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Advancing treatment of Secondary organic aerosols in CESM using the VBS-MAM approach

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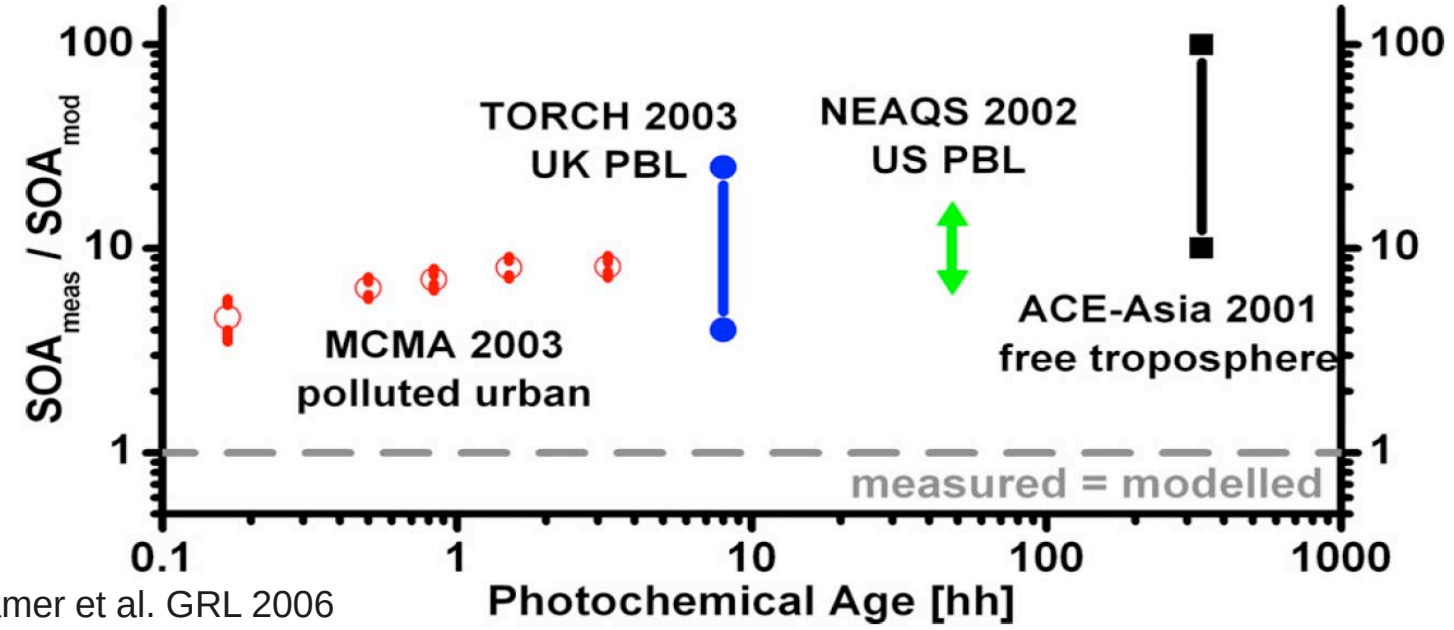
CESM AMWG-CCWG Joint Session, 11th February 2014

Acknowledgement: DOE SciDAC ACES4BGC project

Models often underpredict SOA loadings



Volkamer et al. GRL 2006

- Models often under-predict SOA loadings by a factor of ~10
- Discrepancy between model and data increases with photochemical age
- What is responsible for this discrepancy between models and measurements?

Model assumptions are inconsistent with laboratory and field data

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Traditional Modeling Approach Semivolatile SOA (SVSOA)

- Model treats SOA as rapidly mixing and evaporating solution
- Model assumes SOA particles are at **equilibrium** with the gas phase

