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Global transformation and fate of SOA using a modified volatility basis-set approach

MANISH SHRIVASTAVA
RICHARD EASTER, XIAOHONG LIU, ALLA ZELENYUK, BALWINDER SINGH, KAI ZHANG, PO-LUN MA, DULI CHAND, STEVEN GHAN, JOSE L. JIMENEZ, QI ZHANG, JEROME FAST, PHILIP J. RASCH, PETRI TITTA

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Recent studies reflect large uncertainties in predicting SOA radiative forcing

- Previous estimates of SOA direct radiative forcing (DRF) differ by an order of magnitude

Studies	DRF (W m^{-2})
AeroCom Phase II Intercomparison experiments (Myhre et al. 2013)	-0.01 to -0.21 (mean: -0.06)
Spracklen et al. 2011 (observationally constrained but mostly near surface and in North Hemisphere)	-0.26±0.15 (anthropogenic controlled SOA)

- Most of the AeroCom models had very crude SOA treatments, mostly dominated by biogenics, & very few treated biomass burning as a source of SOA

- Biogenic and biomass SOA sources were not well constrained in Spracklen et al. 2011 due to limited observations in those regions

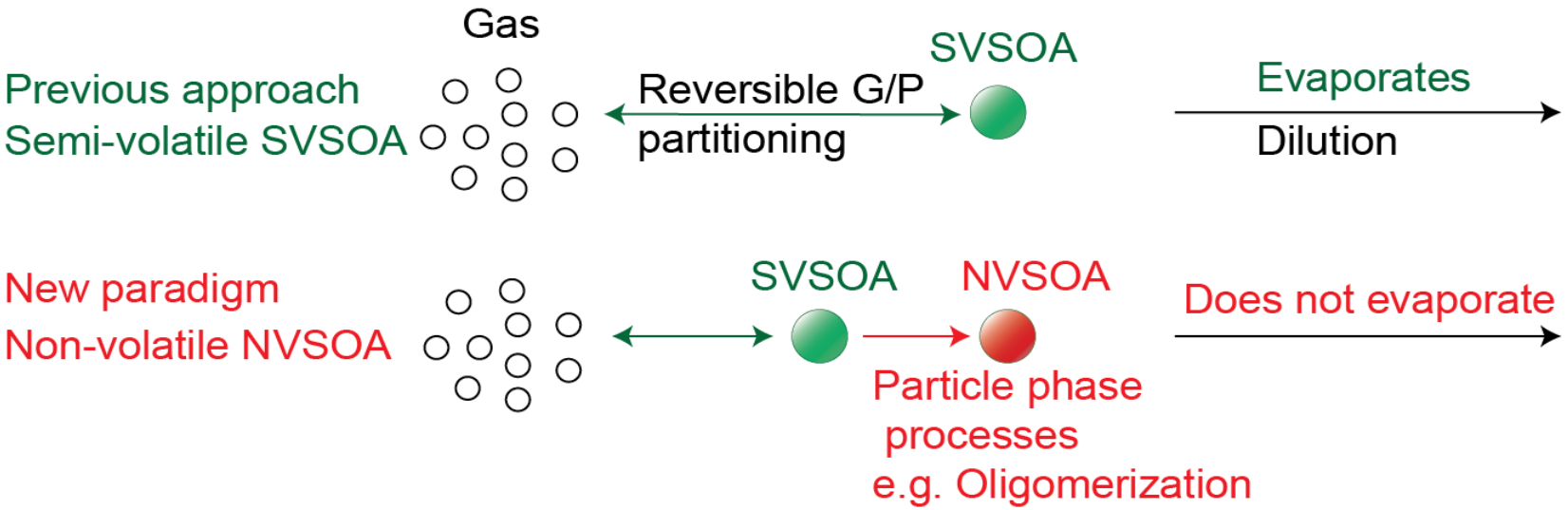
Current treatment of SOA in most global models

- "Traditional" SOA from biogenic VOCs (and anthropogenic VOCs in some models)
- Fixed yields and simplified chemistry
- But…

When it is about SOA it's not that simple…

- Gas-phase multigenerational chemistry of precursors should be realistic: Include both gas-phase functionalization & fragmentation reactions (e.g. Kroll et al. 2011)
- SOA properties change with aging and time: e.g. volatility reductions due to particle phase reactions such as oligomerization (e.g. Ziemann and Atkinson, 2012)
- Models that treat SOA as semi-volatile throughout its entire lifecycle are clearly missing these changes in SOA properties with atmospheric aging
- Most global models do not treat semi-volatile and intermediate volatility precursors emitted from combustion sources as biomass burning (e.g. Yokelson et al. 2013)

SOA paradigms: non-volatile vs semi-volatile



- NVSOA, Non-volatile SOA, formed due to condensation & subsequent decrease in volatility due to heterogeneous/multiphase chemistry

  (*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, Lopez-Hilfiker et al. 2015, Ziemann and Atkinson, 2012*)

- NVSOA starts as semi-volatile SOA, and is rapidly transformed to much less volatile and much more viscous SOA than previously assumed in most models

- Some global models treat SOA as non-volatile for simplicity, but the global scale impacts of this treatment needs to be investigated

Methodology: Global modeling

Shrivastava et al. 2015, JGR

- CAM5 (1.9× 2.5°), nudged to ERA-Interim reanalysis
- Mozart gas chemistry coupled to modal aerosol module (MAM3)
- Modified VBS approach for SOA in 3 source classes: fossil-fuel, biomass burning and biogenic
- Compare different model treatments of SOA particles:

