Satellite Observations of Tropospheric Ammonia, Methanol, and Formic Acid

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1. Motivation

Ammonia (NH_3)

Ammonia is an integral part of the nitrogen cycle

- **Nitrogen in ammonia is deposited to the Earth's surface and leads to:**
  - Nutrient imbalances
  - Changes in ecosystem composition
  - Algal blooms and hypoxia (oxygen depletion)

Secondary Inorganic Aerosol Formation

- **Ammonia (gas) reacts with sulfate and nitric acid**
  - **Produces ammonium sulfate and ammonium nitrate (aerosol-phase)**
  - Air Quality
    - **Responsible for 10-20% of fine particulate matter (PM2.5)**
      - Exceeds recommended threshold (WHO, 2003)
    - **Exposure to aerosol concentration is associated with health issues**
      - Cardiovascular disease, inhibited lung development, premature death
  - Climate
    - **Direct radiative forcing of ammonium aerosols**

Methanol (CH_3OH)

Methanol is an important part of the organic carbon cycle

- **The most abundant organic gas in the atmosphere after methane**
- **Global emissions are thought to be equal or greater to those of all anthropogenic VOCs combined**

Methanol has important chemical effects in the atmosphere

- **It is a major source of formaldehyde in the continental boundary layer**
- **It is an important source of CO to the global atmosphere**
- **It plays a role in the tropical ozone and HOx budgets**
  - **(e.g. NOx + VOCs -> Ozone)**

Formic Acid (HCOOH)

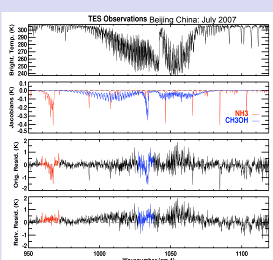
Formic Acid is the most abundant organic acid in the atmosphere, along with acetic acid

- **Formic acid is an important source of free acidity in precipitation "acid rain", especially in remote areas**
- **Influences pH-dependent chemical reactions in clouds**
- **An important sink for OH(aq) in clouds**

Why Measure from Space?

- **Lack of observations to help with large uncertainties in modeled emissions**
- ***In situ* (mostly surface) measurements are sparse**
- **Uncertainty in the seasonal and spatial variability**
  - **For example:**
    - CMAQ (regional) : NH_3 peak emissions during fertilization application in spring (April)
    - GEOS-Chem (global) : NH_3 peak emissions with high temperatures in summer (July)
- **Satellite measurements have potential to constrain the emissions**

2. TES NH_3, CH_3OH, HCOOH Spectral Signal

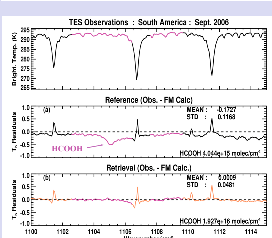


TES Observation

NH_3 and CH_3OH Jacobians

TES - LBLRTM (IG)

TES - LBLRTM (Retv)



TES Observation

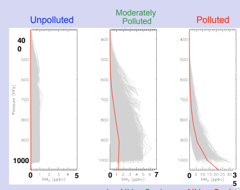
TES - LBLRTM (IG)

TES - LBLRTM (Retv)

3. TES Sensitivity Studies : NH_3 Example

GEOS-Chem NH3 Profiles

- Obtained from **GEOS-Chem monthly mean** output for 2005
- **Binned** by lower tropospheric ammonia amounts

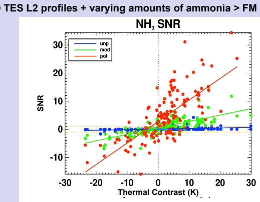


Binning Thresholds → NH_3 < 1ppbv | 1 < NH_3 < 5ppbv (below 500 mb) | NH_3 > 5ppbv (surface)

- **Retrieval input profiles for initial guess and a priori**
- **Polluted, Moderate, and Polluted profiles**

Sensitivity Test : Strength of NH_3 Signal

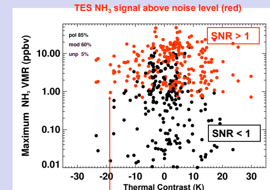
- **540 TES L2 profiles + varying amounts of ammonia > FM > simulated spectra**



- **SNR : ($BT_{Background}$ - BT_{NH3}) / NEdT**
- **Thermal Contrast: BT_{sfc} - $Tair_{Bottom}$**

- **Thermal contrast increases sensitivity**
- **Polluted and moderate profiles typically have SNR > 1.**
- **The linear fits are used to determine input retrieval profile.**

Sensitivity Test: Level of Detectability

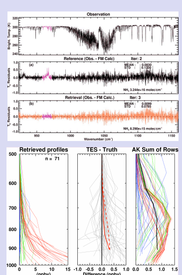


Detectability level ~1ppbv

- **Conservative level as the:**
  - Maximum concentration usually near surface
  - TES most sensitive between 900 and 800 mb

4. TES Retrieval Examples

NH_3 Retrieval Results : TES Simulated Double Emission Profiles



TES Simulated Obs.
- NH_3 profile (GEOS-Chem double emission) + noise (2.3 ppbv@sfc.)