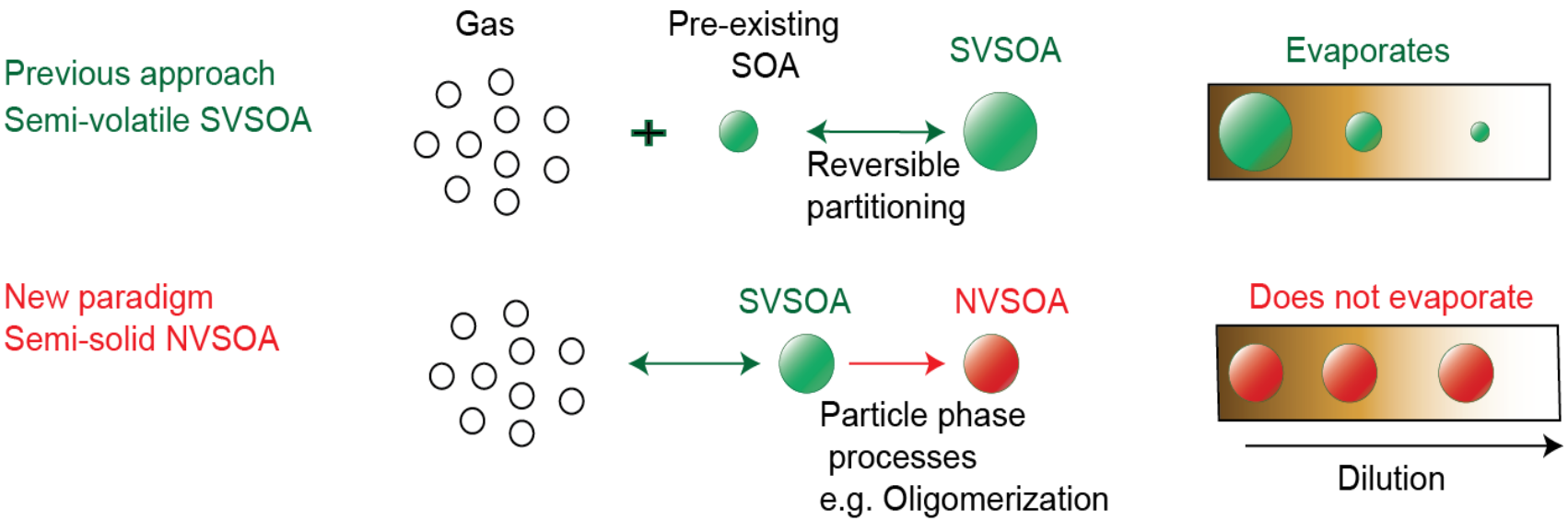
Recent Data Show

- SOA evaporates orders of magnitudes slower than assumed
- SOA is highly viscous semi-solid
- SOA is not at equilibrium with the gas phase

New Modeling Paradigm-Nonvolatile SOA (NVSOA)

- Treat SOA as a non-volatile semi-solid
- Include fragmentation of gas-phase SOA precursors

SOA paradigms: nonvolatile vs semivolatile

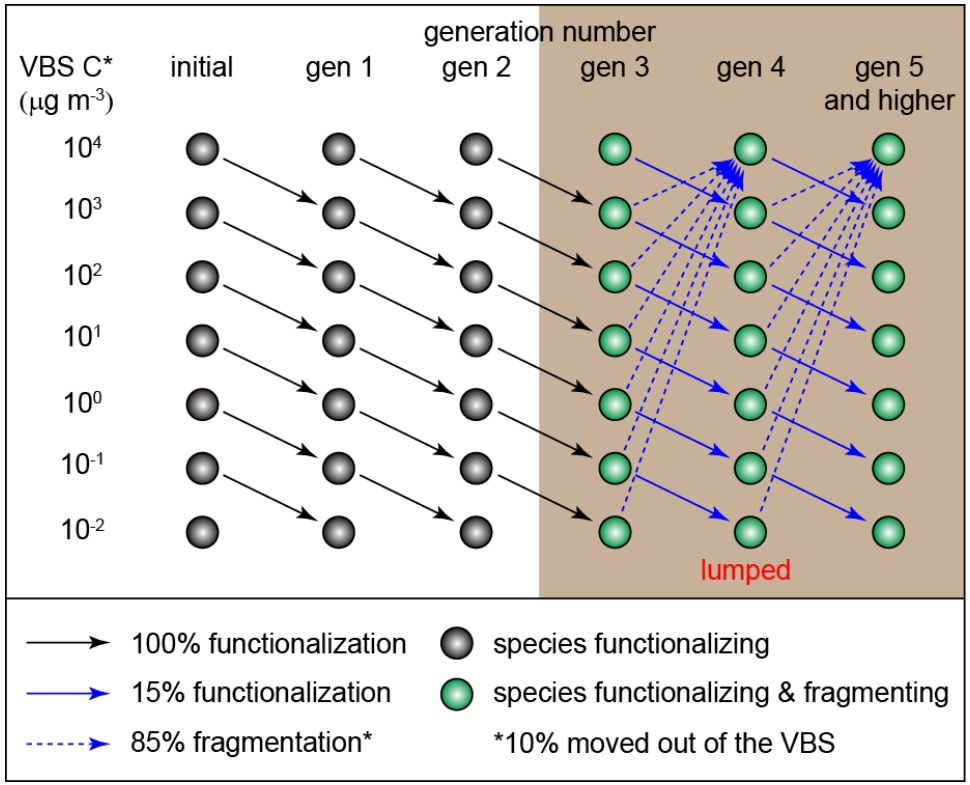


- NVSOA, Highly viscous, non-absorbing, semi-solid

  (*Zelenyuk et al. 2012; Vaden et al. 2011; Vaden et al. 2010; Cappa and Wilson 2011; Saukko et al. 2012; Virtanen et al. 2010; Pierce et al. 2011*)

- SOA particles are almost non-volatile, highly viscous semi-solid and hence non-absorbing

Gas-phase fragmentation of SOA precursors



While we know that fragmentation reactions play an important role in SOA formation, we lack the detailed data required to reliably represent the process.