1. Standard CAM treatment (instantaneously emitted low-volatility gas that quickly condenses to SOA, no chemistry)
2. Revised treatments with explicit oxidation chemistry of SOA precursors:
   a) Semi-volatile SOA paradigm with gas-phase functionalization only
   b) Semi-volatile SOA paradigm with gas-phase functionalization & fragmentation
   c) Non-volatile SOA paradigm with gas-phase functionalization & fragmentation

Results: Standard CAM vs. revised NVSOA treatment

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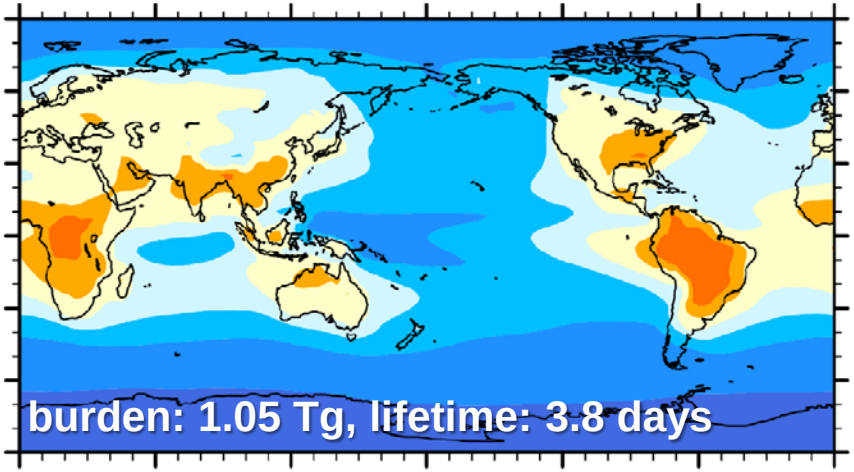
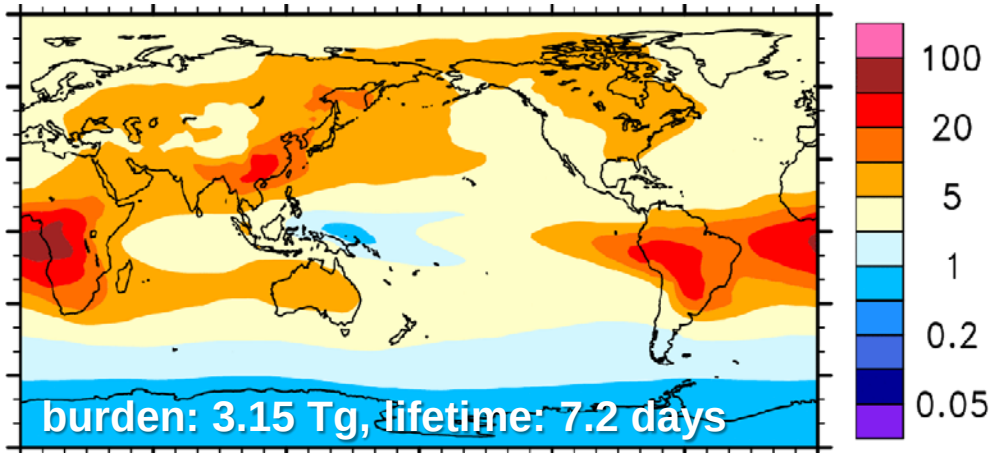
Standard CAM: Liu et al. 2012



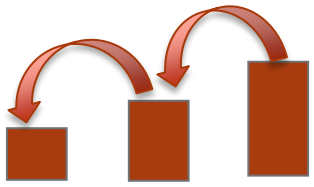
Revised: Non-volatile SOA, Func + Frag



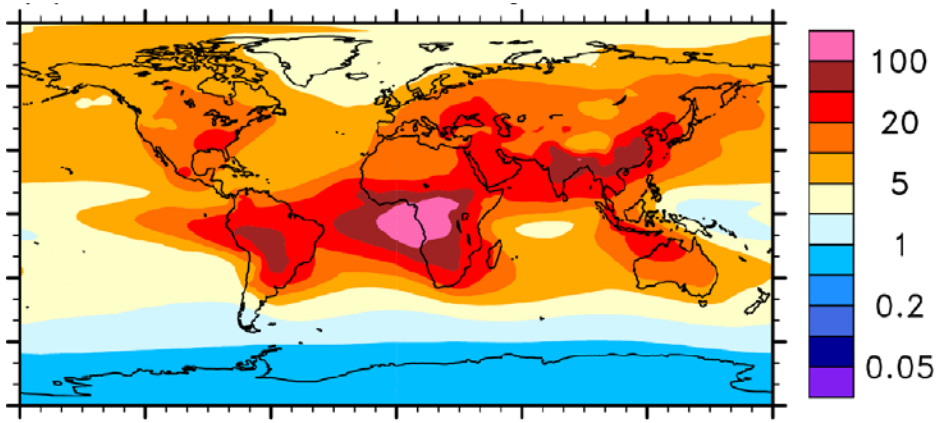
Shrivastava et al. 2015, JGR

- Revised treatment produces higher SOA burden & longer lifetime than Standard CAM
- Standard CAM SOA formed instantaneously close to surface below clouds (no mid/upper troposphere sources & no time lag for chemistry)
- Revised treatment: SOA also has mid/upper troposphere sources from biomass burning, SOA formation continues as organic gases react in the atmosphere

