Motivation

Recent studies analyzing CARES field campaign data suggest anthropogenic biogenic interactions play an important role (Shilling et al. 2012, Setyan et al. 2012)

How can we use the 3D models to understand these interactions?

First we need to consider how well we understand SOA formation in purely anthropogenic vs. biogenic plumes

Approach:
- Look at measurements where there was very little mixing
- Compare to mixed plume conditions

Uncertainties:
- Anthropogenic precursor emissions poorly constrained
- Missing biogenic precursors and their chemistry
WRF-Chem configuration

- 4×4 km grid spacing

- Emissions and chemistry:
  - 2008 CARB emissions inventory
  - SAPRC-99 gas chemistry
  - MOSAIC for inorganic aerosols
  - 2-species VBS anthropogenic SOA (Shrivastava et al. 2011)
  - MEGAN for biogenic emissions
  - NOx dependent biogenic SOA yields
  - OH, O3 and NO3 oxidants
  - 2-species fits for smog chamber biogenic and anthropogenic SOA (C* 0.1 and 10 µg m⁻³)

WRF domain: CARES

OA µg m⁻³
June 28, 3 p.m.
Very limited mixing: June 12th afternoon
No T0 → T1 transport

- Default model underpredicts OA ~ factor of 3
- Expect mostly biogenic SOA downwind of T1 (black box)
- Biogenic SOA likely low ~ factor of 3
Simulated total OA: Afternoon flight 28 June T0→T1 transport (Mixed plumes)

- Default model underpredicts OA → factor of 3 on average
- Model with no VBS anthropogenic SOA → underpredicts OA ~factor of 7
Mixed anthropogenic-biogenics: June 28 afternoon flight

- Model captures timing of CO peaks reasonably well
- Model underpredicts isoprene+MVK+MACR by less than 50%
- But default model underpredicts OA by a factor of 5 in mixed plumes
- Without VBS anthropogenic SOA model underprediction is even large
Conclusions and Discussions

- The non-mixing case (June 12th) suggests model underestimates biogenic emissions ~ factor of 3
- Model underpredicts SOA in mixed plumes on 28th June (~ factor of 5)
- Same VBS parameters predicted SOA well over Mexico City and overpredicted SOA ~ factor of 5 away from Mexico City (Shrivastava et al. 2011)
- Sacramento anthropogenic plumes lot cleaner (lower POA) than previous study in Mexico City which overpredicted SOA (Shrivastava et al. 2011)

Discussions and questions for future work:

- Before quantifying anthropogenic-biogenic interactions we need to better constrain both anthropogenic and biogenic SOA mechanisms in models
- How to improve biogenic SOA estimates? Missing precursors, multi-generational chemistry mechanisms?
- What is the contribution of reactive uptake, oligomerization processes in formation of SOA?
- What is the role of gas-phase fragmentation reactions? (Shrivastava et al. 2013, JGR in press)
- Ongoing work: the CARES dataset are being used to constrain anthropogenic and biogenic contributions to SOA
Biogenic SOA yields

- Default model: NO\textsubscript{x} dependent yields for isoprene, monoterpenes and sesquiterpenes

![Graph showing Mass Yield (%) vs. Isoprene to NO\textsubscript{x} ratio]

- SOA yields depend on VOC:NO\textsubscript{x} ratio through some unknown mechanism during CARES (Shilling et al. 2012, ACP)

- Investigate effects of Isop:NO\textsubscript{x} dependent yields

Kroll et al. 2006 ES&T; Chan et al. 2010 ACP

May 1, 2013
C130 flight during MILAGRO

Shrivastava et al. 2013, JGR
SOA: Very low effective volatility

- SOA evaporation much slower than kinetic mass transfer theory predictions using 7-species VBS
- Fits to SOA evaporation rate imply very low effective volatility
- 2-species VBS → Non-volatile anthropogenic SOA
Modeling SOA during CARES: Implications for anthropogenic biogenic interactions

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