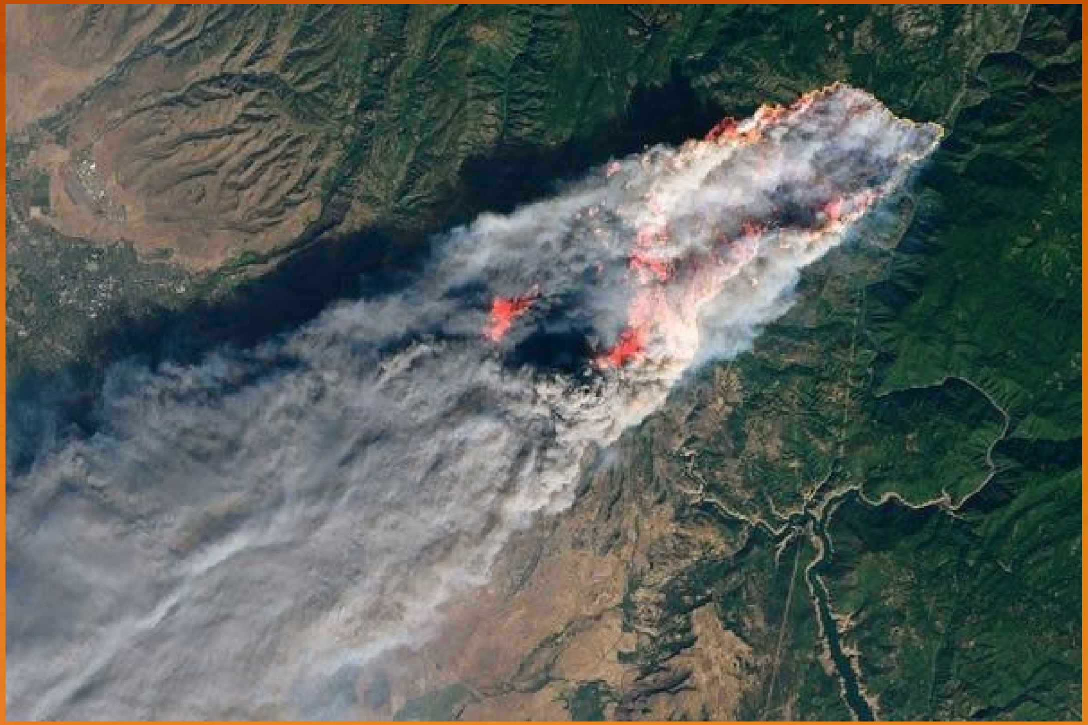
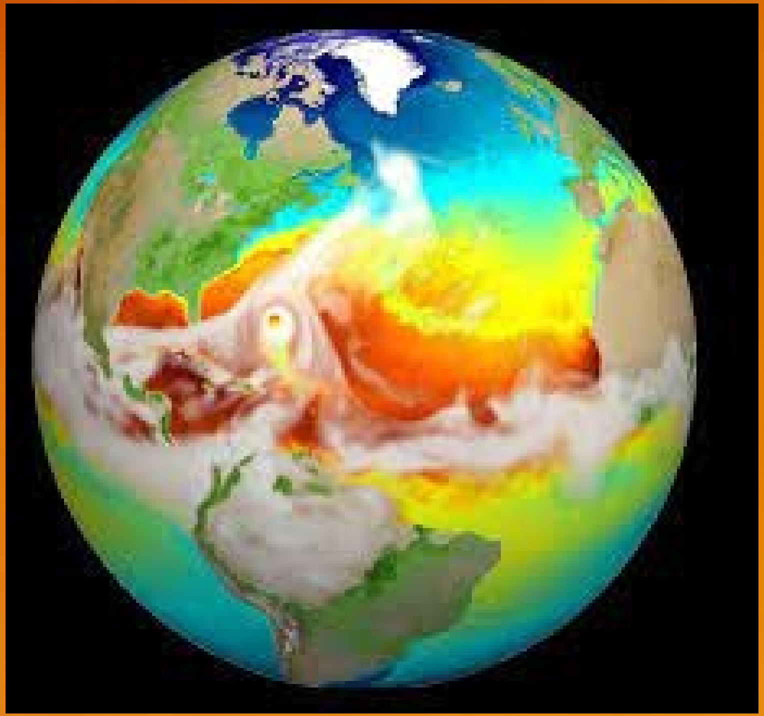
Representation of biomass burning organic aerosols in E3SM and future outlook





E3SM

MANISH SHRIVASTAVA

SIJIA LOU, JIE ZHANG, QUAZI RASOOL, ALLA ZELENYUK, QI ZHANG, JOSE JIMENEZ, PEDRO CAMPUZANO-JOST, MANVENDRA DUBEY, HAILONG WANG, ALEXANDER LASKIN, AND MANY OTHER COLLABORATORS

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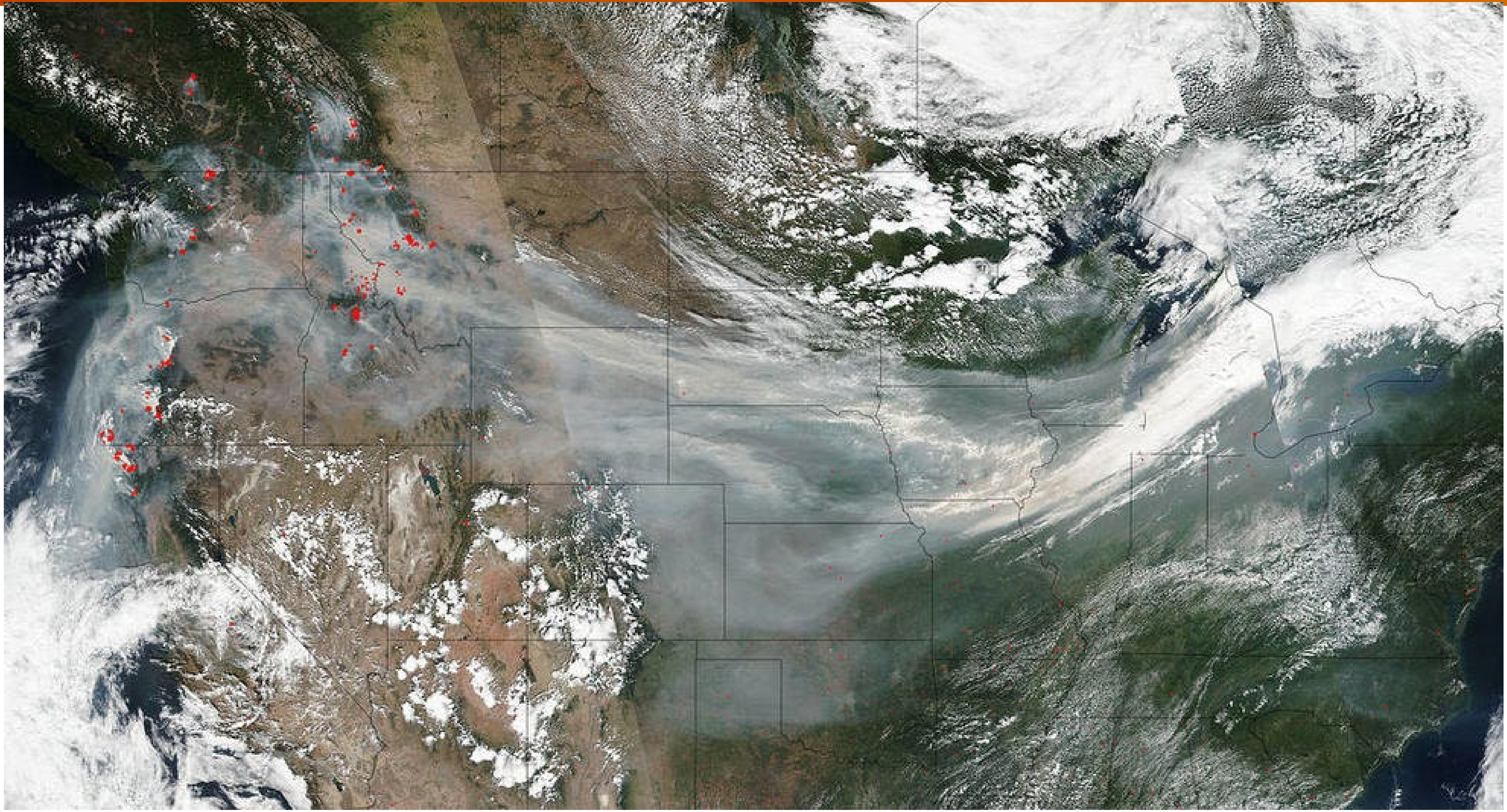
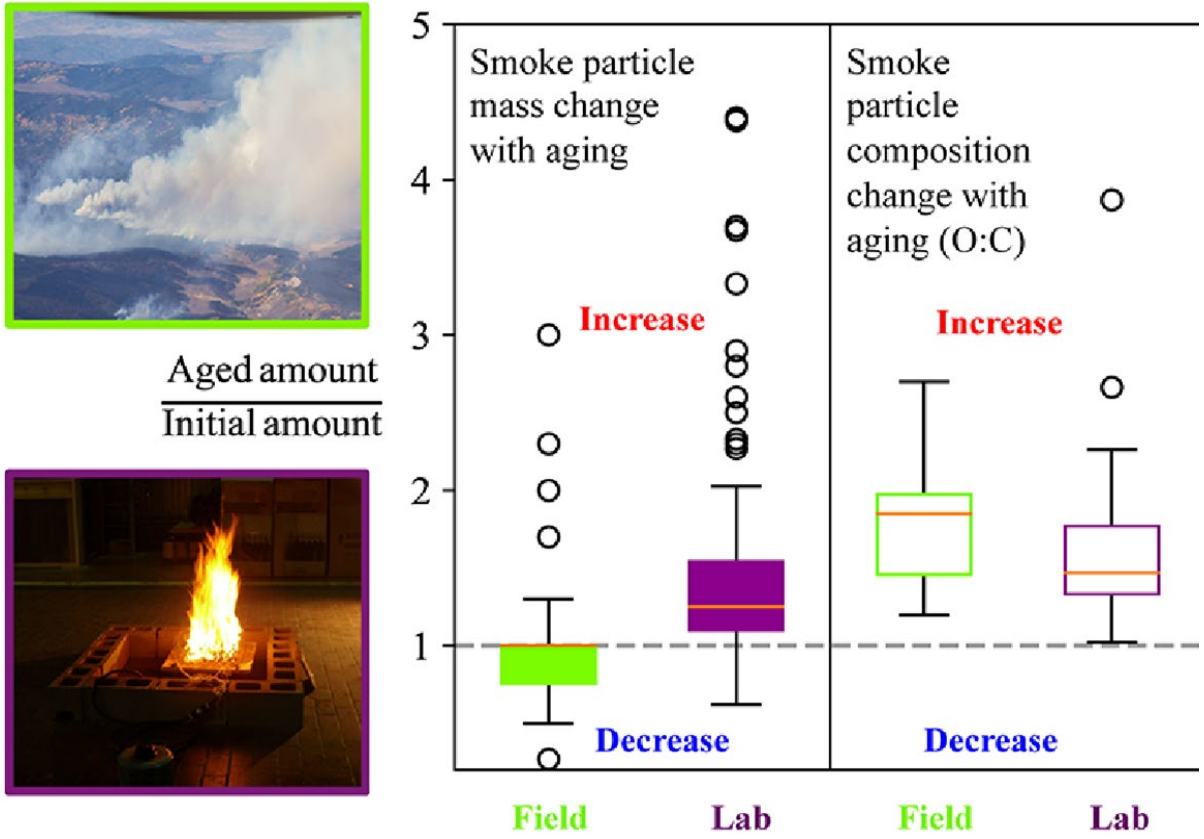
October 23, 2022