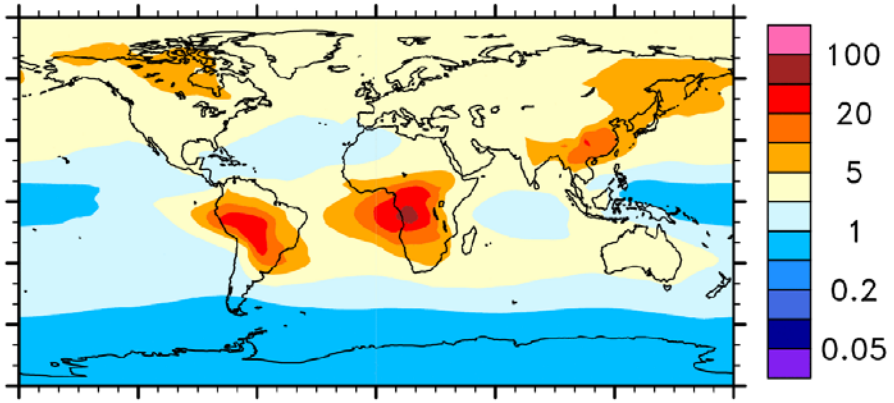
Results: Sensitivity to fragmentation reactions



Functionalize, do not fragment: Burden= 7.5 Tg



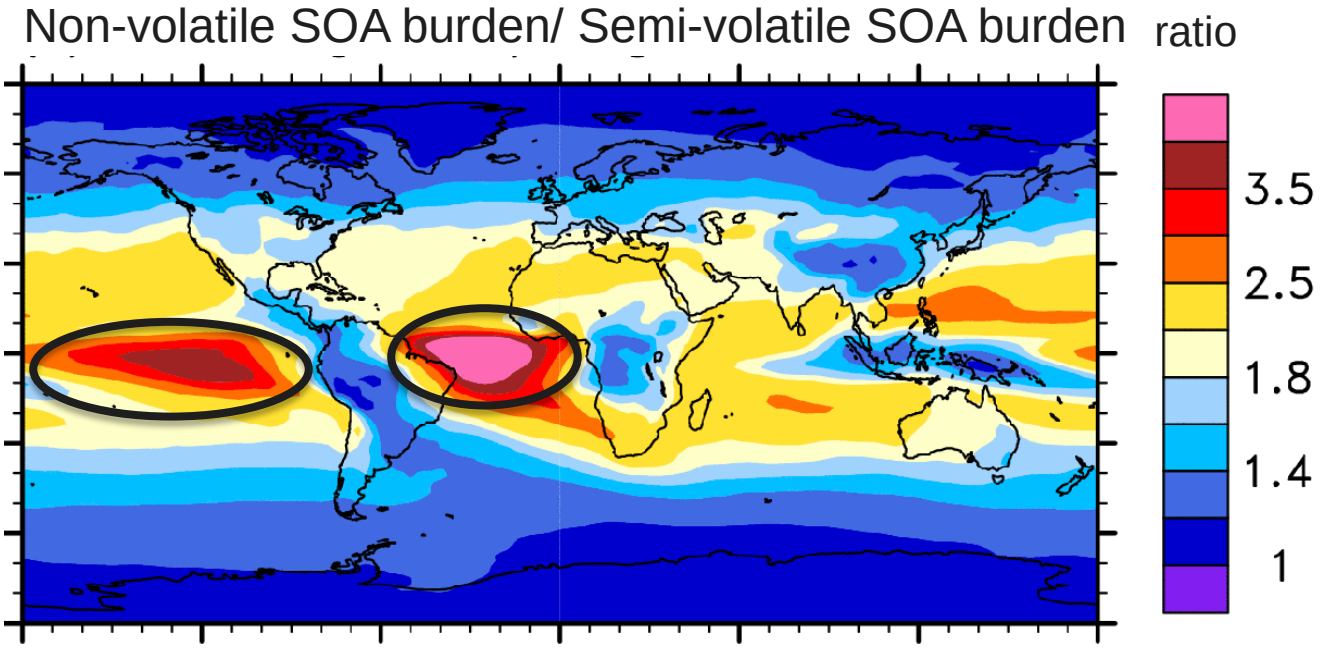
Functionalize + Fragment: Burden = 1.8 Tg



Shrivastava et al. 2015, JGR

- Neglecting fragmentation reactions causes unrealistically high SOA formation since ~96% of SIVOCs are efficiently moved to lower volatility bins due to functionalization reactions
- Fragmentation reactions are the largest sinks of condensable SOA gases
- Take home message: Multigenerational aging parameterizations that include SIVOC emissions need to include fragmentation reactions (in addition to func rxns)