- Fragmentation parameters correspond to the best model-measurement agreement during MILAGRO 2006 (Shrivastava et al. 2013)
- Because data show that precursor gas oxidation by OH yields **higher and lower** vapor pressure products, our model includes fragmentation reactions

Methodology

- CAM5 (1.9× 2.5°), nudged to ERA-Interim reanalysis
- Mozart chemistry coupled to modal aerosol module (MAM3)
- Daily fire emissions using GFED3.1
- 4-bin volatility basis-set (VBS) for biogenic SOA: Isoprene & Terpenes
- Semi-volatile and intermediate volatility organics (SIVOC) from anthropogenic and biomass burning emissions: 5-bin VBS×2
- 62 SOA species (42 SOA particle species and 20 gas phase organic species) + 104 gas-phase tracers from Mozart chemistry
- Flexible SOA modeling framework to easily change SOA species
- SOA species interact with clouds and the optical calculations
- Source-resolved SOA predictions from 3 precursor classes: anthropogenic, biomass burning and biogenic
- Treatment of gas-phase fragmentation and semi-solid SOA

Model configurations

1. Default SOA treatment that directly emits SOA (Liu et al. 2012, GMD)
2. Semi-volatile SOA, functionalization only (Func,no fragmentation)
3. Semi-volatile SOA, Func + Frag
4. Non-volatile semi-solid SOA, Func + Frag

Results: Annual average column burden

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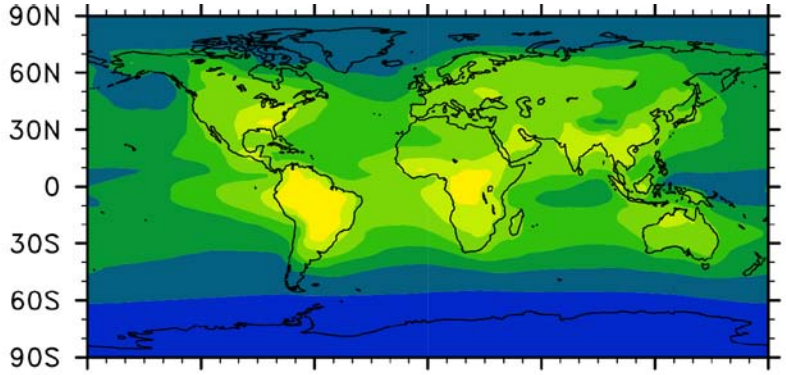
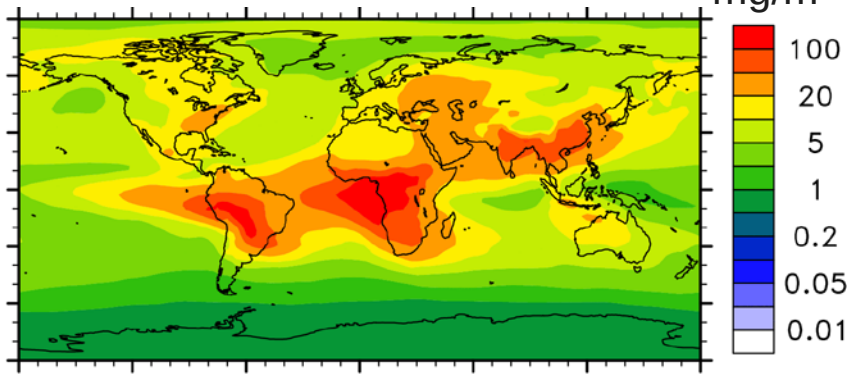
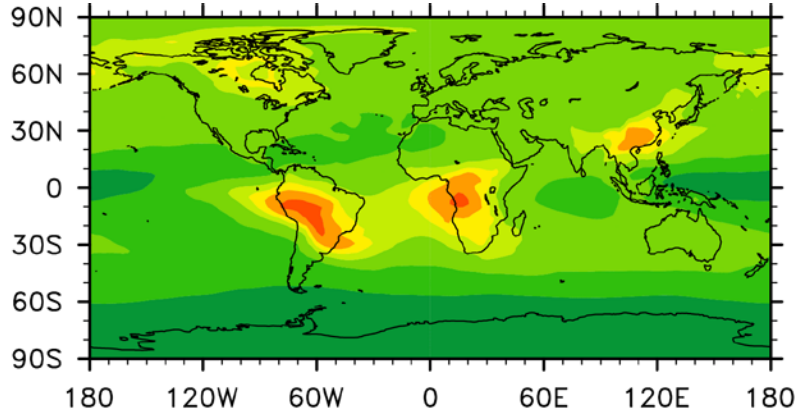
Previous SOA: 1.07 Tg, 3.8 days
Liu et al. GMD