Smoke from wildfires transported thousands of miles: Space Satellite Images



Jeff Schmaltz LANCE/EOSDIS MODIS Rapid Response Team, GSFC

Field and laboratory measurements differ in how aging increases biomass burning particle mass



Hodshire et al. 2019, ES&T

- Laboratory measurements show increase in particle mass with aging, inconsistent with field data
- Evidence of increased aging ratio is seen both in the field and laboratory: Evidence of SOA formation
- Possibilities: Dilution, fire size, background and initial OA, wall losses in laboratory measurements

Evolution of biomass burning aerosols from local, regional to global scales

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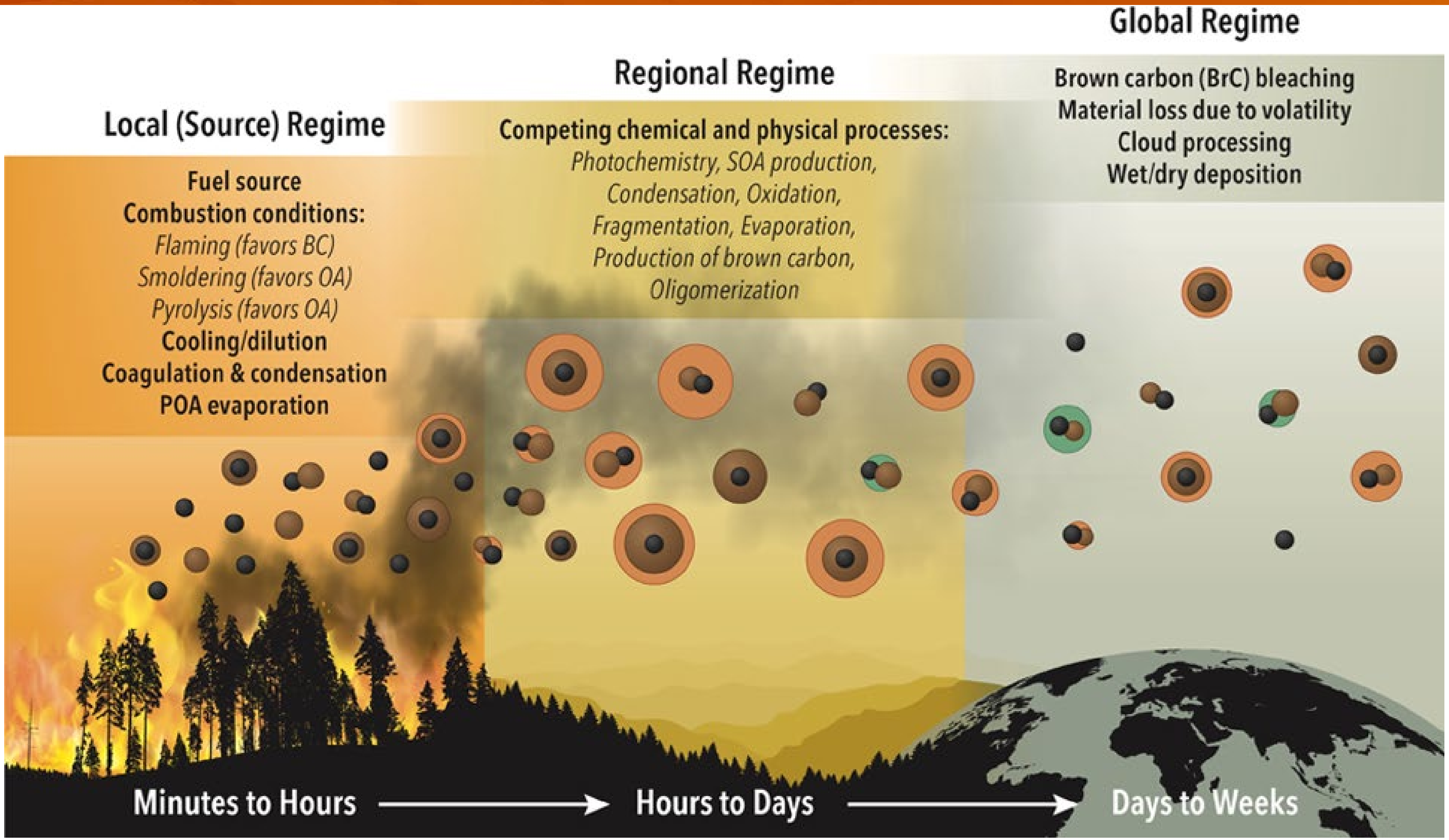