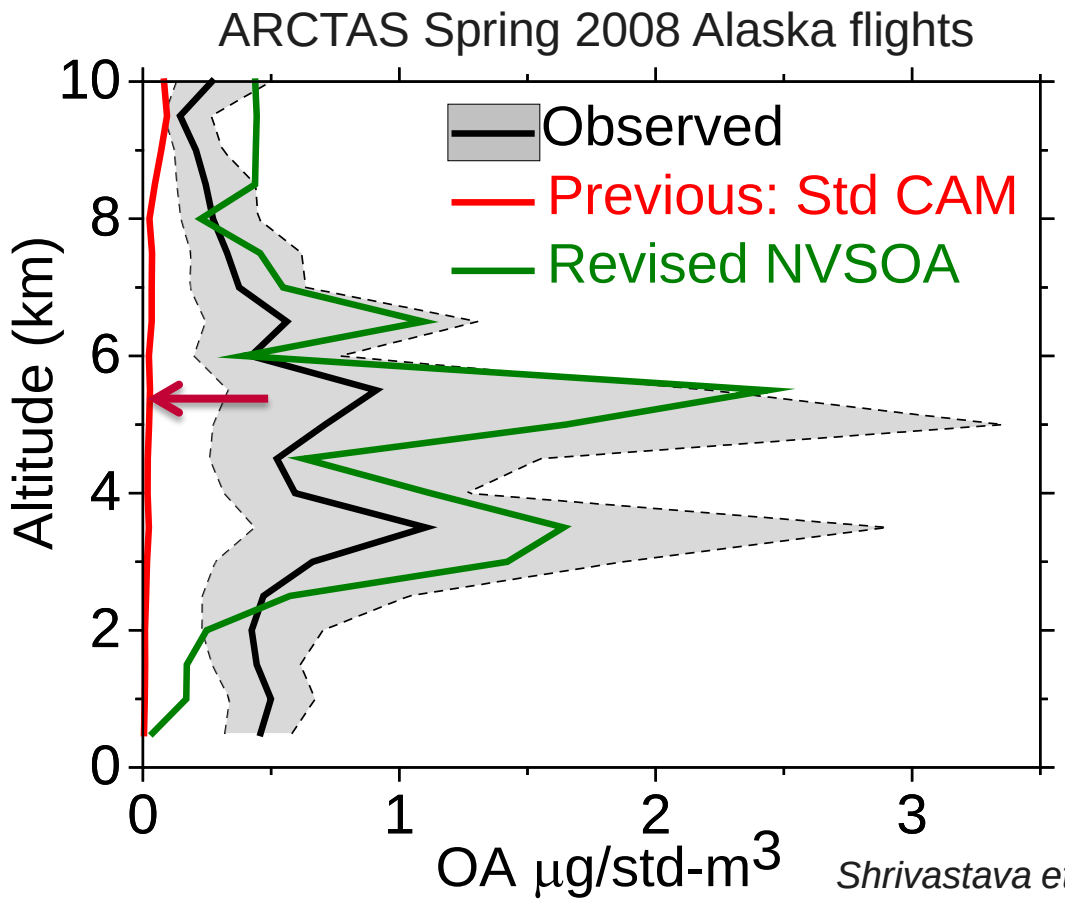
Non-volatile vs. semi-volatile SOA : Ratio of column burdens



Shrivastava et al. 2015, JGR

- Treating SOA as non-volatile increases global average SOA burdens by a factor of ~ 2 compared to semi-volatile SOA
- Even larger increases in SOA burdens due to its non-volatile treatment correspond to pollution outflow over the oceans due to evaporation of semi-volatile SOA

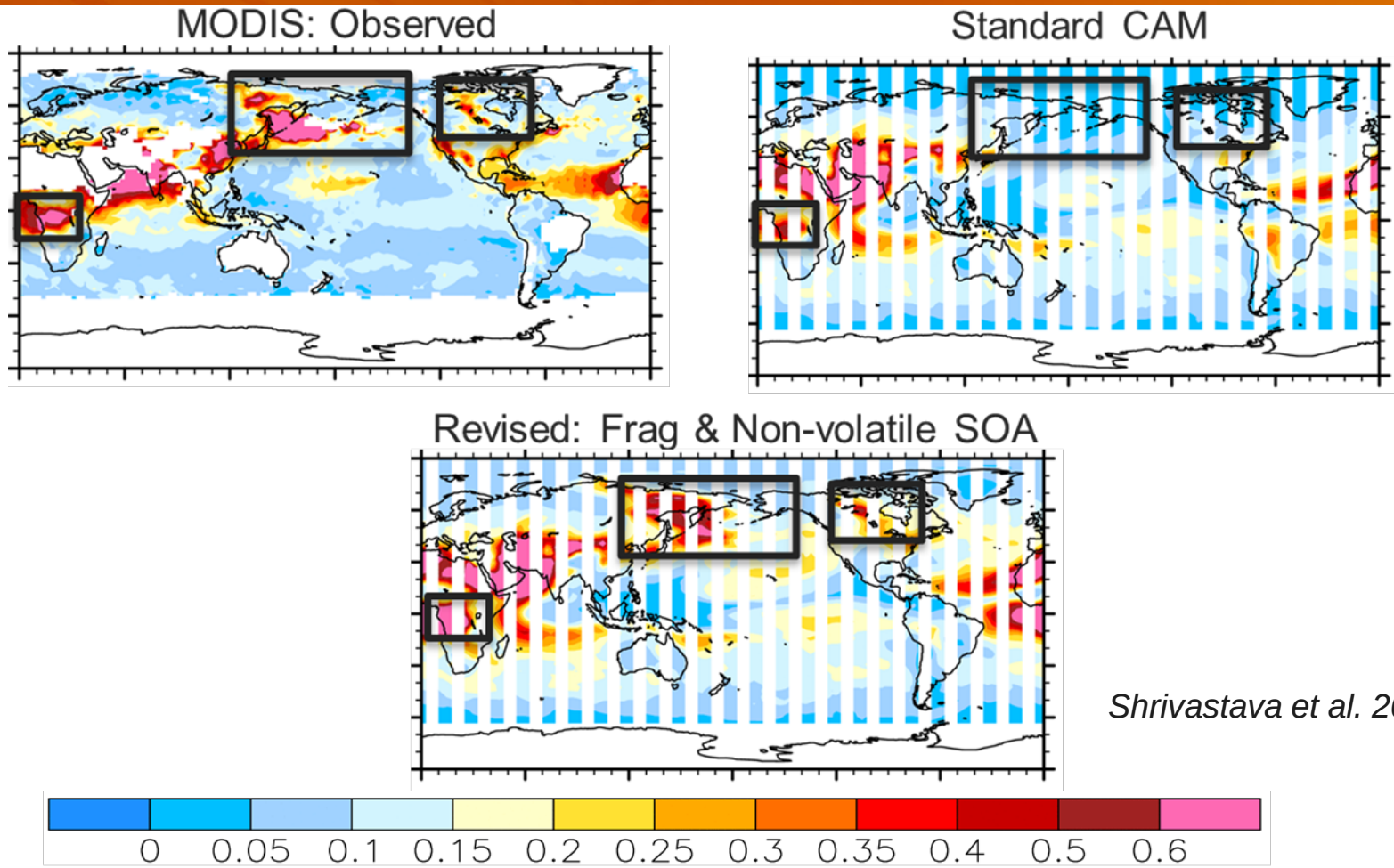
Evaluation using aircraft vertical profiles in wildfire affected regions in the Arctic



