Heterogeneous Chemistry Research at the Center for Energy and Environmental Resources – University of Texas at Austin

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♦There have been many laboratory studies investigating heterogeneous chemistry. In principle these apply to tropospheric chemistry.

♦ We want to use cases with ambient evidence to better understand what is really important in the atmosphere.

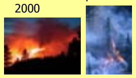
♦ A main tool will be the comparison of modeled behavior and ambient data.

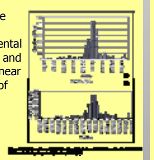
Previous Work – Examination of Heterogeneous Chemistry During a Fire Episode in 2000

Buzcu et al (2006) Journal of Geophysical Research-Atmospheres 111 (D1) Art. No. D10S13
Nopmongcol et al (2006) Atmospheric Environment, 40, S524-S537
Nopmogncol (2005) Dissertation, University of Texas at Austin

Sulfate Formation During Wood Smoke Episodes

Dramatic spike in sulfate particle concentrations observed during continental scale fire event in 1998 and in a forest fire episode near Houston in September of 2000



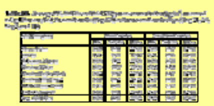


Investigating the Source of the Sulfate Spike During the 2000 Fire Episode

- Possible sources investigated and excluded
  - Direct emissions of sulfate
    - Sulfate not a major constituent of wood smoke
    - Wood smoke tracers indicate that fire particles contributed 10-30% of the elevated particulate matter concentrations
  - Displacement of Chloride in fire emissions by sulfate
    - Calculations show that this has the potential to account for a maximum of 5% of increased sulfate mass
    - High potassium concentrations would be expected, but were not observed
  - Gas phase SO_2 oxidation
    - Elevated OH concentrations would be required to account for the peak in sulfate
    - No elevated OH concentrations were observed
  - Condensed phase (aqueous) SO_2 oxidation
    - Calculations were performed to estimate increased aqueous phase due to wood smoke hydration
    - Based on maximum possible dissolved SO_2 concentrations and maximum oxidation rate, calculated sulfate formation was minimal compared to measured levels
- Heterogeneous Reactions (SO_2 oxidation on carbonaceous wood smoke particle surfaces) are the only explanation left
  - Similar chemistry has been observed in laboratory studies
  - Photochemical model results show that sulfate increases can be explained by chemical mechanisms which are a function of total particle surface area density in the atmosphere

Organic Carbon from Fires

- During the 2000 fire episodes there was also a spike in OC concentrations.
- Was the OC primary or secondary?



Estimates of Primary OC Based on Ambient Measurement of Molecular Markers (potassium and levoglucosan)

- Estimates based on source profiles from several studies predicted that wood smoke emissions of OC would result in concentrations that were higher than total measured ambient OC concentrations.
- Estimates based on the profile from Schauer et al (2001) predicted reasonable wood smoke contributions (31-36% of total OC) on non-smoke days.
- Source apportionment based on Schauer et al showed:
  - 60-70% of OC could be accounted for from primary sources on non-wood smoke days
  - 30-50% of OC could be accounted for from primary sources on wood smoke days (included estimates of primary fire emissions)
- This suggests there is some unaccounted secondary formation mechanism occurring on wood smoke days

Schauer, J. J., M. J. Kleeman, G. R. Cass and B. R. T. Simoneit (2001). "Measurement of emissions from air pollution sources. 3. C1-C29 organic coumpounds from fireplace combustion of wood." Environmental Science & Technology 35: 1716 - 1728.

Photochemical Modeling of SOA Formation

- Two separate SOA formation mechanisms were modeled
  - Condensation of semivolatiles on increased number of seed particles from primary fire emissions
  - Acid catalyzed heterogeneous SOA formation on the surface of fire particles
- The model predicted that the condensation pathway would account for less than 10% of the SOA formation. (This was not significant on fire days).
- Temporal patterns predicted by the model suggest that heterogeneous isoprene condensation was not important in this episode
- Temporal and spatial patterns predicted by the model show a correlation between predicted aldehyde concentrations from heterogeneous reactions and measured SOA increases.

Previous Work – Modeling Effects of Heterogeneous N_2O_5 Hydrolysis in Southeast Texas

N_2O_5 chemistry

- NO_2 photolyzed during the day – reaction 1 driven to the left
- N_2O_5 accumulates at night – fate at night effects NO_2 concentrations in the morning
- Reaction 2 can happen in the gas phase or on particle surfaces
- HNO_3 is lost from the atmosphere via deposition

Reaction 1

$$NO_2 + NO_3 \leftrightarrow N_2O_5$$

Reaction 2

$$N_2O_5 + H_2O \leftrightarrow 2HNO_3$$

Why N_2O_5?