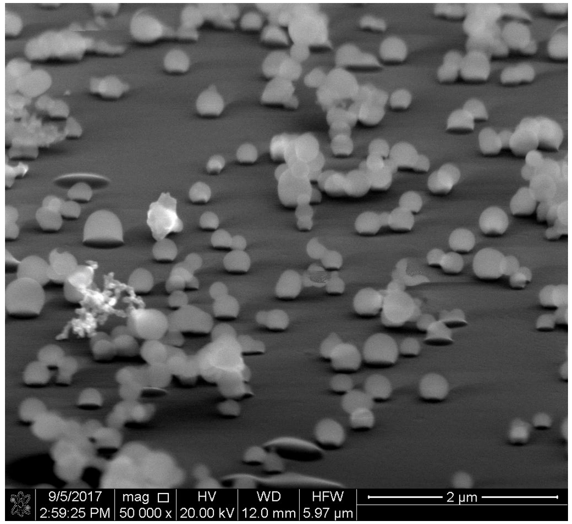

2017 SEM image of ambient tar balls in Richland, Courtesy: C. Zezhen, S.China

Sedlacek et al. 2022

Mass ratio of nonrefractory (organic) coating to core black carbon particles

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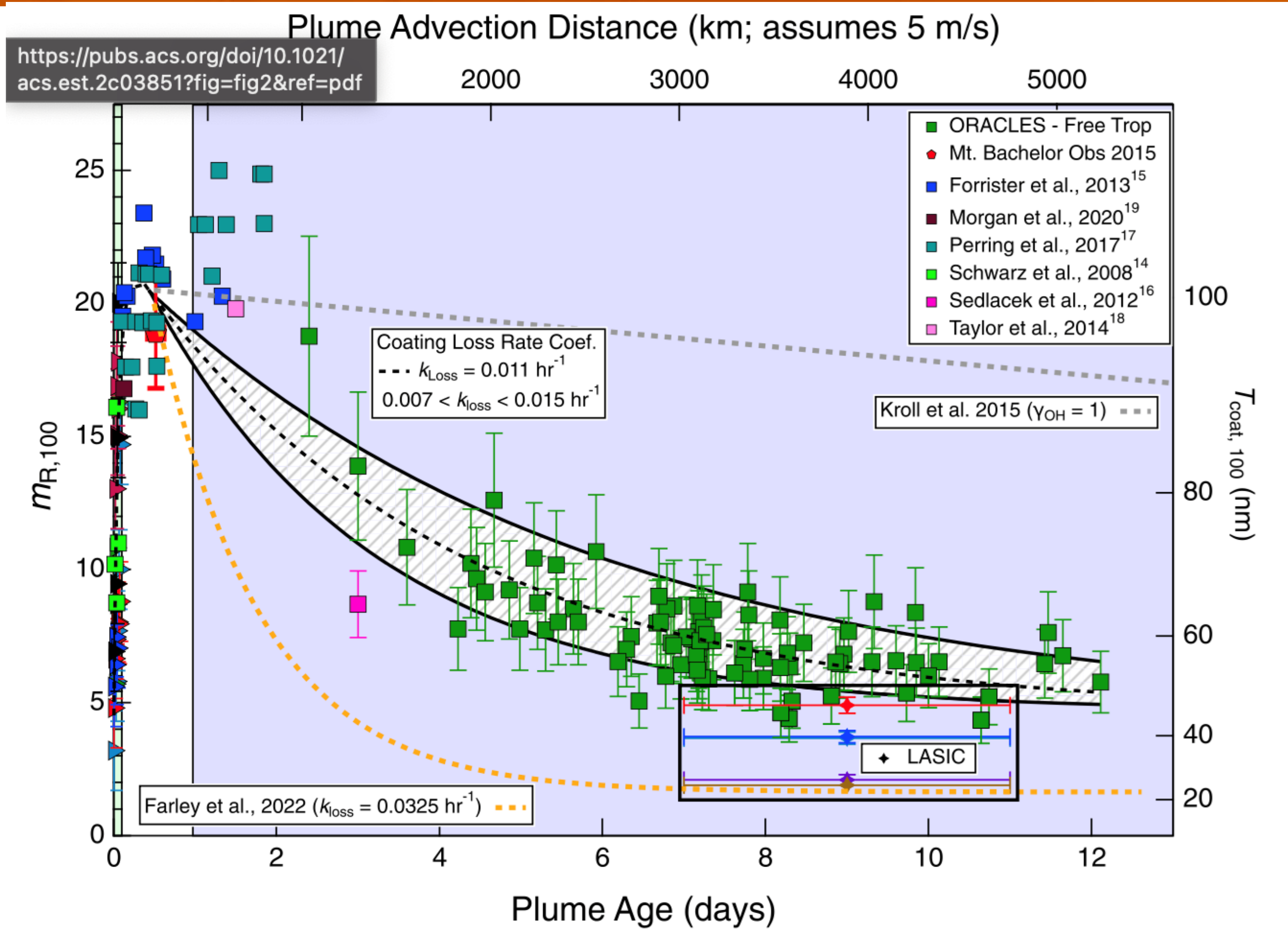

Sedlacek et al. 2022

- Local scales ~minutes-hours: Coating thickness grows rapidly mostly due to organic aerosols
- Regional ~day: Growth rates decrease, coating thickness and OA to CO ratio remains constant
- Global scales in free troposphere: Slow loss by heterogeneous oxidation with OH radicals, photolysis

Parameterizing gas-phase multigenerational oxidation Functionalization and Fragmentation reactions: Local scales

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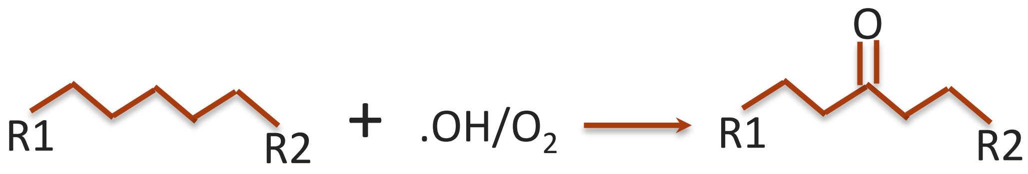
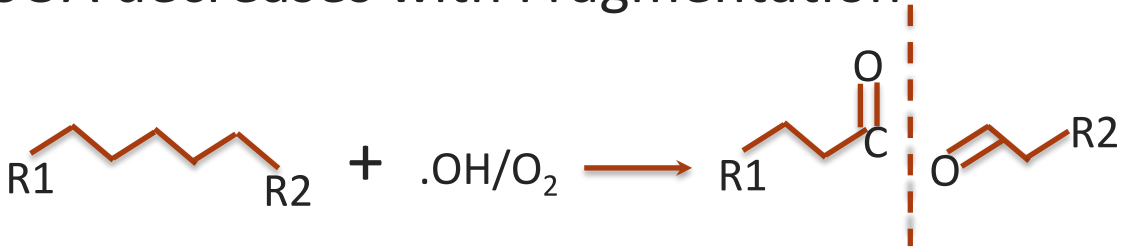
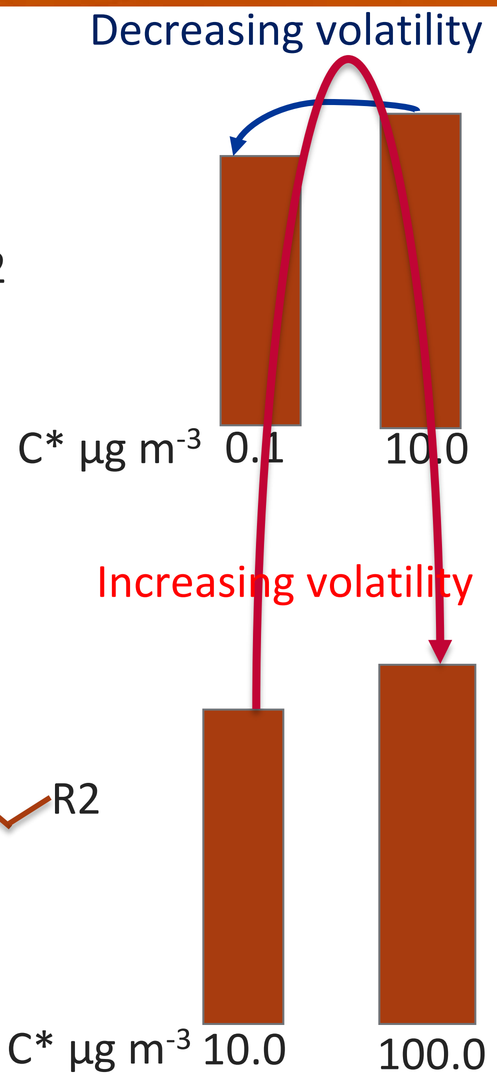
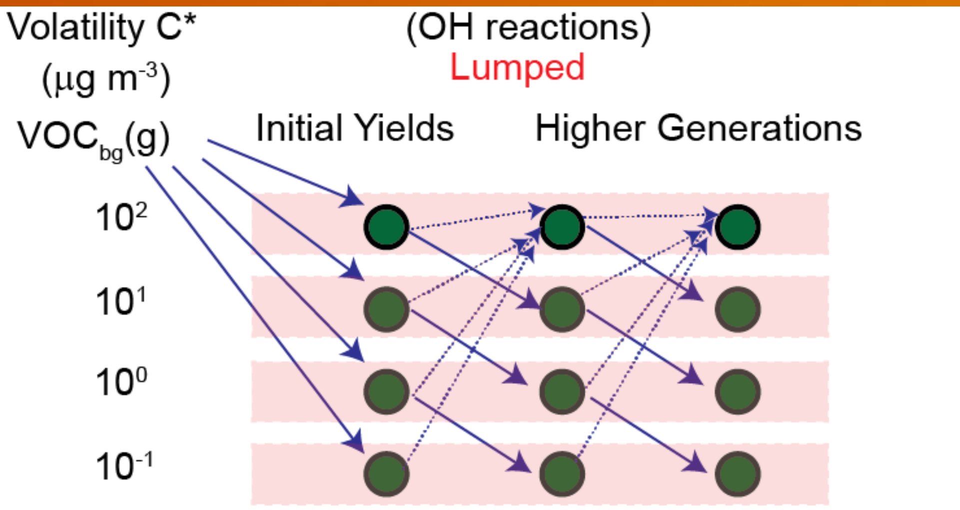
SOA increases with Functionalization



