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
- NO_x dependent biogenic SOA yields
- **OH**, O_3 and NO_3 oxidants
- 2-species fits for smog chamber biogenic and anthropogenic SOA (C*0.1 and 10 µg m⁻³)



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
- Mostly fresh SOA (Vaden et al. 2011, Setyan et al. 2012 Shilling et al. 2012) → Measured SOA yields not representative of field data

Simulated total OA: Afternoon flight 28 June T0→T1 transport (Mixed plumes)





- Default model underpredicts $OA \rightarrow$ factor of 3 on average
- Model with no VBS anthropogenic SOA \rightarrow underpredicts OA ~factor of 7

Mixed anthropogenic-biogenics: June 28 afternoon flight





Observed Default model VBS anth. and biogenic SOA

Only biogenic SOA i.e. No VBS anthropogenic SOA

- 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)
- Dicussions 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, multigenerational 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_x dependent yields for isoprene, monoterpenes and sesquiterpenes



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

- SOA yields depend on VOC:NOx ratio through some unknown mechanism during CARES (Shilling et al. 2012, ACP)
- Investigate effects of Isop:NOx dependent yields May 1, 2013

C130 flight during MILAGRO



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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 \rightarrow Non-volatile anthropogenic SOA



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Modeling SOA during CARES: Implications for anthropogenic biogenic interactions

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