Shrivastava et al. 2015

- Standard CAM treatment under-predicts OA by orders of magnitude
- Revised model treatment dominated by biomass burning SOA significantly improves OA predictions

Evaluation using satellite AOD (July 2008)



Shrivastava et al. 2015

- Standard CAM underpredicts AOD over biomass burning regions in Eastern Russia, Northern Canada and Central Africa
- Revised treatment shows much better agreement: Biomass burning is predicted as the largest contributor to OA globally

Direct radiative forcing (DRF) of SOA

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Studies	DRF (W m^{-2})
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Spracklen et al. 2011	-0.26±0.15 (anthropogenic controlled SOA)
Shrivastava et al. 2015: Ageing & Non-volatile SOA	-0.50
Shrivastava et al. 2015: Ageing & Semi-volatile SOA	-0.26

- DRF of SOA from Shrivastava et al. 2015 is at the high end of previous estimates
- Semi-volatile SOA DRF in Shrivastava et al. is same as Spracklen et al. 2011
- The dominant OA sources are very different: Biomass burning (Shrivastava et al. 2015) vs. anthropogenically controlled natural OA (Spracklen et al. 2011)

Conclusions

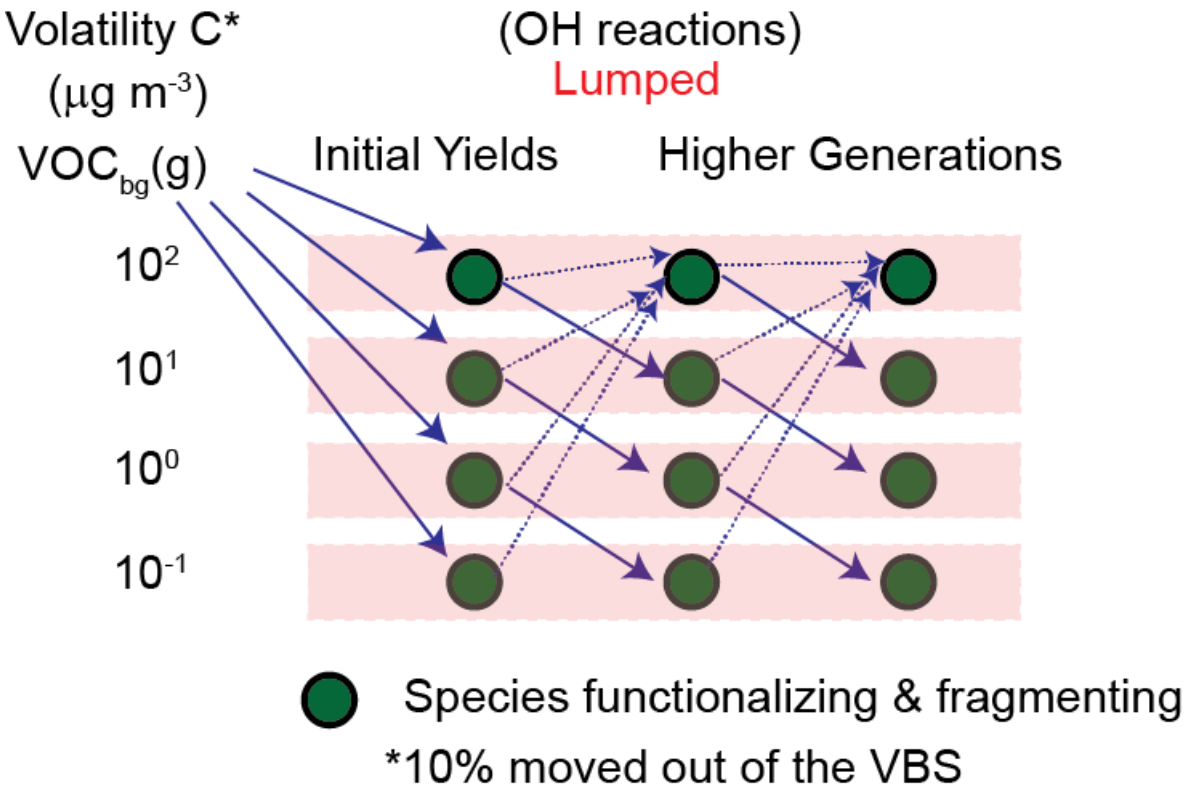
- Fragmentation reactions are the dominant sinks of condensable organic gases, and strongly affect simulated SOA loadings
- The non-volatile SOA treatment increases global SOA burdens compared to semi-volatile SOA, and larger increases are over pollution outflow to pristine regions
- Biomass burning is the largest simulated global source of OA (POA+SOA): supported by satellite & aircraft evaluations in biomass affected regions
- The POA-SOA split for biomass burning is uncertain and model inputs needs to be observationally constrained
- Biomass burning OA (POA & SOA) have much larger impacts on radiative climate forcing than previously thought
- Simulated direct radiative forcing of SOA in this study is at the higher end of previous global model estimates