SOA decreases with Fragmentation







Species functionalizing & fragmenting

*10% moved out of the VBS

Another approach: Developing a simple model for BBOA consistent with field measurements

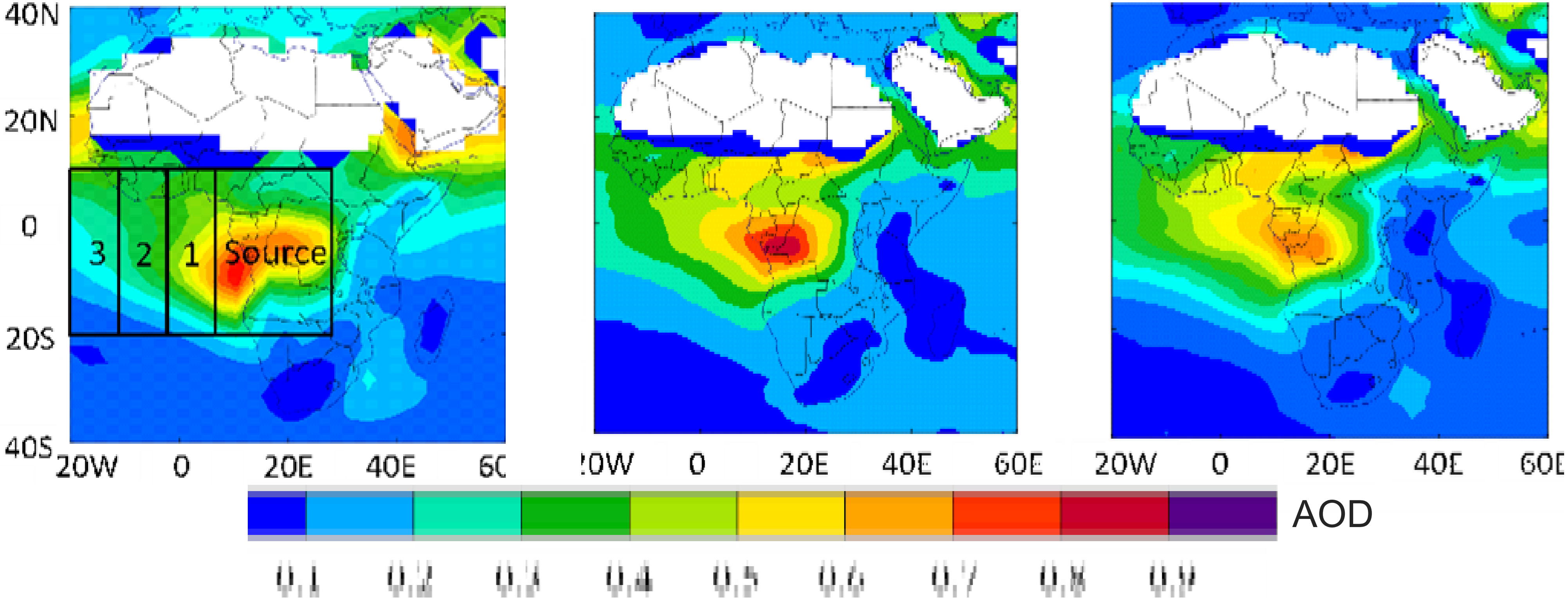
- Organic aerosol/CO ratio is constant but OA constantly oxidizes (O/C ratio increases)
- Reasonable first order assumptions for modeling free tropospheric evolution of BBOA
  - Measured primary biomass burning organic aerosol (BBOA) includes rapid OA formed near plumes
  - Assume this measured BBOA includes the net OA formed by evaporation and re-condensation of semi-volatile and intermediate volatility organics
  - Increase in oxidation and hygroscopicity: Convert BBOA to SOA at e-folding timescale of 1 day
- SOA formed by oxidation of more volatile organics like phenols through gas-phase and aqueous chemistry: Needs to be included separately

Satellite AOD over African biomass burning outflow: Complex and simple model predictions are similar in outflow

Satellite observed AOD

Complex E3SM Model: Functionalize & Fragment

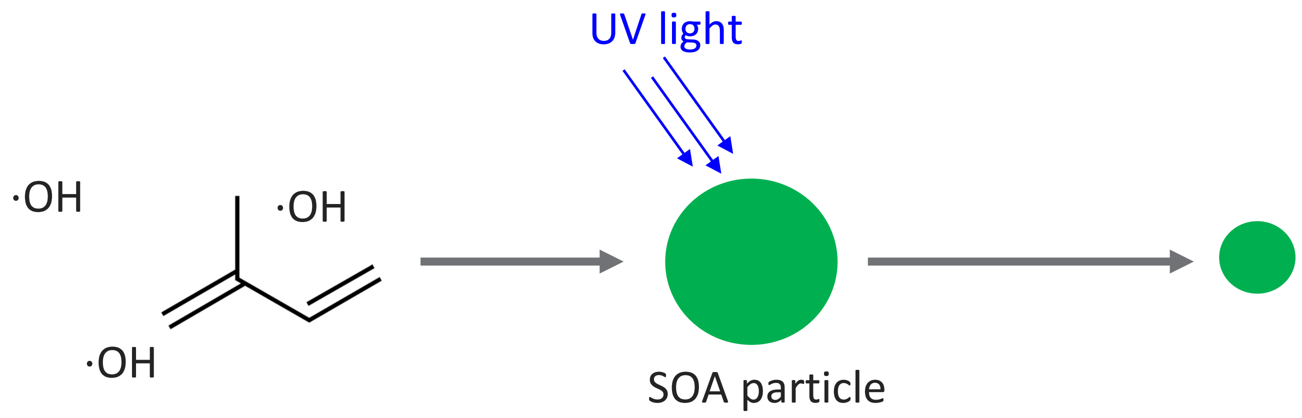
Simple E3SM Model: BBOA assumed non-volatile & converted to SOA ~1 day

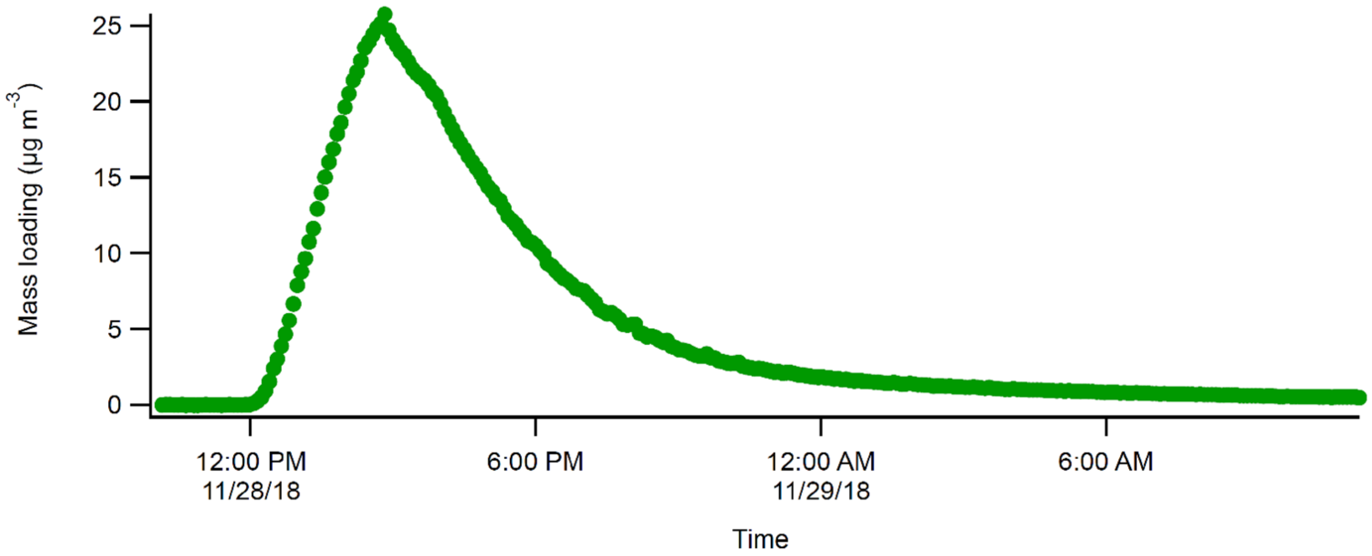


Lou, Shrivastava et al. 2020

- Simple BBOA aging in E3SM predicts similar AOD as complex multigenerational oxidation
- The simple BBOA aging accounts for constant OA/CO ration and increase in hygroscopicity during oxidation of BBOA

