Fresh constraints on the global reactive nitrogen budget through new TES NH$_3$ and PAN observations

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NH$_3$ and PAN play critical roles in atmospheric chemistry.
**NH$_3$**

What can TES observations tell us about process-based emissions of ammonia?

**PAN**

What can TES PAN observations tell us about the sources and transport of PAN and O$_3$ with attention to anthropogenic intercontinental transport, biomass burning, and lightning?
GEOS-Chem was used to derive 3 a priori profiles of TES NH$_3$.

- Sensitivity peak: 700-900 hPa.
- Bias: $\sim +0.5$ ppb (at 825 hPa).
- Detection limit: $\sim 1$ ppb. (Shephard et al., 2011)
- TES NH$_3$ spatial and seasonal trends verified by surface obs. (Pinder et al., 2011)
Optimized NH₃ profiles more closely resemble TES retrieval.

- 4D-Var inversion (GEOS-Chem adjoint) to adjust NH₃ emissions. (North America, 2006 – 2009)

- Prior NH₃ profiles lower than TES retrieval.
- Optimized model still underestimates TES retrievals.
- Reductions of the cost function: 66% for April, 42% for July, 57% for October.

Zhu et al., 2013
TES improves the model in the central and western US consistent with other studies.

- Changes in CA consistent with Walker et al. [2012] and Nowak et al. [2012]
- Central US underestimates noted from IIASI [Clarisse et al., 2009; Heald et al., 2012]

Zhu et al., 2013
TES assimilation improves the comparison with AMoN in April & October.

AMoN: 21 sites with 2-week long observation, Middle & Eastern US

- Model values below 1 ppb did not change significantly due to TES detection limit.

Zhu et al., 2013
TES assimilation overestimates AMoN in July.

- Possible reasons for July bias:
  - Sampling bias due to TES level-of-detectability (i.e., lack of low values) or spatial sampling.
  - TES overpass time (1:30 AM & PM) points to missing model diurnal variability; new diurnal variability scheme improves comparison with SEARCH obs.
  - Bi-directional exchange was neglected in GC (Zhu et al., in prep).

Zhu et al., 2013
TES sampling strategy leads to a +30% bias in surface concentration.

All CMAQ NH₃ Over US

CMAQ NH₃ At TES Sampling Locations

Future solution:
Include more retrievals with peak value of profile below 1 ppbv.

Zhu et al., 2013
A new GEOS-Chem PAN simulation was used to develop 6 a priori profiles.

Tropic

Outside tropics

Detection limit: 0.2 ppbv

Payne et al. 2014, ACPD
East Asia is a major PAN export region. We are focusing here first.

- 45°E – 90°W, 15°N – 80°N
- trop avg: average of levels between 800 mbar and tropopause
Elevated TES PAN is associated with elevated CO in fire plumes.

- TES observations from July 2008 ARCTAS campaign
- Colored points: DOFS > 0.6
- Previously identified by Alvarado et al. 2010

*Payne et al. 2014, ACPD*
Spring 2008 was an extreme year for biomass burning in East Asia.

TES, trop avg value, East Russia

MODIS Fire Radiative Power
April 2008

TES PAN and CO reflect this.
In April 2008, fires are a main source of extreme PAN and strong relationships with CO and O₃.
There is evidence of fire PAN and CO being exported over the Pacific in April 2008.
Conclusions

- Fires are a main source of extreme PAN in April 2008 and we see strong relationships with CO and O₃ in East Asia.
- Elevated TES PAN is associated with elevated CO in fire plumes.
- There is evidence of fire PAN and CO exported over Pacific.

Preliminary Conclusions

- TES NH₃ values are higher than initial model but potentially biased.
- TES assimilation enriches our understanding of NH₃ emissions in the West and Midwest US.
- TES assimilation better captures the range and variability of surface NH₃ in April and October, but it is biased high in July.
Thanks!

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NH₃ has large impacts on human health and the environment.

PM₂.₅ causes bronchitis, asthma, premature mortality...

Smog
Decreases visibility.

Eutrophication
Alga blooms; Hypoxia; Cloudy, colored water.

Soil acidification
Nitrification of NH₄⁺ into NO₂⁻, releasing H⁺.

Large uncertainties in NH₃ inventories.
PAN is the route for $\text{NO}_x$ to reach the remote troposphere.

$\text{PAN} \quad (\text{CH}_3\text{C(O)O}_2\text{NO}_2) \quad \rightarrow \quad \text{PAN}$

$\text{C}_x\text{H}_y \quad \rightarrow \quad \text{NO}_x \quad \rightarrow \quad \text{HNO}_3$

Transport at cold temperatures

thermal decomposition

$\text{NO}_x \quad \rightarrow \quad \text{HNO}_3$

$\text{O}_3 \text{ and OH}$

$\text{NO}_x \quad \text{Source Region}$

Remote Atmosphere

Jacob 1998
Implementing diurnal variability for livestock NH$_3$ emissions reduces bias.

\[ E_h(t) = E_d \times N_{\text{met}}(t) \]

\( t \): hour, 1, 2, ..., 24;  
\( E_d \): daily NH$_3$ emission;  
\( E_h(t) \): NH$_3$ emission at hour \( t \);  
\( N_{\text{met}}(t) \): fraction of NH$_3$ emission diurnal variation, depends on \( T \), \( R_a \), aerodynamic

\[ N_{\text{met}}(t) = \frac{H(t)/R_a(t)}{\sum_{1}^{n}(H(t)/R_a(t))} \]  

\( H(t) = \frac{161500}{T}e^{-10380/T} \)  
(Nemitz et al., 2000)

Scheme developed based on field studies downwind of livestock facilities in North Carolina (Bash et al., in prep.)
Implementing diurnal variability for livestock NH$_3$ emissions reduces bias.

- NH$_3$ decreased at night by several ppb; increased in day up to 1 ppb.
- Monthly average surface NH$_3$ (and NO$_3$) decreased.
- NH$_3$ concentration (at TES overpass time 13:30) can be impacted without changing total emissions.
- Improves TES assimilation results compared to Zhu et al. 2013.