SOA formation due to multiphase chemistry over SouthEast USA: Implications from integrated model measurement studies with WRF-Chem in other regions like SGP site and the Amazon

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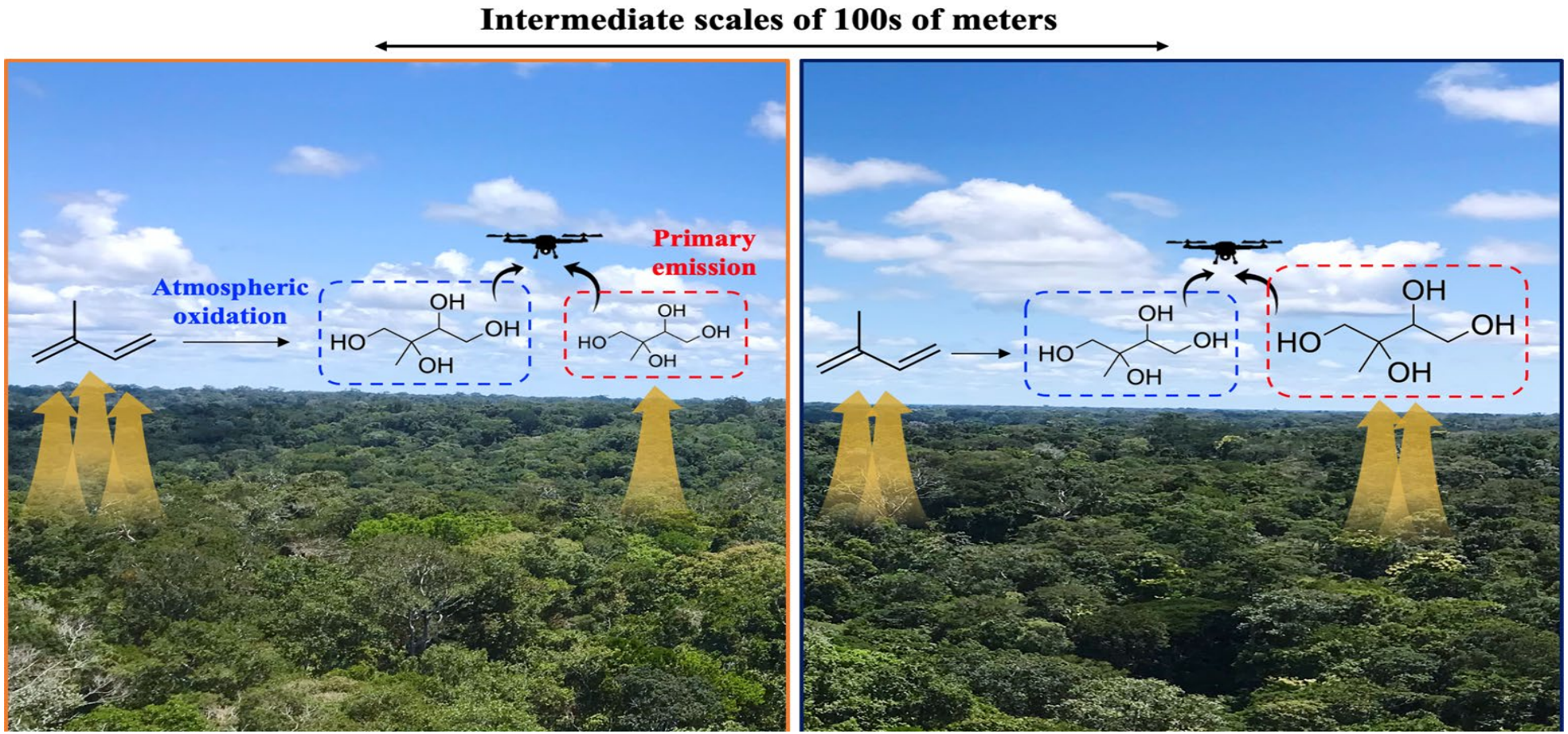
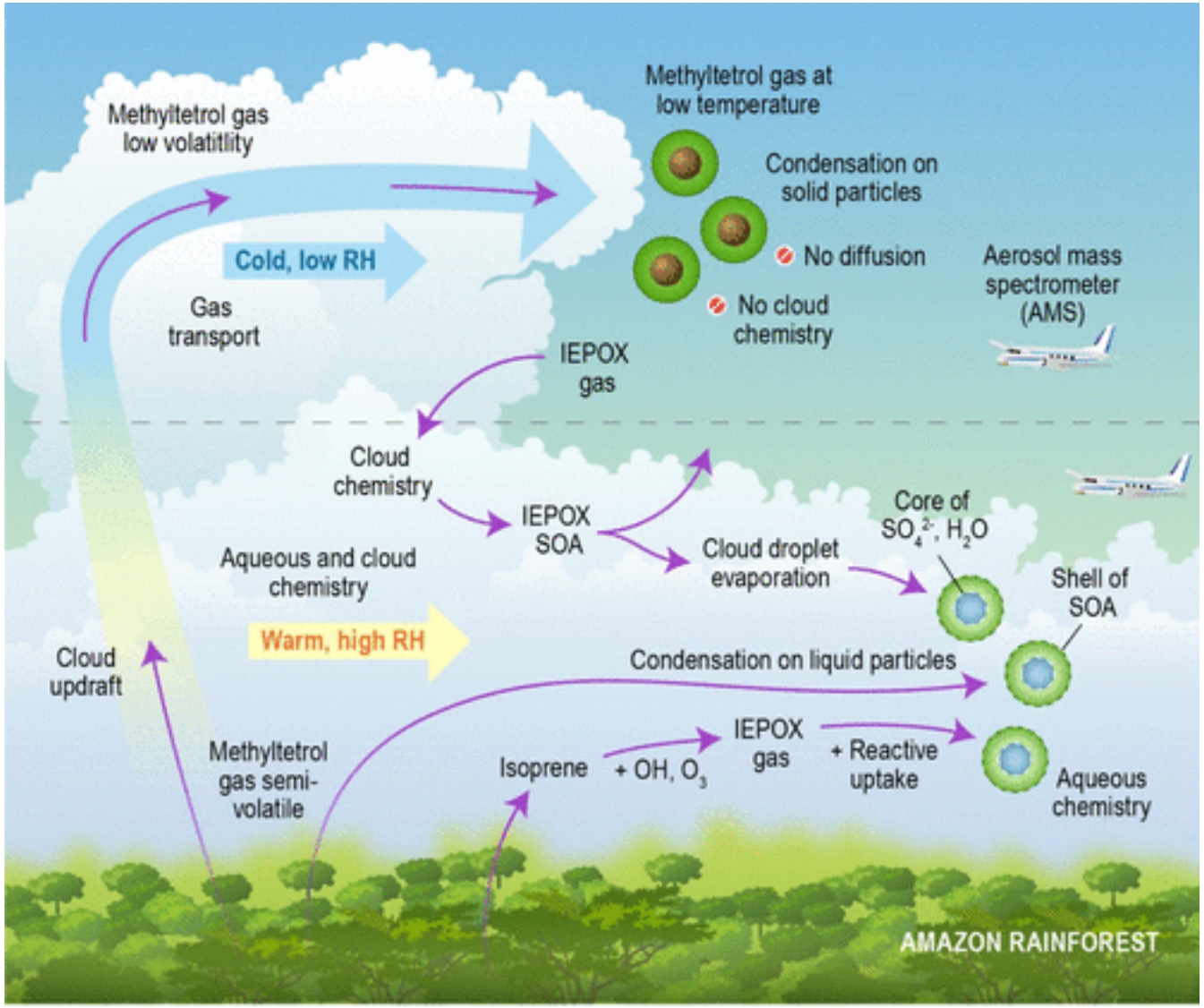
