Modeling the Fate and Transport of Tropospheric Nitrogen Compounds

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EPA Science Advisory Board
Integrated Nitrogen Committee
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Outline

• Questions from the SAB
  ▪ Summarize Robin Dennis’ conference call presentation
  ▪ Can the modeling framework provide nitrogen emissions and deposition estimates?
  ▪ Is there a link between EPA atmospheric modeling (N-deposition) and deposition networks (CASTNET, NADP)?
  ▪ What is needed to improve those networks and data provided to EPA by these networks?

• This briefing: Address the broad-questions posed by the SAB and use them to highlight current modeling challenges and data needs
CMAQ Model

Model uses “1st principles” parameterizations of the physics and chemistry that are generalized.

An evolving conceptual framework to synthesize our current understanding

Inputs: Hourly

- Meteorology from a Weather Model
- Emissions from the EPA National Inventory

Air Quality Model: CMAQ

- Transport
- Transformation: Gas Chemistry, Aqueous Chemistry, Aerosol Processes
- Loss Processes

Outputs: Hourly

- Air Concentrations: $O_3$, $PM_{2.5}$

- Wet and Dry Deposition:
  - $SO_2$ gas
  - $SO_4$ aerosol
  - $SO_4^{wet}$
  - $Hg^{0}$
  - RGM
  - $Hg$(part.)
  - $Hg$ wet
  - NO
  - $NO_2$
  - $N_2O_5$
  - $HNO_3$ gas
  - $NO_3$ aerosol
  - Organic $NO_3$
  - $NO_3^{wet}$
  - PAN’s
  - $NH_3$ gas
  - $NH_4$ aerosol
  - $NH_4^{wet}$
The NO\textsubscript{x}-SO\textsubscript{x}-NH\textsubscript{x} System

Atmospheric fate and lifetimes of reduced and oxidized nitrogen are linked

Adapted from: Meng et al. (1997); Warneck (1988)
CMAQ is able to capture main spatial pattern and magnitude of wet deposition.
NH₄⁺ Wet deposition

NH₃ emissions are quite uncertain
- Inverse modeling used to determine monthly emissions
- Wet deposition is relatively unbiased because of inverse modeling
Oxidized Nitrogen Wet Deposition

Annual bias: 25% low
Summer: factor of 2
Winter: unbiased

Variability in precipitation also contributes to predicted variability and bias in wet deposition
Ambient NH$_3$

Low Ammonia Site in Raleigh, NC (12-Hr)

Millbrook (Raleigh) Ammonia July 2004
12-hour Averages: 6am-6pm

High Ammonia Site in Sampson County, NC

Kenansville Ammonia July 2004
12-hour Averages: 6am-6pm

Lack ambient NH$_3$ (NH$_x$) measurements to adequately constrain emission estimates
Issues with Representation of Oxidized and Reduced Nitrogen

- **NH₃** provides a pathway for formation of aerosol NO₃⁻
  - Accurate representation of tropospheric NHₓ cycling is critical
  - Uncertainties still exist in sources and sinks (VdanH₃)

- Representation of reaction probability for N₂O₅ hydrolysis (currently based on Riemer et al., 2003; JGR)
  - Overestimation can cause NO₃⁻ over-prediction
  - Recent studies (Evans and Jacob, 2005, GRL and Brown et al., 2006, Science) suggest lower values

- Examine impacts of process level uncertainties through sensitivity experiments (2001-2003)
  - Heterogeneous production of HNO₃ from N₂O₅
    - *Reduced reaction probability by factor of 7*
  - Dry deposition NH₃ flux
    - Uncertainties arising from lack of measurement data, soil emission, and bi-directional nature of NH₃ flux
    - Comparisons with European measurements suggest VdanH₃ in CMAQ may be high
    - Made NH₃ deposition velocity to be similar to that of SO₂
Impacts on ambient levels

$\text{NH}_4^+$, Top Panel (Summer), Lower Panel (Winter)

**Winter:** reduce gamma, reduce TNO$_3$, reduce $\text{NH}_4^+$, reduce $V_d\text{NH}_3$, increase ambient NH$_x$, increase $\text{NH}_4^+$

*Uncertainty impacts in opposite direction*
Impacts on ambient levels

$\text{HNO}_3 + \text{NO}_3^-$, Top Panel (Summer), Lower Panel (Winter)

Reducing gamma, reduces TNO$_3$ bias in both summer and winter
Reducing $V_d\text{NH}_3$, increases TNO$_3$ (more NO3 in the aerosol phase)
Dry Deposition Monitoring Needs
Modeled spatial trends vs. CASTNET location