Future work

- Development of a reduced tracer computationally efficient version of SOA treatments for ACME

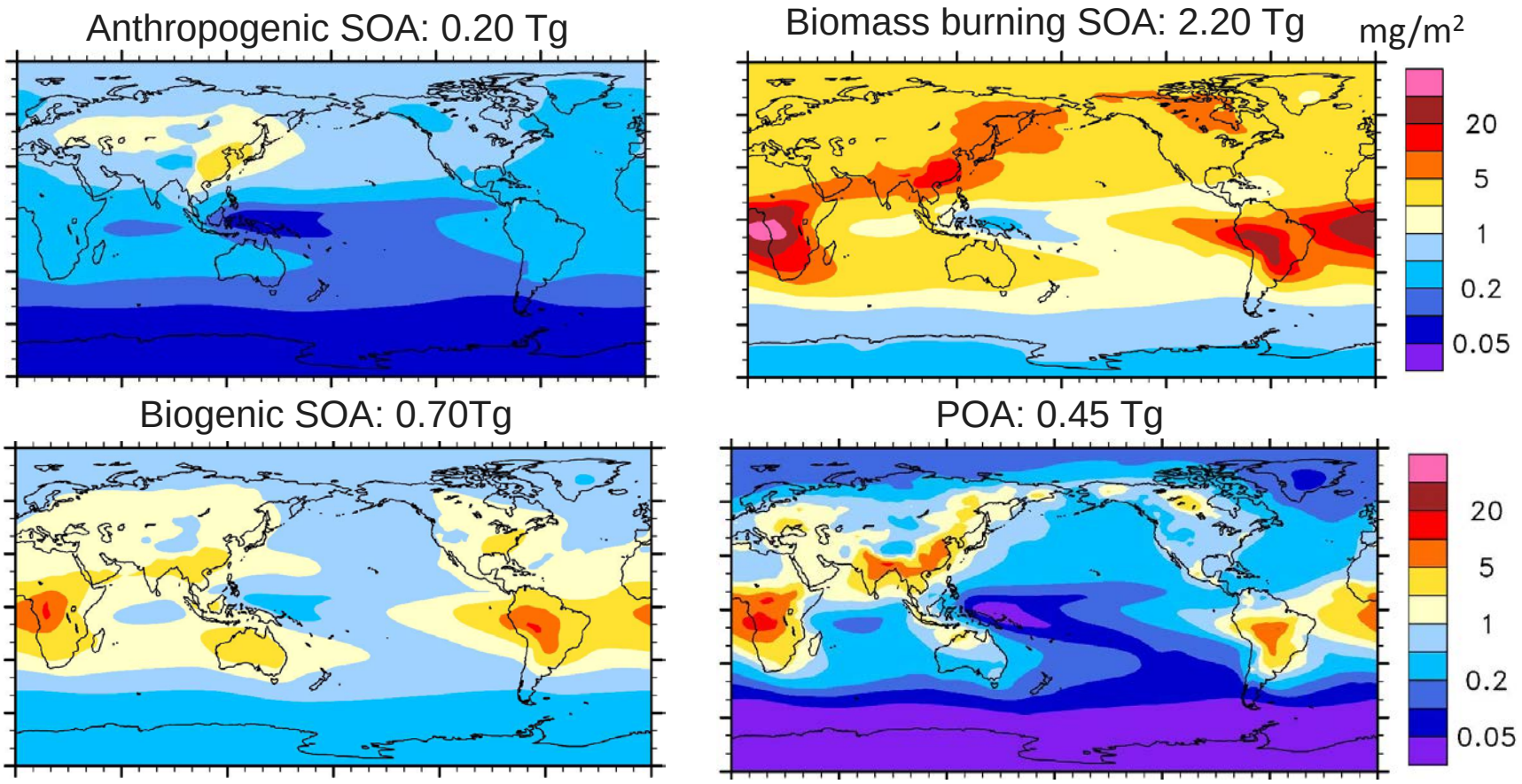
- The framework developed for treating SOA in Shrivastava et al. (2015) is being used for other SOA developments based on GECKO in CESM (Hodzic, Tilmes, Shrivastava et al.)