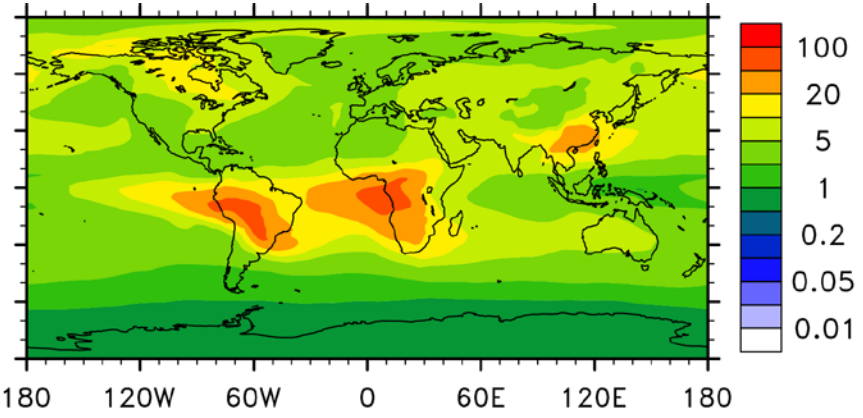
SVSOA, Func only: 8.42 Tg, 5.6 days



SVSOA, Func + Frag: 2.18 Tg, 7.0 days

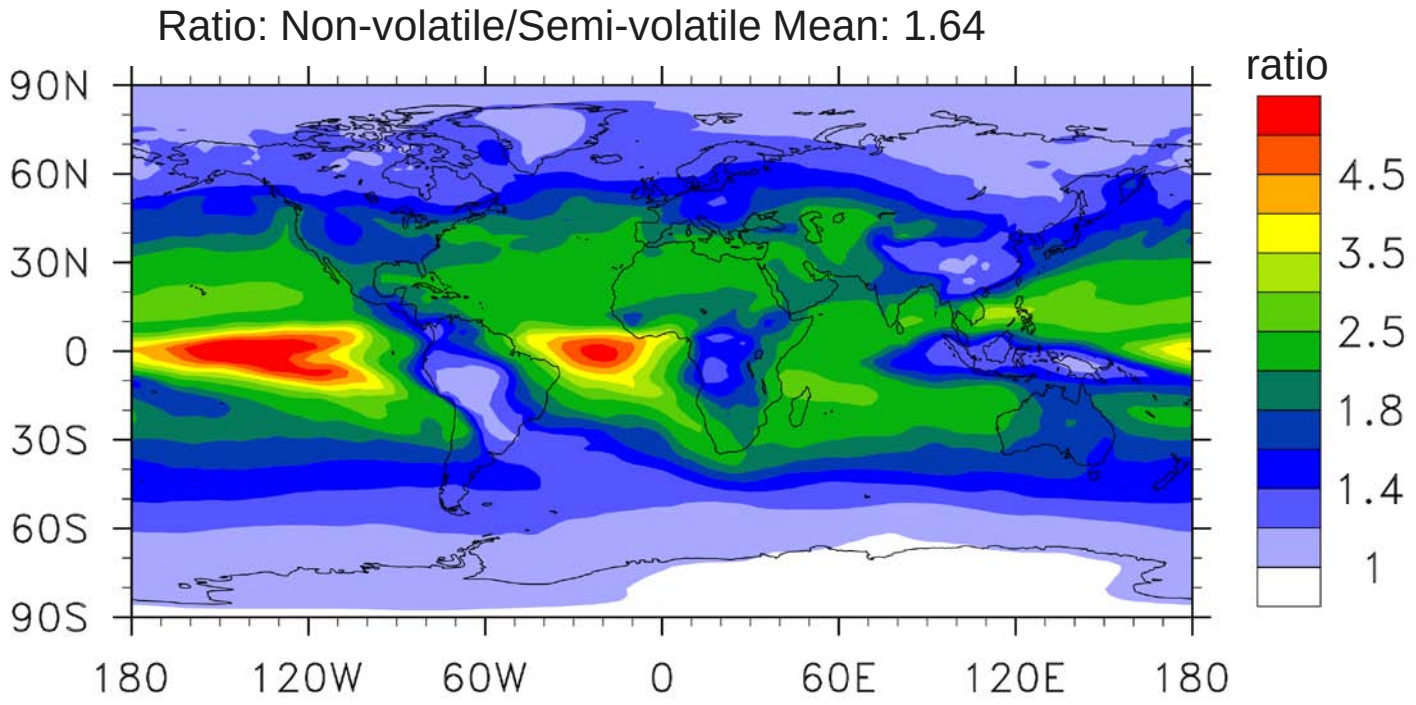


NVSOA, Func + Frag: 3.84 Tg, 7.14 days



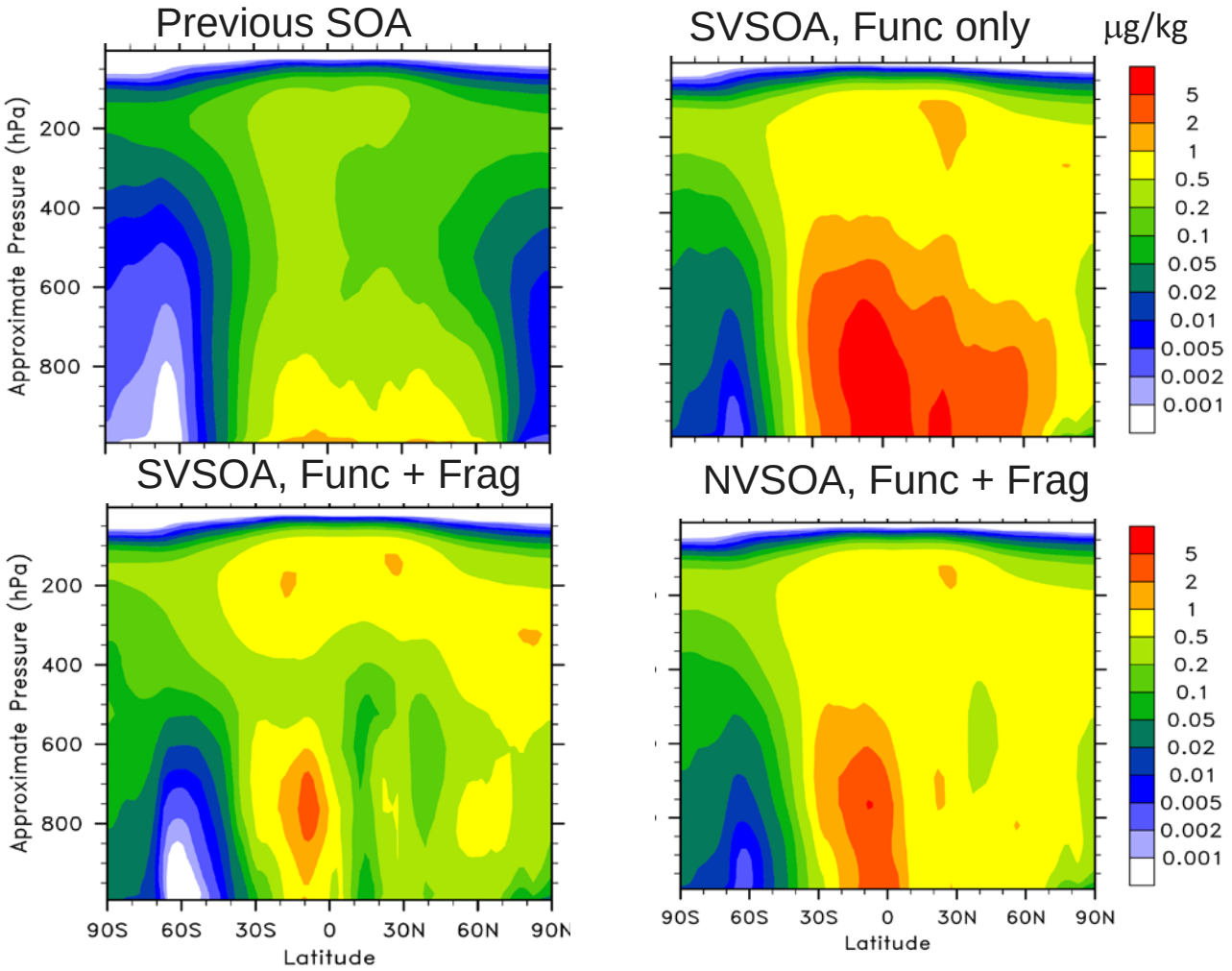
- New model configurations produce higher SOA burden and lifetimes than Liu et al. 2012
- Gas-phase fragmentation reduces average global SOA burden by a factor of ~2-3
- Treatments with fragmentation yield 25% higher SOA lifetime than without fragmentation

Results: Ratio of column burdens



- Treating SOA as a non-volatile semi-solid increases global average SOA burdens by a factor of ~ 2