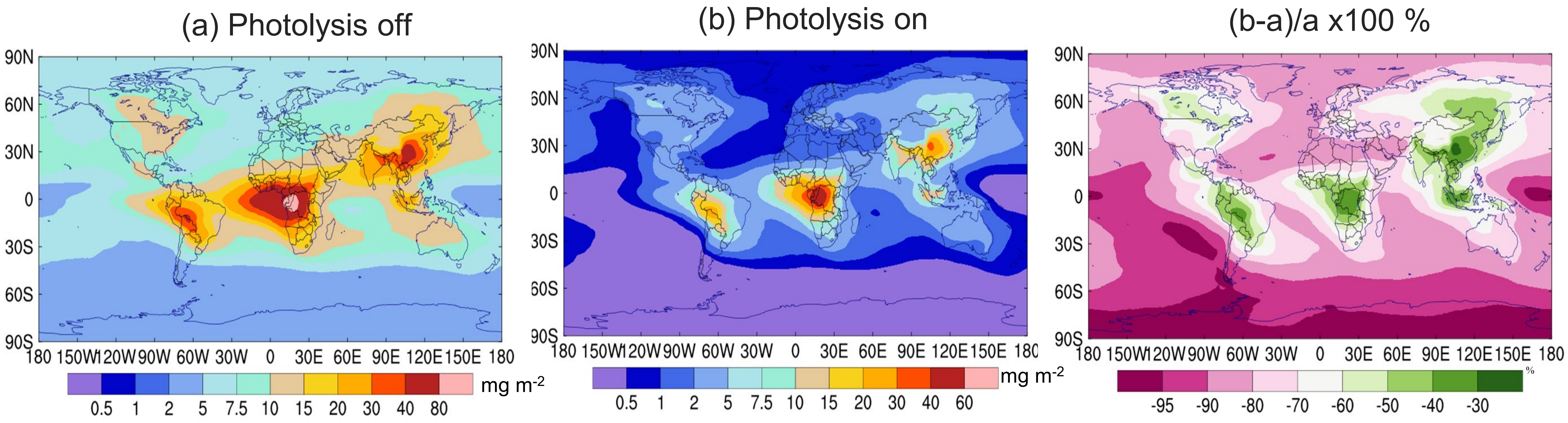
Photolysis is an important sink of SOA found by laboratory measurements





- Isoprene SOA decreases by upto 80% within 10-12 hours upon exposure to UV light in PNNL smog chamber measurements (*Zawadowicz et al. 2020*)

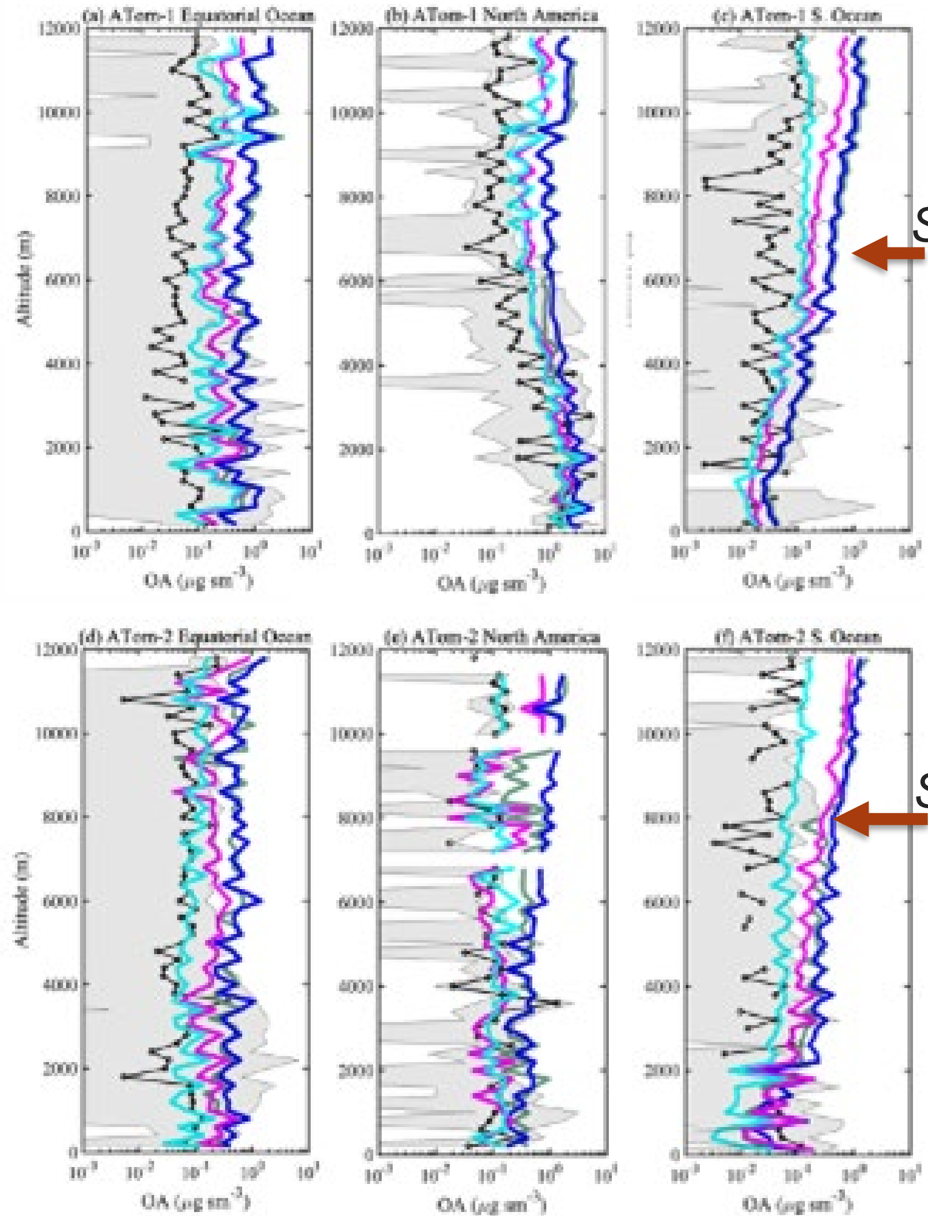
Particle-phase photolysis is an important sink of SOA



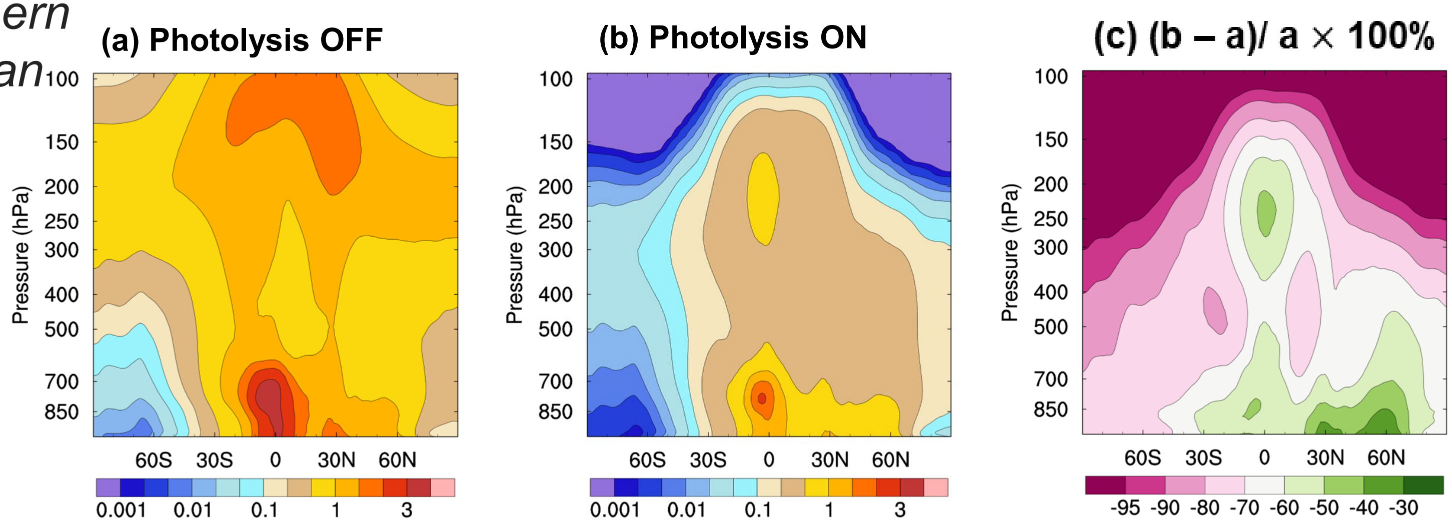
Lou, Shrivastava et al. 2020, JAMES

- Particle-phase photolysis decreases SOA by 30-50% over source regions
- Stronger (80-90%) decreases are seen over remote oceanic regions & high altitudes