Further aging of biogenic VOCs creating SVOC/IVOC



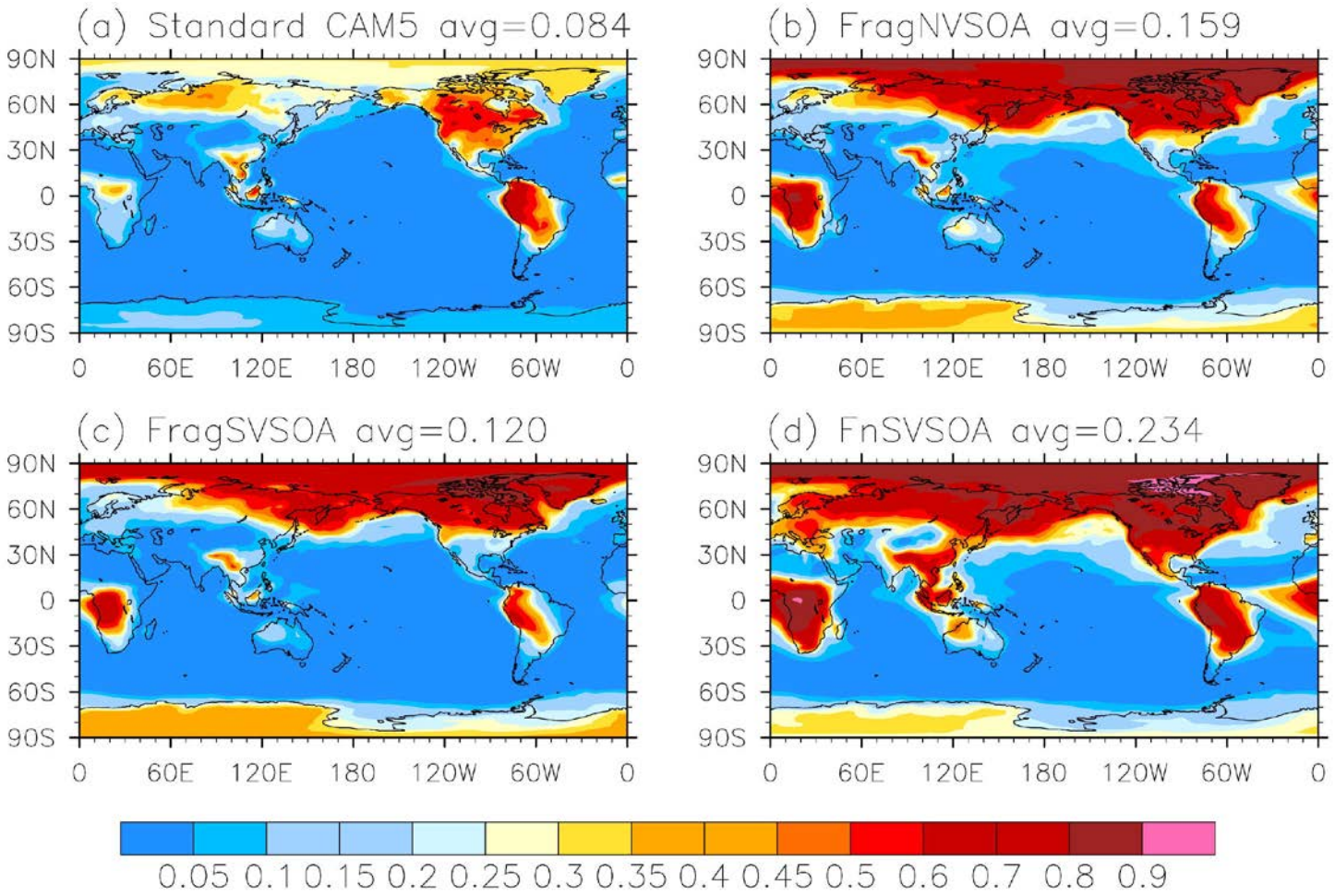
- Initial yields → fits to smog chamber data (reflect aging timescales of few hours)
- Further aging of these species results in both functionalization (decreasing volatility) and fragmentation reactions (increasing volatility)

Revised model SOA Source contributions



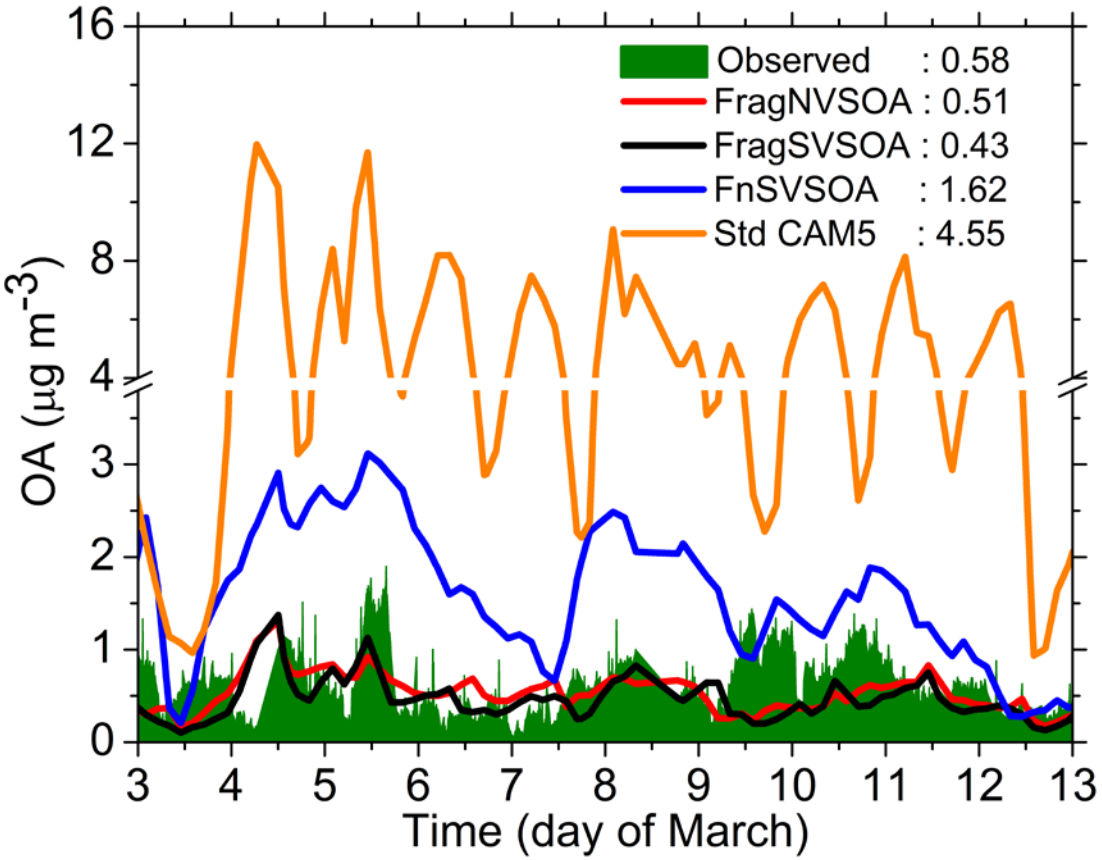
- Biomass burning is the largest source of SOA globally
- SOA from either biomass burning or biogenic sources is much larger than anthropogenic SOA
- In contrast ~85% of SOA in standard CAM5 is biogenic (similar in other studies)