- Largest increases in SOA burdens (> factor of 5) due to its non-volatile treatment correspond to pollution outflow over the oceans
- Large potential implications on radiative forcing of climate

Results: Zonal average SOA



- New model configurations produce much higher SOA over both surface and the free troposphere compared to the previous model (explains higher lifetime)

Results: Source contributions to SOA

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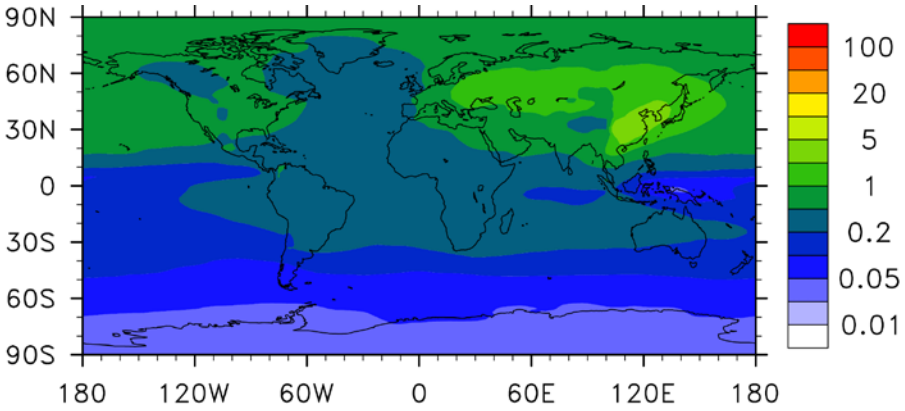
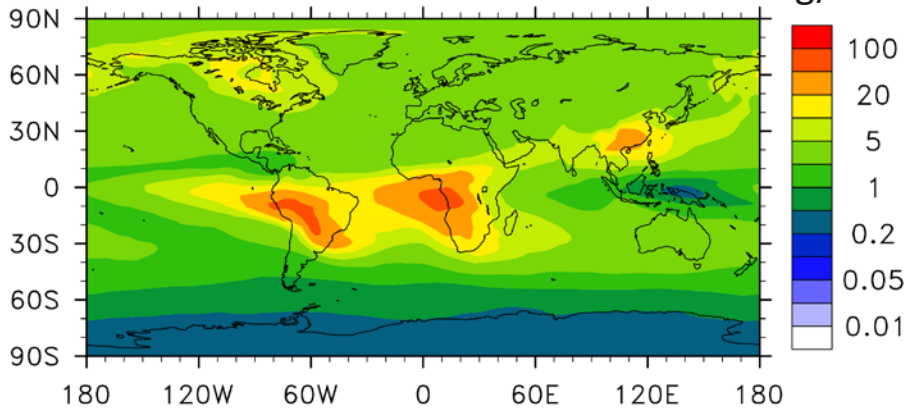
Fragmentation and Nonvolatile SOA