Oxidized-N

Reduced-N

Current coverage is not representative

Need for greater spatial coverage
**Dry Deposition of Reactive N is Important**

**Important Fraction of Dry Deposition Not Being Measured**

<table>
<thead>
<tr>
<th>Specie</th>
<th>Kg-N (x10⁶)</th>
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</thead>
<tbody>
<tr>
<td>Dry Ox-N</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>4.22</td>
</tr>
<tr>
<td>NO₂</td>
<td>14.53</td>
</tr>
<tr>
<td>PAN's</td>
<td>5.42</td>
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<tr>
<td>Other</td>
<td>5.71</td>
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<tr>
<td>HNO₃</td>
<td>55.12</td>
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<tr>
<td>aNO₃⁻</td>
<td>1.63</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>86.62</strong></td>
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<tr>
<td>Wet Ox-N</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>57.25</strong></td>
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</tbody>
</table>

- Dry Ox-N > Wet Ox-N

<table>
<thead>
<tr>
<th>Specie</th>
<th>Kg-N (x10⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Red-N</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>34.75</td>
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<tr>
<td>aNH₄⁺</td>
<td>7.52</td>
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<td><strong>Total</strong></td>
<td><strong>42.27</strong></td>
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<tr>
<td>Wet Red-N</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>45.79</strong></td>
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</tbody>
</table>

- Dry Red-N < Wet Red-N

- Not Being Measured (34%)
- Not Being Measured (82%)
A Modest Reduction in NH$_3$ $V_d$ by 30% Makes a Difference

Uncertainty Response for Single NC Maximum Cell

We define the Range of Influence as the distance by which 50% of the emissions attributable to that source deposit. (This is consistent with earlier work)
1-D Model Parameterization: bi-directional NH$_3$ exchange

Preliminary comparison of modeled and measured NH$_3$ flux averaged over 8-weeks in summer 2002 for soybeans in North Carolina

Courtesy: J. Pleim, AMD
New Challenges
How well do existing chemical mechanisms perform for aloft and night-time conditions?
New Challenges
Performance aloft: Comparisons with ICARTT NOAA-P3 data

Possible role of lightning NO\textsubscript{x}?  

L. Jaegle, Science, 2007
New Challenges

Representation of HONO sources and heterogeneous pathways

- HONO photolysis produces OH in the atmosphere
  - especially important in the morning when other sources of OH are relatively small

A: Current model
B: A+Mobile Emissions
C: A+B+ 2NO2+H2O
D: A+B+ C+ surface-photolysis

Courtesy: G. Sarwar, AMD
Simulating impacts of emission controls
2020/2001 Deposition Ratios

Controls: NO$_x$ SIP Call, Clean Air Interstate Rule, Mobile emission reductions
SO$_2$ (-35%); NO$_x$ (-40%); NH$_3$ (+13%)

Reduction in oxidized nitrogen deposition
Increase in reduced nitrogen deposition
Reduction in total nitrogen deposition except in NH$_3$ rich regions

Courtesy: R. Pinder, AMD
Looking ahead: Possibilities with Remote Sensing Information
Evaluation of Modeled Spatial Distributions; NO$_2$ Columns: Summer 2004

**CMAQ**

**SCIAMACHY**

**On-going efforts:**
- Test and Improve NO$_x$ Emission Inventories
- Accountability studies
  - Track impact of regulations on observed regional and local AQ
- AQ over time using both model and observations

**Comparable spatial distributions**
- SCIAMACHY higher in rural areas
  - higher regional background
  - missing source (lightning), or
  - chemistry (NO$_x$ $\rightarrow$ NO$_y$) too rapid
- CMAQ higher downwind of urban areas (e.g., Atlanta), Point sources
  - Opposite trend compared to GEOS-CHEM (resolution/chemistry)
  - air mass factor from GEOSCHEM (NO$_x$ lifetime difference due to resolution)
Looking Ahead
Leveraging NOAA-EPA Partnership in Air Quality Forecasting

- Developing an archive of continuous model data
  - Continuous archive of oxidized and reduced nitrogen ambient-levels and wet and dry deposition amounts
  - Exploration of bias-adjustment, reanalysis, and data-fusion techniques

RESEARCH & DEVELOPMENT
Building a scientific foundation for sound environmental decisions
Summary

• Can the modeling framework provide nitrogen emissions and deposition estimates?
  ▪ Yes, detailed emission inventories are key inputs and deposition outputs are the primary modeled sink-terms in the mass-conservation equations of the model

• Is there a link between EPA atmospheric modeling (N-deposition) and deposition networks (CASTNET, NADP)?
  ▪ Model verification and evaluation
  ▪ CASTNET: Dry-deposition estimation algorithms
    ▪ Using CASTNET process-level $V_d$ algorithm to scale to CMAQ grid-scale

• What is needed to improve those networks and data provided to EPA by these networks?
  ▪ Need $NH_x$ measurements to verify model budgets
  ▪ More frequent measurements (e.g., bi-directional $NH_3$)
  ▪ Dry deposition measurements for other oxidized-N species
  ▪ Greater spatial coverage
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The maximum Vd for NH$_3$ can equal that for HNO$_3$. This is pretty high.

The pattern of maximum Vd is similar for SO$_2$ and NH$_3$.

Setting the CMAQ NH$_3$ Vd equal to the SO$_2$ Vd should preserve many aspects of the Base NH$_3$ deposition pattern.

June 25, 2002