Fractional contribution of SOA volume to total aerosol



- SOA and associated water is major contributor to aerosol volume (and associated AOD) over Eastern Russia, Northern Canada and Central Africa

Evaluation: AMAZE-2008 campaign north of Manaus, Brazil



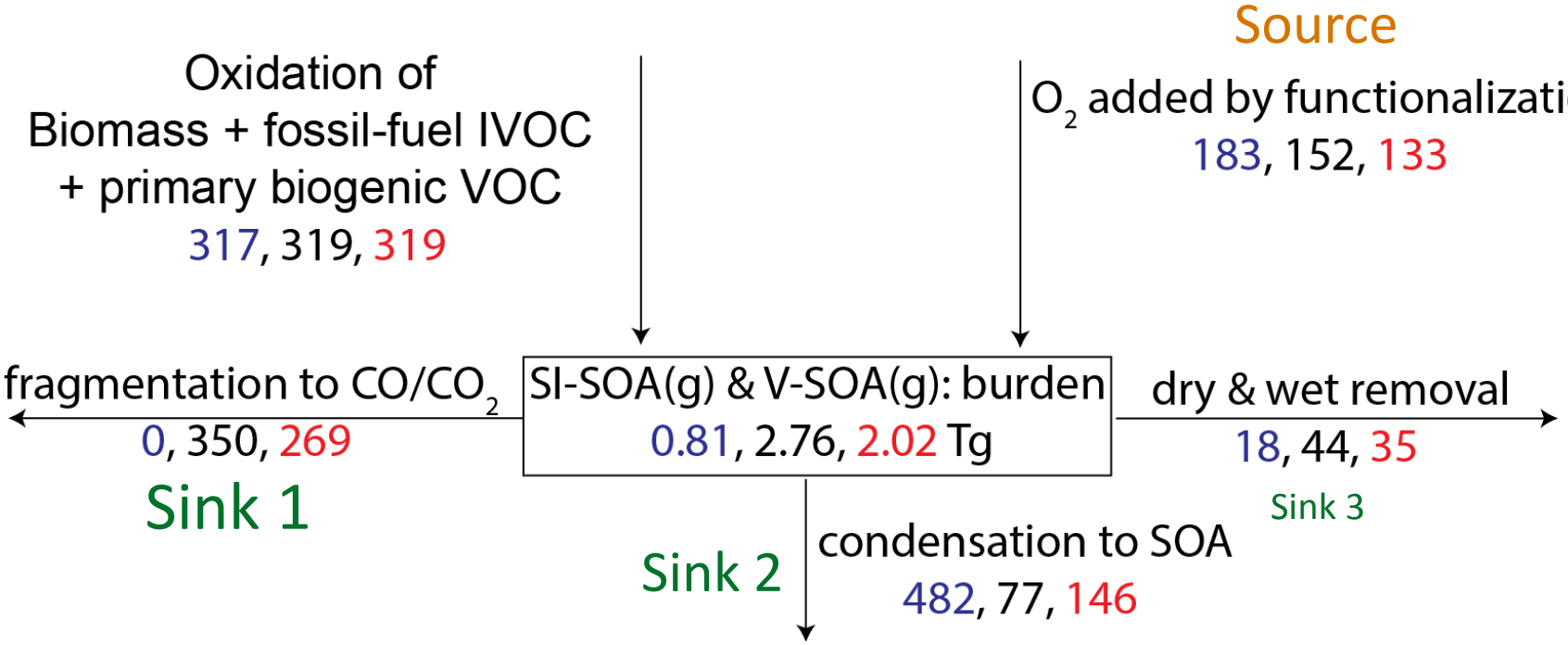
- Median OA from FragNVSOA agrees best with observed OA
- Standard CAM5 overpredicts OA, consistent with its overpredictions at other biogenic dominated sites in the USA
- Higher isoprene emissions, yields and instantaneous SOA formation in standard CAM5

Global budgets for condensable SVOC/IVOC reaction products

No fragmentation (just functionalization)

Fragmentation and semi-volatile SOA

Fragmentation and non-volatile SOA



- Fragmentation is largest sink of SOA precursors→ mass lost to CO/CO_2
- Treatment neglecting fragmentation corresponds to largest condensational rate → SOA formation