Photolysis is an important sink of SOA needed to explain aircraft measurements mainly above 5km altitude



Observed
Photolysis ON
Photolysis OFF



Lou, Shrivastava et al. 2020, JAMES

- Including photolysis improves simulated SOA vertical profiles significantly compared to Atom2016 aircraft measurements
- At high altitudes (above 5 km), wet removal is not efficient
- Photolysis is needed to explain observations at high altitudes

Photolysis decreases CCN more strongly at high altitudes

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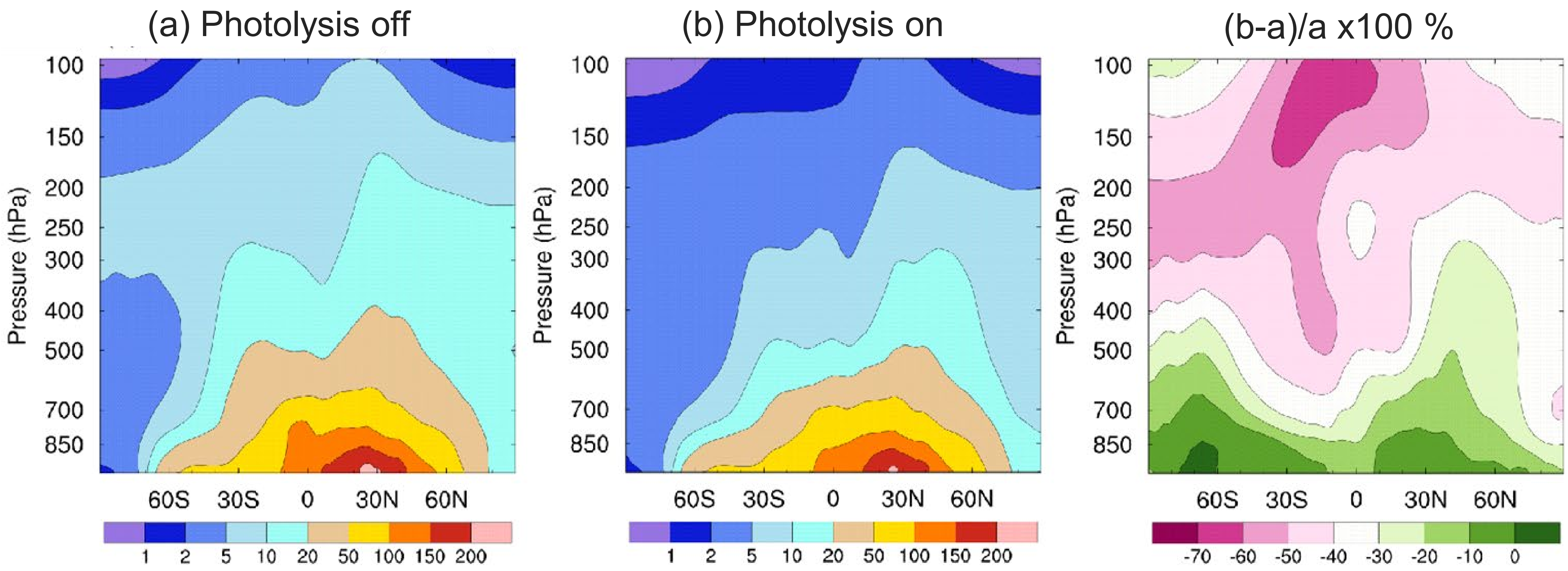


Lou, Shrivastava et al. 2020, JAMES

- Photolysis decreases CCN concentrations by 10-30% near surface and 50-70% at high altitudes
- However, photolysis of BBOA might not be as efficient at global timescales (*Sedlacek et al. 2022*)

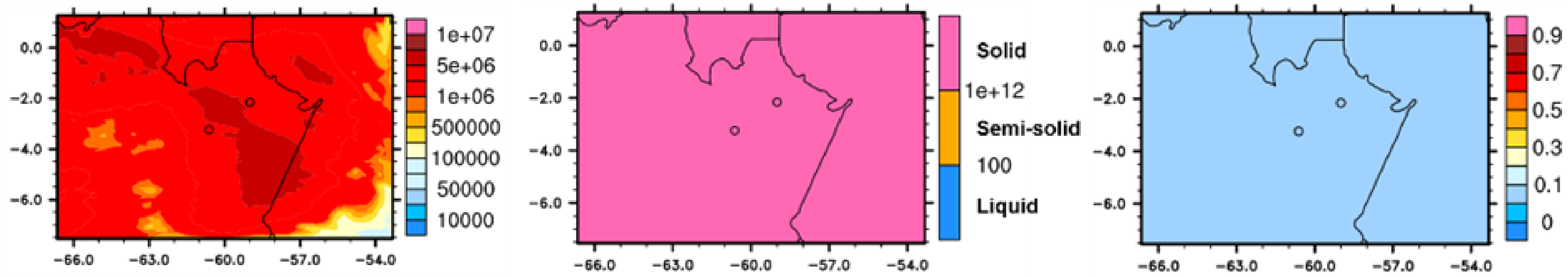
Future work

- Processes not yet included in E3SM
  - Heterogeneous aging of BBOA by OH radicals
  - Viscosity and phase state of BBOA
  - Gas-phase, aqueous-aerosol phase and cloud chemistry of volatile organic gases emitted by wildfire and their SOA formation source
  - Change in optical properties i.e. brown carbon from primary and secondary BBOA and its bleaching

Heterogeneous oxidation by OH as a key chemical sink in the upper troposphere: Varies with viscosity of OA

[OH] (molecules/cm³) | OA viscosity (Pa.s) | OH uptake coefficient

Upper Troposphere (UT)

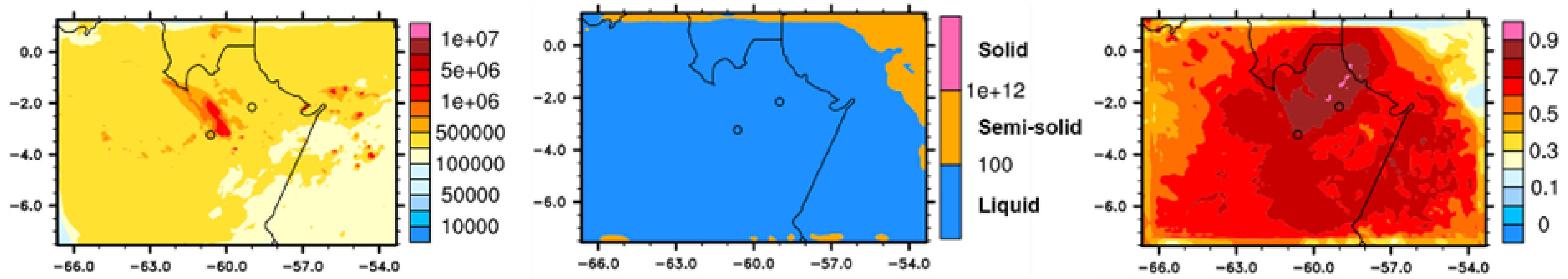


[OH] ~ order of magnitude higher in UT. Pollution plumes at surface also have high [OH]

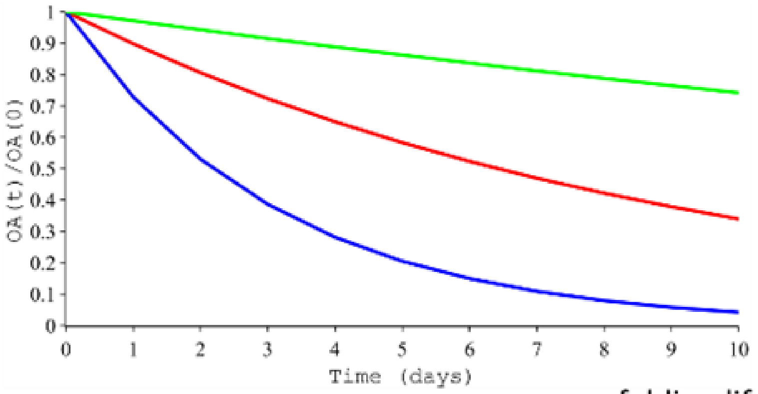
OA viscosity predominantly solid at UT compared to predominant liquid OA at Surface