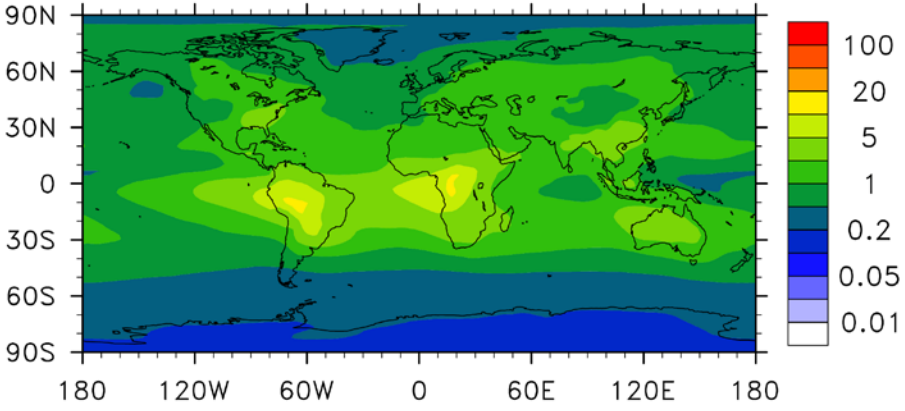
Anthropogenic SOA: 0.39 mg m^{-2}



Biomass SOA: 4.62 mg m^{-2}

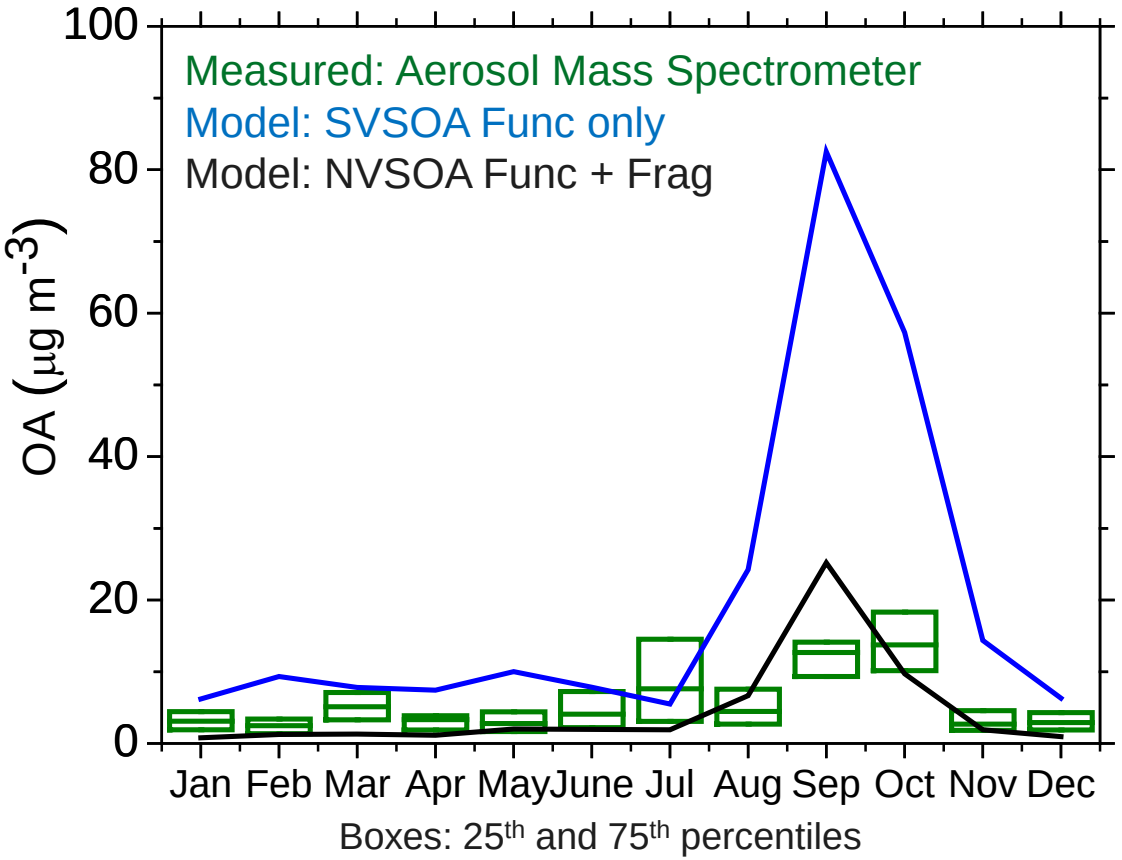


Biogenic SOA: 1.09 mg m^{-2}



- Biomass burning is the largest source of SOA globally (peaks over biomass burning regions)
- SOA from either biomass burning or biogenic sources is much larger than anthropogenic SOA

