Evaluating CMAQ Simulations of Ammonia Sources and Impacts using Surface, Aircraft, and Satellite Data

C. R. Lonsdale¹, J. D. Hegarty¹, K. E. Cady-Pereira¹, M. J. Alvarado¹, D. K. Henze², M. Turner², S. Capps², J. B. Nowak³, J. Murphy⁴, M. Markovic⁴,⁵, T. VandenBoer⁴,⁶ and R. Ellis⁴

¹Atmospheric and Environmental Research, Inc.
²University of Colorado – Boulder
³Aerodyne Research, Inc.
⁴University of Toronto
⁵NOAA ESRL and CIRES
⁶Memorial University of Newfoundland

NH₃ is an important PM₂.₅ precursor

\[ \text{NH}_3 + \text{HNO}_3 \leftrightarrow \text{NH}_4\text{NO}_3 \]
\[ 2 \text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 \]

- Long-range export
- Long-range import

PM₂.₅

Nitrogen Deposition

- Increase incidence of cardiovascular and respiratory diseases
- Increase number of CCN
- Harmful algal blooms
- Loss of species diversity

SO₂, NOₓ decreasing but NH₃ forecast to increase

Global NH₃ Emissions
NH₃ sources are not well known

- Biomass burning
- Industry
  - Fertilizer
  - Coal Mining
  - Power generation
- AGRICULTURE
  - Animal waste (temperature dependent)
  - Fertilizer application
- Automobiles (catalytic converters)
  - Large urban centers
  - 50% of NH₃ in LA area (Nowak et al., GRL, 2012)
Monitoring $\text{NH}_3$ is difficult

$\text{NH}_3$ is highly reactive

- highly variable in space and time

- $\text{NH}_3$ from an Open path Quantum Cascade Laser (QCL) on a moving platform in the San Joaquin Valley during DISCOVER-AQ 2013.

Miller et al., AMT 2013
Better emissions with TES NH$_3$

- Used GEOS-Chem adjoint with TES NH$_3$ profiles, averaging kernels and error covariances to optimize model
- Optimized GC shows better agreement with AMoN network measurements

Largest changes western US and Mexico

Zhu et al., 2013, JGR
• Using TES NH$_3$ data, along with surface and aircraft data, to investigate NH$_3$ emissions during 2010 CalNex Campaign.

• Using the Cross-Track Infrared Sounder (CrIS) to investigate NH$_3$ sources in California and Southeast US.
CalNex 2010 field campaign

- Combined satellite, aircraft and ground-based measurement campaign focused on the California Central Valley and Los Angeles Basin during May – June 2010.
- Provides rich data set for studying NH$_3$ emissions.

- Bakersfield site – mostly agricultural sources
- Los Angeles site – urban setting: agricultural, industrial and mobile sources
WRF and CMAQ Modeling

- WRF-ARW v3.5 with 3 nest levels of 36, 12 and 4 km
  - 41 levels, 1\textsuperscript{st} layer \sim50 \text{ m}
- CMAQv5.0.1 run on inner 4 km domain only.
  - cb05 photochemistry with updated toluene chemistry
  - ae6\_aq - aerosol module 6 with aqueous chemistry
  - No bi-directional NH\textsubscript{3} flux
- CMAQ boundary conditions provided by GEOS-Chem on a 2.0\textdegree \times 2.5\textdegree grid.
- Emissions provided by California Air Resources Board (CARB)

Lonsdale et al., in prep.
Bakersfield and SJV: No Diurnal Cycle
CARB NH₃ Emissions

LA and SoCAB: Step Function Diurnal Cycle Due to Industrial NH₃ Emissions

LA NH₃ Area Sources
8:00 – 16:00

Natural Gas

Industry

NH₃ (MOLES/S)

Data Min = 0.0, Max = 3.5
- 6 TES transect days during CALNEX campaign at ~1:30 pm local time
- CMAQ and TES generally agree on the locations of the high and low NH$_3$.
- CMAQ seems to be biased low compared to TES for the highest NH$_3$ RVMRs.
Bakersfield:
- CMAQ low during day, matching TES
- But too high at night

Los Angeles
- Opposite pattern

Results aren’t sensitive to BCs, gas-aerosol partitioning, or diurnal changes in transport directions.
Are PBL height errors responsible?