TES Simulated Obs. - TES FM Calc. (IG)
- polluted initial guess profile (13 ppbv@sfc.)

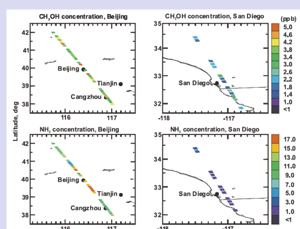
TES Simulated Obs. - TES FM Calc. (retv)
- retrieved NH_3 profile

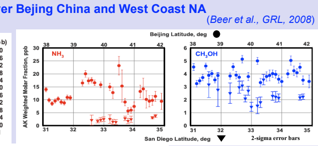
Simulated TES Retrieval Results

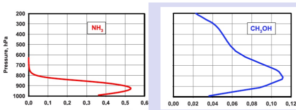
- **TES - Truth(with AK and *a priori* applied)**
  - **Std. : ~ ±0.3 ppbv (red dashed line)**
  - **Mean diff : +0.1 ppbv (red solid line)**
- **Avg. ~1 DOF (piece of information)**
- **Avg. peak sensitivity at ~1.5 - 2 km (~825mb)**
  - **higher than for China (tower hermal contrast)**
- **Avg. ~2 km vertical resolution**

NH_3 and CH_3OH TES obs. over Bejing China and West Coast NA

(Beer et al., GRL, 2008)







Elevated NH_3 amounts over Beijing, China, July 10, 2007

- NH_3
  - **Avg. values : ~12 ppbv**
  - **Avg. uncertainty : ~ ±0.5 ppbv (1σ)**
- **CH_3OH**
  - **Avg. values : ~4 ppbv**
  - **Avg. uncertainty : ~ ±0.30 ppbv (1σ)**

Lower NH_3 amounts over West Coast N.A, June 2007

- NH_3
  - **Avg. value: ~2.5 ppbv**
  - **Avg uncertainty : ~ ± 0.5 ppbv (1σ)**
  - **Minimum value : 1.3 ppbv**
- **CH_3OH**
  - **Avg. value: ~2.4 ppbv**
  - **Avg uncertainty : ~ ± 0.25 ppbv (1σ)**
  - **Minimum value : 1.4 ppbv**

NH_3

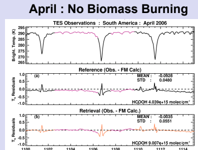
- **Peak Sensitivity: ~900 mb**
- **Vertical Resolution: ~1-2 km**

CH_3OH

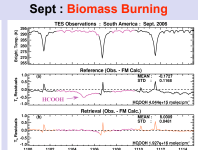
- **Peak Sensitivity: ~800 mb**
- **Vertical Resolution: 3-4 km**

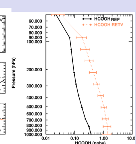
TES HCOOH Retrieval Example over South America

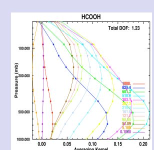
April : No Biomass Burning



Sept : Biomass Burning







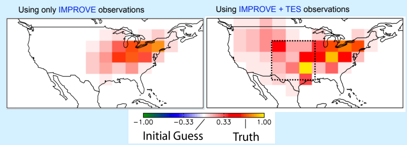
Elevated TES HCOOH observations associated with Biomass Burning

- **~1.2 DOFs**
- **Peak sensitivity: ~3 - 5 km (~700 - 500mb)**
- **Retrieved Values reaching ~1.5 ppbv**

5. TES Observations for Emissions: NH_3 Example

Can TES reduce the large uncertainties in NH3 emissions?

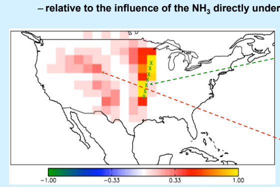
- **Inversion modeling to obtain NH_3 model emission scaling factors**
  - **Input TES NH_3 retrievals from simulated radiance over Midwest.**
  - **Inversion initial guess emission scaling factors were set to zero**
  - **Emission scaling factors after 4 iterations of the inversion**
    - **usually perform more iterations (~20)**



- **Emission scale factors are moving in the correct direction**
  - **from initial guess (0.0) towards the double emission truth [ln(2)=0.69]**
- **Effects on emissions "upwind" of TES obs.**

How sensitive are TES measurements to changes in NH_3 emissions?

- **Show the influence of the NH_3 emissions from any model grid box (from up to a week prior) on the amount of NH_3 that TES observes (marked by X)**
  - **relative to the influence of the NH_3 directly underneath the TES track**



Sensitivities scaled relative to the maximum values (yellow)

TES Obs are most sensitive to NH_3 emissions directly underneath the track (X)

TES is sensitive to NH_3 emissions away from obs.
- e.g. TES is ~40% as sensitive to emissions here compared with directly beneath (X)

NH_3 lifetime increased :
- NH_3 (gas) -> NH_4 (aerosol-phase)
- Bi-directional flux (biosphere and atmosphere)