OH uptake ~ 7xtimes lower at UT, directly influenced by OA viscosity

Surface



Away from sources, in polluted condition OA lifetime would be in order of 1-2 weeks (Box model)



	e-folding lifetime
Upper Troposphere	10 days
Surface (Polluted)	3-4 days
Surface (Background Amazon)	~1 month

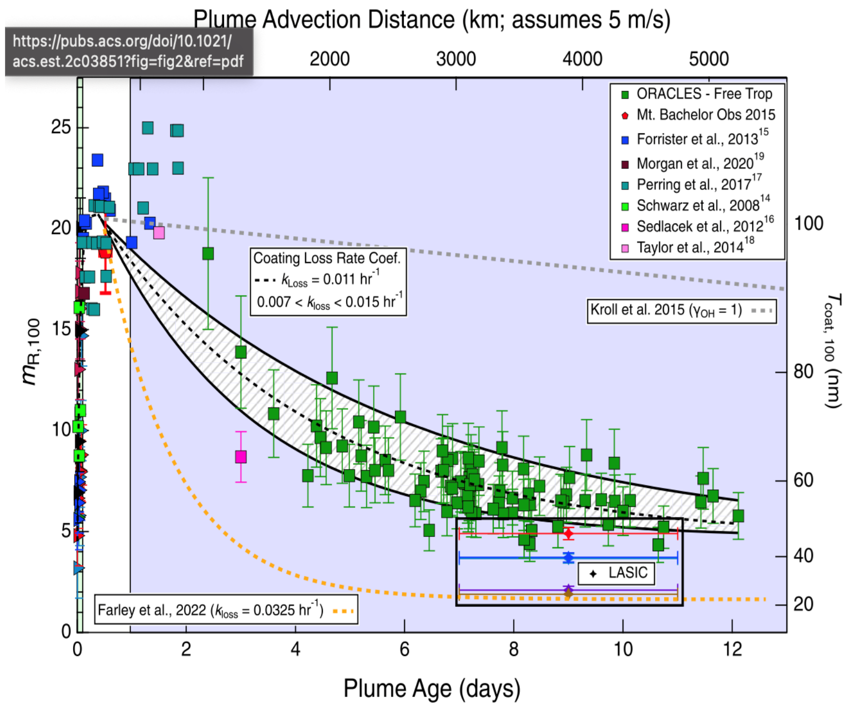
Near sources, with fresh OA (WRF-Chem) OA decay as predicted by Box model is impeded

Rasool, Shrivastava et al. 2022, In preparation

- Heterogeneous loss of organic aerosols by OH oxidation depends on viscosity and OH concentrations
- Lifetime is ~10 days in the upper troposphere, and 3-4 days near surface in polluted regions

As biomass burning aerosols are transported, their physical, chemical, optical properties change continuously

- As BBOA evaporates and/or chemically degrades within first few days:
  - It becomes less volatile as more volatile components leave the particle
  - It become more brown as remaining low volatility components are likely richer in brown chromophores
  - It become more viscous
- At longer timescales of several days to week:
  - Slow loss of BBOA due to heterogeneous oxidation



A new volatility basis set statistical oxidation model (VBS-SOM) captures dynamics of laboratory biomass burning SOA

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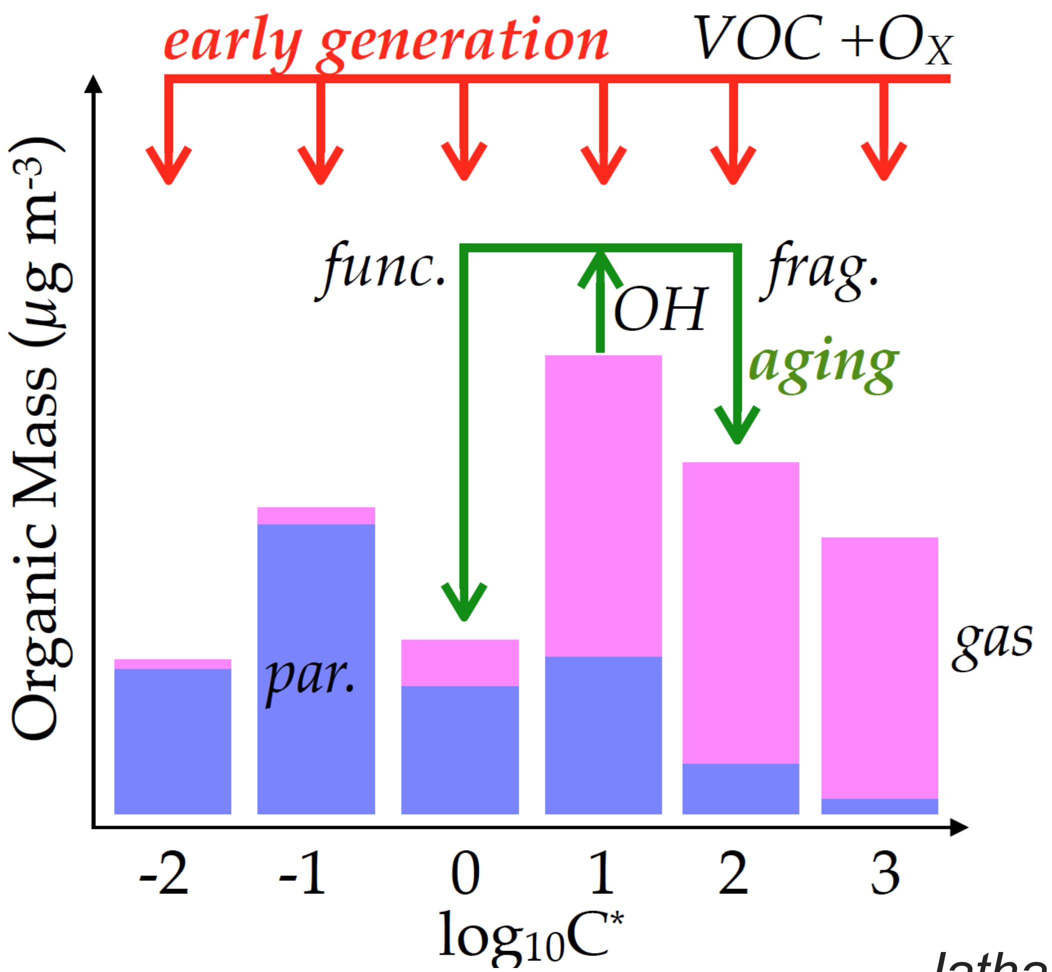

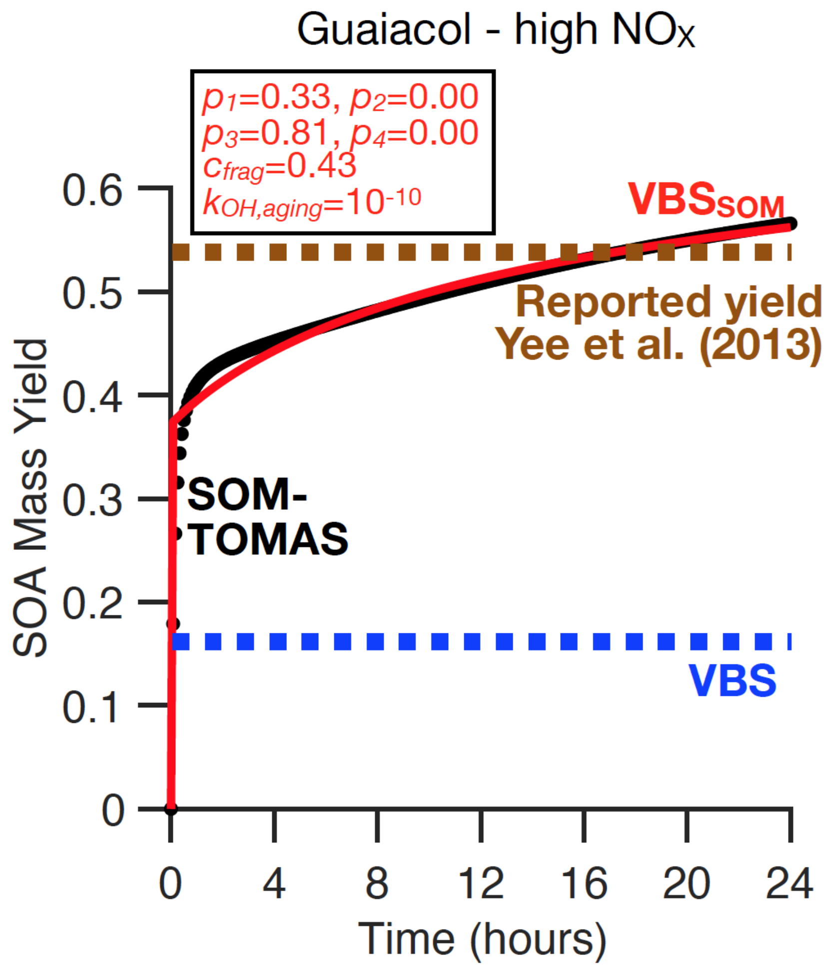

Jathar et al. 2022

- Could be used to predict SOA formation due to gas-phase oxidation of more volatile organics like phenols and their substituted derivatives