**SJV:** PBL errors negligible.

**LA:** Celiometer suggests PBL errors negligible, but HSRL shows negative bias consistent with daytime NH$_3$ overestimate.

HSRL data from Scarino et al., ACP, 2014.
Celiometer data from Haman et al., JAOT, 2012.
For Bakersfield, satellite, surface, and aircraft data give a consistent picture.

- Afternoon flights also show CMAQ underestimating NH$_3$ by a factor of 2, consistent with surface and satellite data.
- No such underestimate seen for CO.
- Since HSRL data suggests WRF PBL is good in SJV, most likely explanation is an error in the diurnal cycle and/or daily magnitude of SJV NH$_3$ emissions.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time (PST)</th>
<th>NH$_x$ Slope</th>
<th>NH$_x$ R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20100524</td>
<td>16:00-22:00</td>
<td>0.20 ± 0.07</td>
<td>0.17</td>
</tr>
<tr>
<td>20100614</td>
<td>11:00-18:00</td>
<td>0.76 ± 0.07</td>
<td>0.73</td>
</tr>
<tr>
<td>20100616</td>
<td>11:00-18:00</td>
<td>0.56 ± 0.04</td>
<td>0.55</td>
</tr>
<tr>
<td>20100618</td>
<td>11:00-18:00</td>
<td>0.52 ± 0.08</td>
<td>0.64</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.51 ± 0.13</td>
<td></td>
</tr>
</tbody>
</table>
LA is more complicated. CMAQ gives reasonable NH$_x$/CO slopes relative to aircraft data...

- Only using data in LA urban core. Does not include data from dairy farms downwind of LA.
- Model NH$_x$/CO slopes consistent with afternoon aircraft data and analysis of Nowak et al., GRL, 2012.

<table>
<thead>
<tr>
<th>Date</th>
<th>FLIGHT NH$_x$/CO</th>
<th>CMAQ NH$_x$/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>20100508</td>
<td>0.028 ± 0.005</td>
<td>0.029 ± 0.004</td>
</tr>
<tr>
<td>20100514</td>
<td>0.035 ± 0.002</td>
<td>0.019 ± 0.001</td>
</tr>
<tr>
<td>20100516</td>
<td>0.024 ± 0.001</td>
<td>0.024 ± 0.001</td>
</tr>
<tr>
<td>20100519</td>
<td>0.036 ± 0.002</td>
<td>0.032 ± 0.001</td>
</tr>
<tr>
<td>20100620</td>
<td>0.029 ± 0.002</td>
<td>0.020 ± 0.003</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>0.030 ± 0.006</strong></td>
<td><strong>0.025 ± 0.005</strong></td>
</tr>
</tbody>
</table>
...but aircraft data suggest CMAQ underestimates \( \text{NH}_x \) in afternoon in LA, opposite of surface data.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time (PST)</th>
<th>( \text{NH}_x )</th>
<th>Slope</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20100508</td>
<td>11:00-18:00</td>
<td>0.61 ± 0.09</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>20100514</td>
<td>10:00-16:00</td>
<td>0.42 ± 0.03</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>20100516</td>
<td>11:00-18:00</td>
<td>0.84 ± 0.07</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>20100519</td>
<td>11:00-16:00</td>
<td>0.51 ± 0.04</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>20100620</td>
<td>11:00-17:00</td>
<td>0.70 ± 0.10</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.62 ± 0.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Outline

• Using TES NH$_3$ data, along with surface and aircraft data, to investigate NH$_3$ emissions during 2010 CalNex Campaign.

• Using the Cross-Track Infrared Sounder (CrIS) to investigate NH$_3$ sources in California and Southeast US.
Why switch to CrIS?

- **TES** is past its design lifetime, taking little new data, and has low spatial coverage.
- **CrIS** could monitor global NH$_3$ with high spatial coverage for many more years (>2022).