- Many global modeling studies on heterogeneous N_2O_5 hydrolysis (Dentener and Crutzen, 1993 and others)
  - In combination with heterogeneous NO_3 loss, caused up to 49% decrease in global tropospheric NO_x
  - In combination with heterogeneous NO_3 loss, caused up to 9% decrease in global tropospheric O_3
- One urban ozone study (Reimer et al, 2003)
  - Mixed results on ozone
  - Increased HNO_3 formation lead to increased $PM_{2.5}$
- Lots of laboratory data on parameters effecting reaction rate
- Direct measurements of N_2O_5 and its hydrolysis and photolysis products planned for field program in August

Method – CMAQ model

- 36 km (TX and surrounding states) and 12 km (TX) grids used
- Episode: September 13-20, 1999
- RADM2 chemical mechanism used
- CMAQ version used already included this heterogeneous reaction
  - $\gamma = 0.1$
  - Reaction modeled on aqueous aerosol particles

Method – CAMx Model

- 36 km (TX and surrounding states), 12 km (TX), and 4 km (Texas coast) grids used
- Episode: September 13-20, 1999
- CB4 chemical mechanism used
- Added FORTRAN code to modeling program to perform calculations using following equations
- Used $\gamma = 0.1$ as upper bound
- Reaction modeled on sulfate aerosols

$$-\frac{d[N_2O_5]}{dt} = k[N_2O_5] = \frac{\gamma\omega A}{4}[N_2O_5] = \gamma Z$$

$$A = \frac{6V}{D_p} = \frac{6W}{\rho D_p} \qquad \omega = \sqrt{\frac{8RT}{\pi MW}}$$

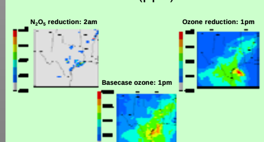
Measured Reactive Uptake Coefficients from the Literature for Heterogeneous N_2O_5 Hydrolysis

Aerosol Type	Range for γ
Water	0.005 - 0.06
Sulfuric acid	0.024 – 0.15
Ammonium sulfate	0.00094 – 0.09
Ammonium bisulfate	0.001 – 0.069
Ammonium nitrate	0.00042 – 0.001
Sodium bisulfate	0.0002 – 0.018
Sodium nitrate	00.0018 – 0.001
Aqueous malonic acid	0.002 – 0.033
Solid malonic acid	0.001
Solid azaleic acid	0.0005
Sea salt	0.005 – 0.03
Soot	0.00004 – 0.0002
Sodium sulfate	0.037
Dust	0.01

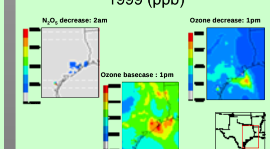
Results

- CMAQ
  - Maximum basecase daily ozone: 95-119 ppb
  - Maximum daily ozone decrease from heterogeneous reaction: 1.8-4.5 ppb
- CAMx
  - Maximum basecase daily ozone: 81-141 ppb
  - Maximum daily ozone decrease from heterogeneous reaction: 0.01-0.257 ppb
  - Maximum daily ozone increase: 0.03 - 1.0 ppb

CMAQ Plots – September 20, 1999 (ppb)



CAMx Plots – September 20, 1999 (ppb)



Results Summary

- CMAQ model runs showed that this chemistry is potentially quite significant
- CAMx model runs showed mixed results
  - Effect on some days was almost zero
  - Effect on a few days was somewhat significant
  - Area of effect was very limited
  - Chemistry caused both increases and decreases in ozone
- Difference between CMAQ and CAMx results is likely due to:
  - Order of magnitude difference in gas-phase N_2O_5 hydrolysis rates used for the two models
  - Different gas-phase chemical mechanisms (RADM2 vs. CB4)

Conflicting Modeling Results

- Dentener and Crutzen: up to 9% change in global average tropospheric ozone conc.
- CMAQ: generally less than 5% change in daytime urban 1-hr ozone conc.
- CAMx: generally less than 1% change in daytime urban 1-hr ozone conc.
- 3 different models with 3 different answers
  - CAMx: modest implications
  - CMAQ & Dentener and Crutzen: more substantial
- Up next: better define this chemistry using field measurements

Future Work

New Tools for Future Work

- We now have new measurements from TEXAQS II.
- We have recently developed a model-ready primary PM emissions inventory which will allow more accurate modeling.

Future Projects

- Investigate the source of unexplained SOA
- Refine modeling to investigate the importance of heterogeneous N_2O_5 hydrolysis
- If any fire plumes are identified in the TEXAQS II data, further investigate heterogeneous sulfate formation on fire particles

Characterizing Unexplained SOA – Testing Hypothesis 1: Heterogeneous Formation from Condensation of Aldehydes on (Acidic?) Aerosols

We Plan to:

- Identify TEXAQS II flights with aerosol and precursor measurements
- Model heterogeneous SOA formation pathways on days with ambient data
- Compare modeled and measured aldehyde concentrations
  - do we see similar enhancement of aerosol concentrations?
  - Does SOA formation from ambient measurements vary with the composition of the aerosol? If so, can models accurately describe this variation?

Characterizing Unexplained SOA – Testing Hypothesis 2: Condensation of On-Road Semivloatile VOCs that are Missing from the Emissions Inventory

- Use predicted semivolatile VOC emission rates from the litterature to adjust the model-ready emissions inventory
- Run the model with the adjusted Emissions Inventory
- Compare the spatial distribution of SOA predicted by the model with measured values

Future N_2O_5 Work

- Look at NO, NO_3, NO_2, N_2O_5, and aerosol measurements to determine what fraction of N species are being heterogeneously processed
- Model heterogeneous chemistry using newly developed primary PM emissions inventory and TEXAQS II data predicting reactive uptake coefficients on Houston aerosol.
- How well do current models capture heterogeneous processing?
  - CAMx does not include heterogeneous chemistry, but the homogeneous rate constant has been adjusted to account for it. Does the model's accuracy at predicting NO_x concentrations vary with particle loading?
  - CMAQ does currently include N_2O_5 hydrolysis on aerosol surfaces
- What are any possible regional implications to complying with 8-hour ozone standards?