsheds are still substantial, although not as large as for oxidized nitrogen.

• Conventional wisdom is distorting interpretations and assessments of responsibility. This needs to be corrected.
Further Elements of the Budget

• Mixing
  – Vertical mixing away from the surface
    • Day – do fairly well
    • Night – we don’t know how to model the nighttime pbl
  – Mixing height
    • We are getting better, though still uncertainty of +/- 25%
  – Aloft transfer to the free troposphere
    • Ignorance reigns

• Transport
  – For averaging time of a month or longer, transport is probably o.k.
Further Elements of the Budget (cont.)

• Deposition
  – Wet – not too bad, but there are some inconsistencies
  – Dry – we need a lot of North American work on dry deposition
    • Out-of-date and erroneous parameterizations. We have been borrowing from the Europeans to improve the parameterizations
    • Issue of bi-directionality and compensation point
Additional Issues Regarding Loads

• Subgrid Hot-Spots
  – Hot-spots are a local loading issue that is not going away.
    • We are typically blind to hot-spots from a monitoring sense, because we try to avoid them. We basically depend on the emissions inventory to identify them. We need some top-down remote-sensing help.
  
  – The grid models dilute their effect, if we even have correct emissions to put into the air quality model.

  – We have not studied them sufficiently to characterize the bias introduced by ignoring or misrepresenting them.
Where Are We At?

• We’ve come a long way, Baby!

• We still have a ways to go!

• The glass is more than half full.
  – Even with their present deficiencies, the model are, nonetheless, useful tools, when carefully applied and results carefully interpreted.

• We will get a boost from fine particle research.
  – We need to state our needs from our perspective and participate.
How to Improve:

Research Recommendations

• Subdivided into 6 Areas:
  – Emissions
  – Dry Deposition
  – Methods
  – Studies
  – Third Dimension/Remote Sensing
  – Loading
Research Recommendations - Emissions

• Need more work on emissions inventories for ammonia
  – better, more complete activity data; better spatial data
  – improved emissions factors, leading to development of emissions models for ammonia
  – better representation of diurnal patterns of emissions
  – look for missing sources
    • Natural (e.g., animals)
    • Human activity
    • Industrial

• Remote sensing capability is sorely needed to get at missing emissions across space, at hot-spots and suggest missing categories.
Research Recommendations – Dry Deposition

• Need work on NH$_3$ / NH$_4^+$ dry deposition algorithms
  – compensation point and other effects.
  – Need measurement methods to give diurnal deposition and eddy correlation-based estimates for ground truth

• New NH$_3$ measurement techniques are becoming available with 1 second and better time resolution. We need to take advantage of these (make the investment).
  • Note the burst of ammonia in the a.m. seen by John Walker

• Need work on evasion/flux of NH$_3$ from surface waters

• Need collocated wet and dry deposition measurements
• Need daily wet and hourly dry deposition (not inferred, but directly measured) at several sites.
Research Recommendations -
Methods

• Need to have a full suite of inorganic measurements at all locations
  • $\text{SO}_4^{2-}$, $\text{HNO}_3$, $\text{NO}_3^-$, $\text{NH}_3$, $\text{NH}_4^+$

• Need to transition all sites to measuring the full suite of inorganic species at hourly time resolution.

• Need to replace integrated sampling with hourly measurements as quickly as possible.
  – The new, semi-continuous techniques still need further shake-down, but we need to get ready.

• Need to include coarse particle composition at near-coastal and coastal sites as well.
Research Recommendations – Studies

• Need some North American budget experiments (general and around hot-spots)
  – emissions
  – around hot spots / concentration gradients
  – flux gradients
  – mixed-layer aloft measurements

• Need aircraft measurement in the mixed layer with a full suite of fast-response instruments (Summer 2004 ITCT a target of opportunity).
Research Recommendations – Third Dimension/ Remote Sensing

We need good information in the 3rd dimension

• Need vertical cross-sections via remote sensing:
  – Daytime mixed layer
  – Nighttime planetary boundary layer
    • Active remote sensing - aircraft
    • Passive remote sensing - satellite

• Need flux plane measurements aloft
  – Transfer of mass from the mixed layer into the free troposphere (and reverse direction)

• Need remote sensing of NH\textsubscript{3} in the mixed layer, vertical column and in the free troposphere.

• Hot-spots need to be characterized via remote sensing of NH\textsubscript{3} in a GIS form
  • active or passive remote sensing
Research Recommendations – Loading

• Develop detailed, location-specific deposition budgets for a check on the regional model

• The regional model is still best to develop large-scale regional estimate of loading and estimating long-term average wet-to-dry ratios for use with empirical wet deposition data.

• Apply new, sophisticated space-time techniques to better estimate deposition patterns (e.g., Baysian technique of Montse Fuentes of NC State).
  – These techniques combine model and measurement and are able to address model bias.
  – But, for these techniques to work, we **have** to have NH$_3$ and NH$_4^+$ measurements.