<table>
<thead>
<tr>
<th></th>
<th>TES</th>
<th>CrIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Satellite</td>
<td>AURA</td>
<td>NPP</td>
</tr>
<tr>
<td>Available Data</td>
<td>July 2004-present</td>
<td>October 2011-present</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.06 cm$^{-1}$</td>
<td>0.625 cm$^{-1}$</td>
</tr>
<tr>
<td>Footprint</td>
<td>5x8 km rectangle</td>
<td>14 km diameter circle</td>
</tr>
<tr>
<td>Repeat cycle</td>
<td>Once every 16 days</td>
<td>Daily</td>
</tr>
<tr>
<td>Equatorial crossing</td>
<td>1:30 am and 1:30 pm</td>
<td>1:30 am and 1:30 pm</td>
</tr>
<tr>
<td>Noise in NH$_3$ window</td>
<td>0.09 – 0.12 K</td>
<td>0.03 – 0.06 K</td>
</tr>
</tbody>
</table>
TES and CrIS versus surface NH$_3$

- QCL directly under TES transect in the San Joaquin Valley on January 28, 2013

Shephard and Cady-Pereira, AMT, 2015.
Application of CrIS NH$_3$ to California

California - June 13, 2012

ppbv

Latitude

Longitude

aer
Atmospheric and Environmental Research
Application of CrIS NH$_3$ to SENEX

SENEX - June 11, 2013

ppbv

Latitude

Longitude

aer
Atmospheric and Environmental Research
Satellite, surface, and aircraft data all suggest diurnally constant NH$_3$ emissions in CARB CalNex inventory for California Central Valley are likely incorrect.

For LA, surface observations suggest CARB estimates of industrial NH$_3$ emissions are either too high or are more constant through the day, but aircraft observations give conflicting information.

The CrIS satellite instrument can detect NH$_3$ as well as TES, but has much greater spatial coverage, providing much more data for model evaluation.

Use CMAQ Adjoint, along with CrIS, CalNex, and SENEX data, to constrain NH$_3$ emissions in California and Eastern US.
Acknowledgements

- Juliet Zhu, Colorado State University
- John Walker and Robert Pinder, EPA
- Armin Wisthaler, University of Innsbruck
- Kang Sun and Mark Zondlo, Princeton
- Amy Jo Scarino, NASA Langley
- Jeremy Avise and Leo Ramirez, CARB
- Ming Luo, Jet Propulsion Laboratory, California Institute of Technology
- NOAA CPO AC4 Program Grant Numbers NA13OAR4310060 and NA14OAR4310129
- TES Science Team
- NASA Suomi-NPP Science Team
BACKUP SLIDES
CrlS microwindows and constraints

- Lower spectral resolution of CrIS required different microwindows.
- *A priori* and constraints from TES (Shephard et al., 2011)
  - Polluted, Moderately polluted, and Unpolluted profiles
- *A priori* selected based on signal to noise ratio (SNR) and thermal contrast
NH$_3$ signal from TES and CrIS

Simulated spectra and NH$_3$ signal
18 ppbv at surface

- Detectability is ~1 ppbv under ideal conditions
- But thermal contrast also plays a role
CrIS NH₃ Retrieval: Simulated Spectra
Future Work on CrIS NH$_3$ Retrieval

- Validate against SENEX, FRAPPE, and other field NH$_3$ measurements.
- Use CMAQ adjoint to test ability of CrIS to optimize NH$_3$ emissions.
- Deliver CrIS NH$_3$ retrieval algorithm to NASA.

NH$_3$ mixing ratios (ppbv) measured by the NOAA WP-3 aircraft during SENEX 2013.
(Figure courtesy of Jesse Bash, US EPA NERL.)
• CMAQ with CARB emission inventory generally captures the locations of the NH$_3$ plumes observed by aircraft.

• But absolute concentrations too low.
Both instruments most sensitive to $\text{NH}_3$ between 950 and 600 mbar

TES is more sensitive to amounts lower in the atmosphere

1 piece of information or less: DOFS<1.0

Collapse all information to a single point: RVMR
  - Easier to compare with *in situ* measurements, models and other instruments