Comparison to measurements: biomass burning site Welgegund, South Africa



- Seasonal variation of measured OA captured by the model
- Neglecting fragmentation leads to large over-prediction of OA
- Model that includes fragmentation is closer to measurements

Evaluation with U.S. IMPROVE network OC measurements (2007-2011)

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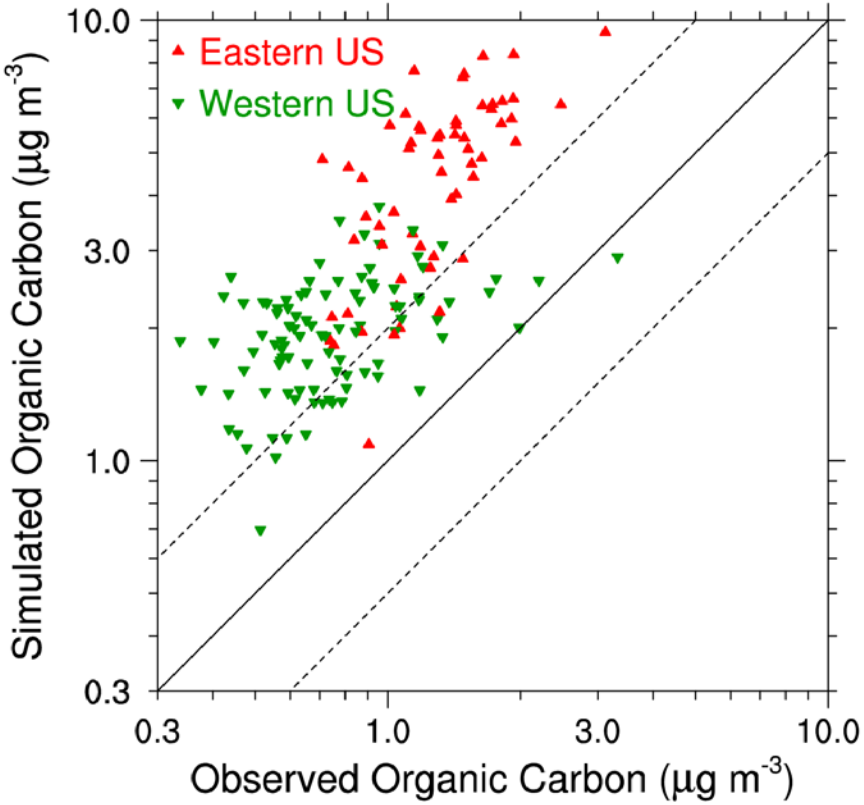
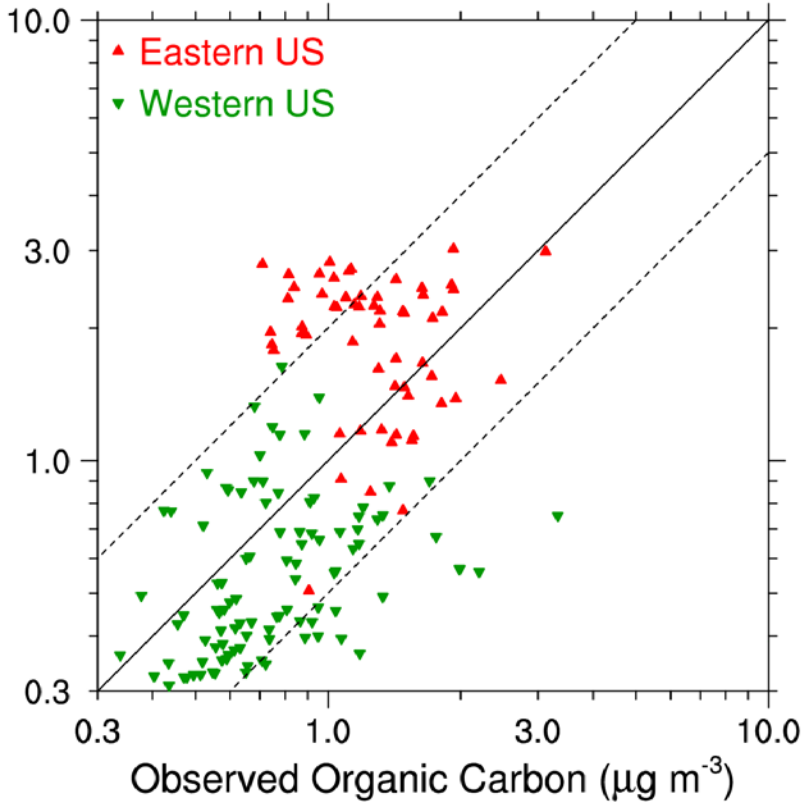
Obs. mean OC: 1.01 μg m^{-3}

Model default: 3.01 μg m^{-3}



NVSOA Func+Frag: 1.09 μg m^{-3}



- Previous default treatment (Liu et al. 2012) overestimates OC
- Revised treatment with non-volatile NVSOA and fragmentation shows much better agreement