Simulated composition of ultrafine particles in wildfire plumes is different from accumulation mode particles

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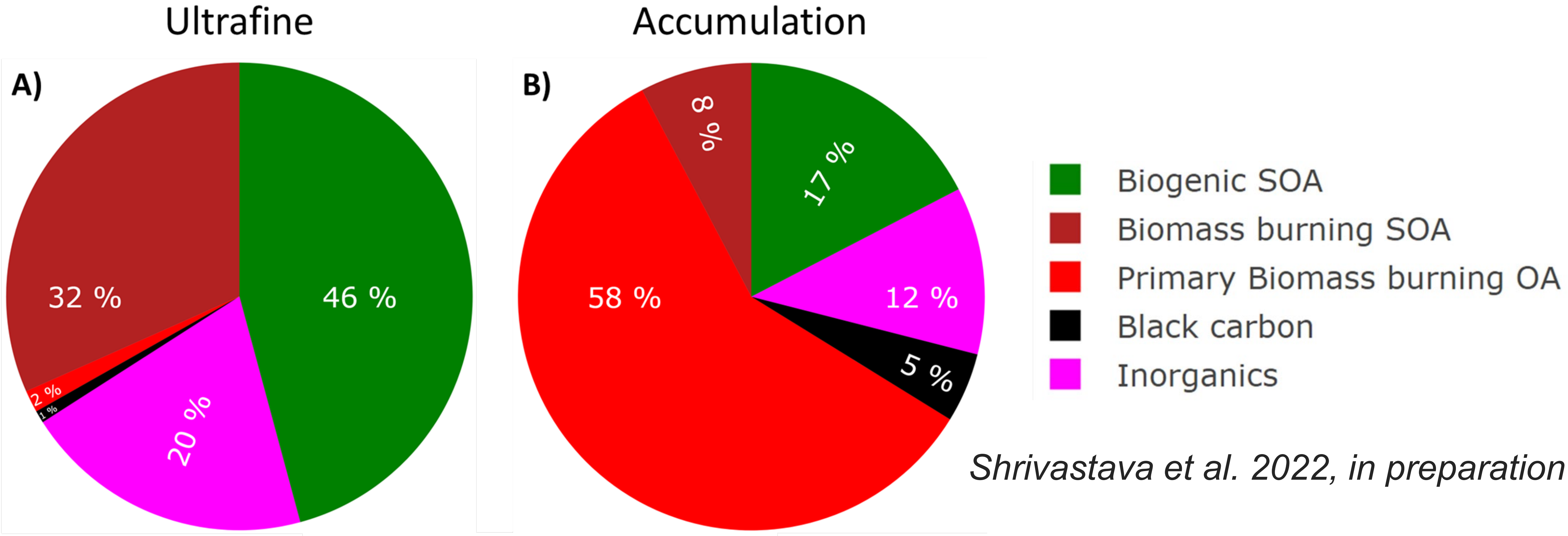
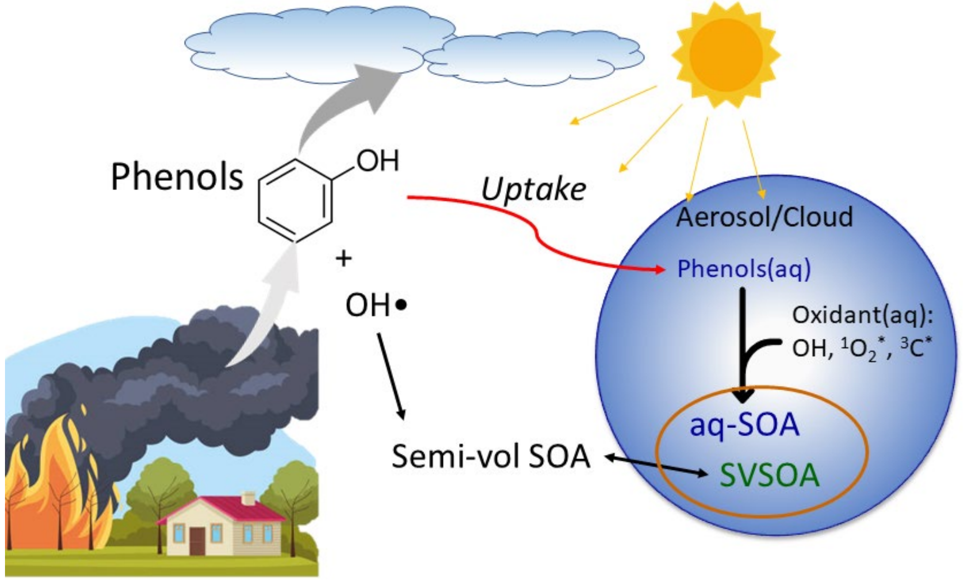


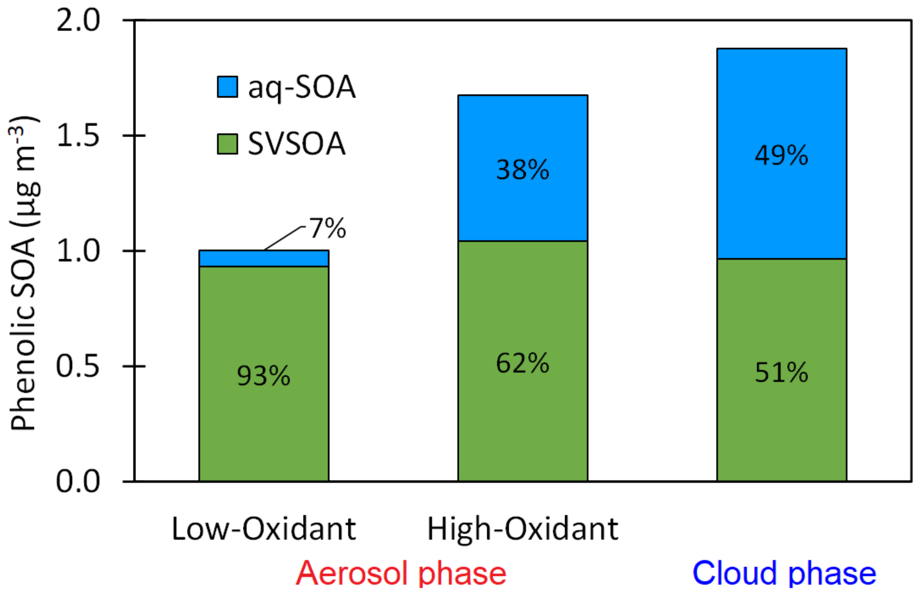
Shrivastava et al. 2022, in preparation

- WRF-Chem predicts ultrafine particles are mainly SOA, accumulation mode is mostly primary OA
- Ultrafine particles (3-25 nm) composition measurements needed to assess early particle growth
- But these measurements are difficult with current approaches

Aqueous and cloud chemistry likely as important as gas-phase chemistry during long-range transport of biomass burning

Preliminary box model runs based on lab measurements of biomass burning SOA in aqueous phase





Aqueous and cloud chemistry is likely as important as gas-phase chemistry for biomass burning SOA formation

Based on measurements from Smith et al. 2014, 2015; Li et al. 2021

- Current models do not include aqueous biomass SOA processes
- Recent field and laboratory measurements show aqueous SOA from biomass burning increases CCN and light absorption
- Single particle measurements at EMSL:
  - Aqueous biomass SOA consists of carboxylic acids and higher molecular weight oligomers
  - Aqueous SOA composition is different from pure gas-phase oxidation products

Future outlook and needs

- Regional and global models could represent the first few hours of rapid BBOA formation assuming BBOA converts to SOA at aging timescale of ~1 day
- Need to include gas-phase oxidation of volatile organic gases emitted by wildfires
- Investigate how aqueous and cloud chemistry forms biomass burning SOA affecting CCN and optical properties at global timescales
- Represent viscosity-dependent OH heterogeneous loss of BBOA in models
- Investigate how chemical, physical and optical properties of BBOA change during aging and their interactions with clouds
- Measurements of the composition of ultrafine particles formed in wildfires needed to understand the early stages of particle growth