Conclusions

- Multi-generational aging of organic vapors increases SOA concentrations throughout the domain
- Fragmentation reduces SOA concentrations by a factor of 2-3
- Treating SOA as non-volatile semi-solid (glassy) increases SOA concentrations compared to its traditional semi-volatile treatment
- Biomass burning is the largest global source of SOA followed by natural biogenic emissions
- Including fragmentation significantly improves model-measurement agreement of OA at Welgegund, South Africa
- Treatment with fragmentation and non-volatile SOA shows much better agreement with IMPROVE network measurements

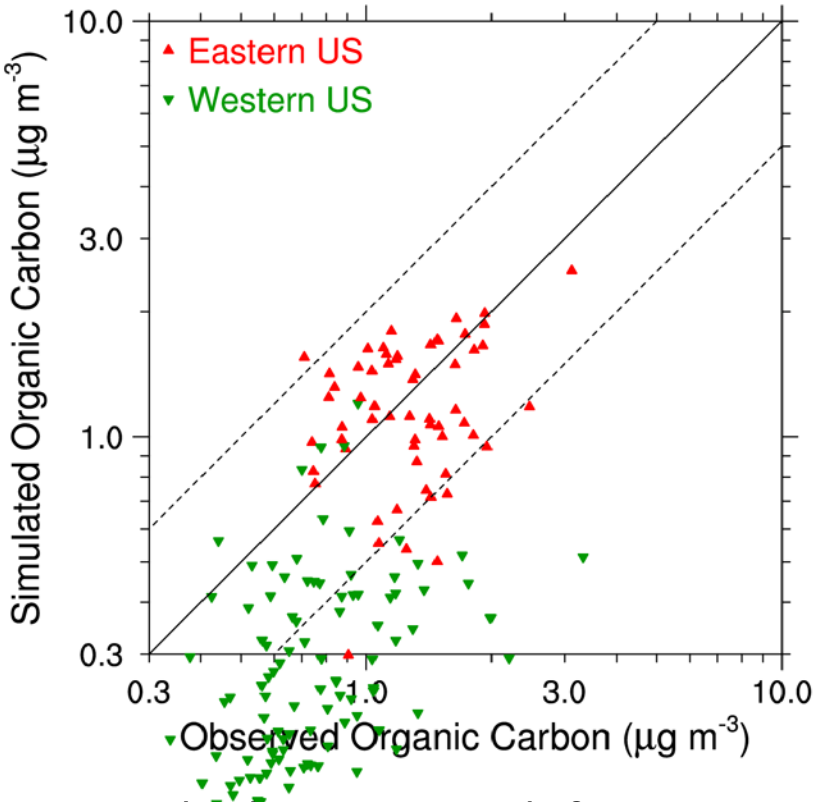
Future work:

- Improving treatment of particle nucleation and growth due to organics
- Evaluating the role of new SOA treatments on radiative forcing of climate
- Developing simpler but more accurate SOA treatments for use in global climate model simulations

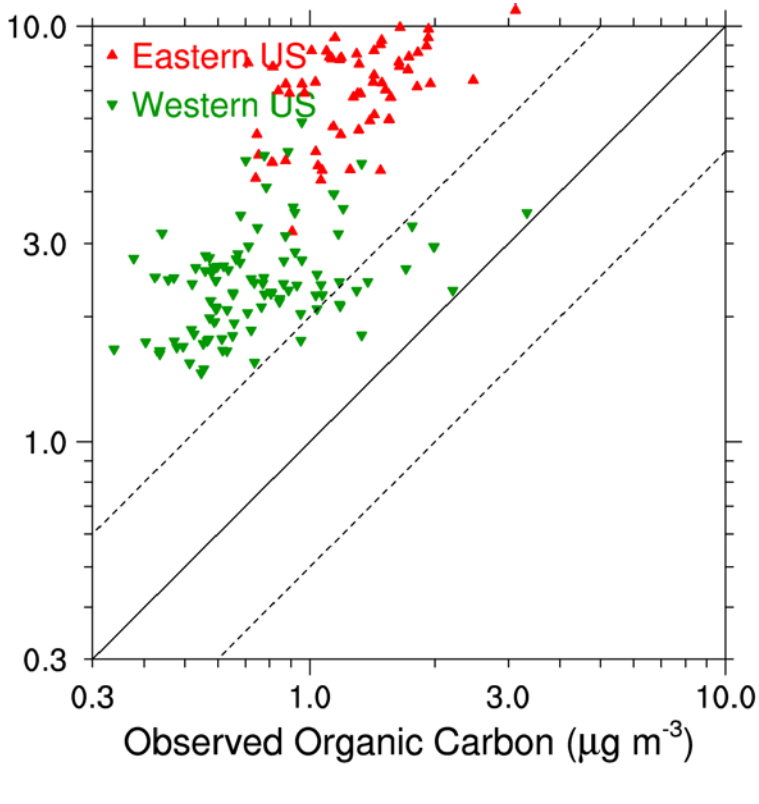
Evaluation with U.S. IMPROVE network OC measurements (2007-2011)

Obs. mean OC: 1.01 μg m^{-3}

SVSOA Func + Frag: 0.65 μg m^{-3}



SVSOA Func only: 4.23 μg m^{-3}



- Semivolatile SVSOA with fragmentation (Func+Frag) underestimates OC
- Semivolatile SVSOA neglecting fragmentation (Func only) significantly overestimates OC