Connecting dots with new UAV measurements: Emissions of 2-methyltetrol semi-volatile gases from the forest



Ye et al. 2021

- 2 methyltetrol gases measured by UAV varied by upto 480% over 100's of meters
- Heterogeneity of isoprene emissions & their oxidation does not explain 2-MT differences
- 2-MT formation needs a heterogeneous medium
- Leaves/soil ubiquitous medium for reactions of deposited IEPOX gases forming 2-MT

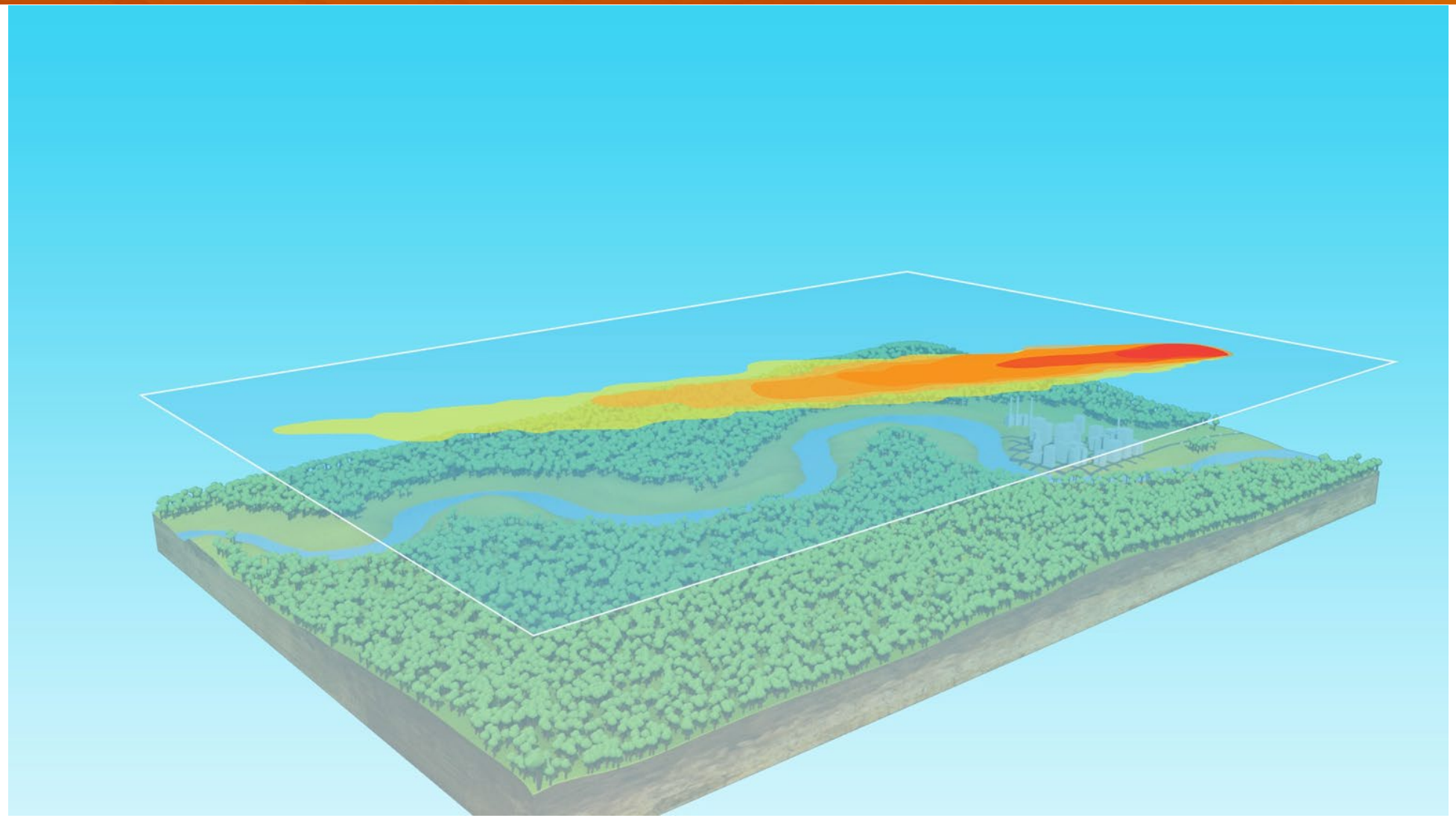
Integrated UAV and aircraft measurements with WRF-Chem: Identified a new process that explains IEPOX-SOA



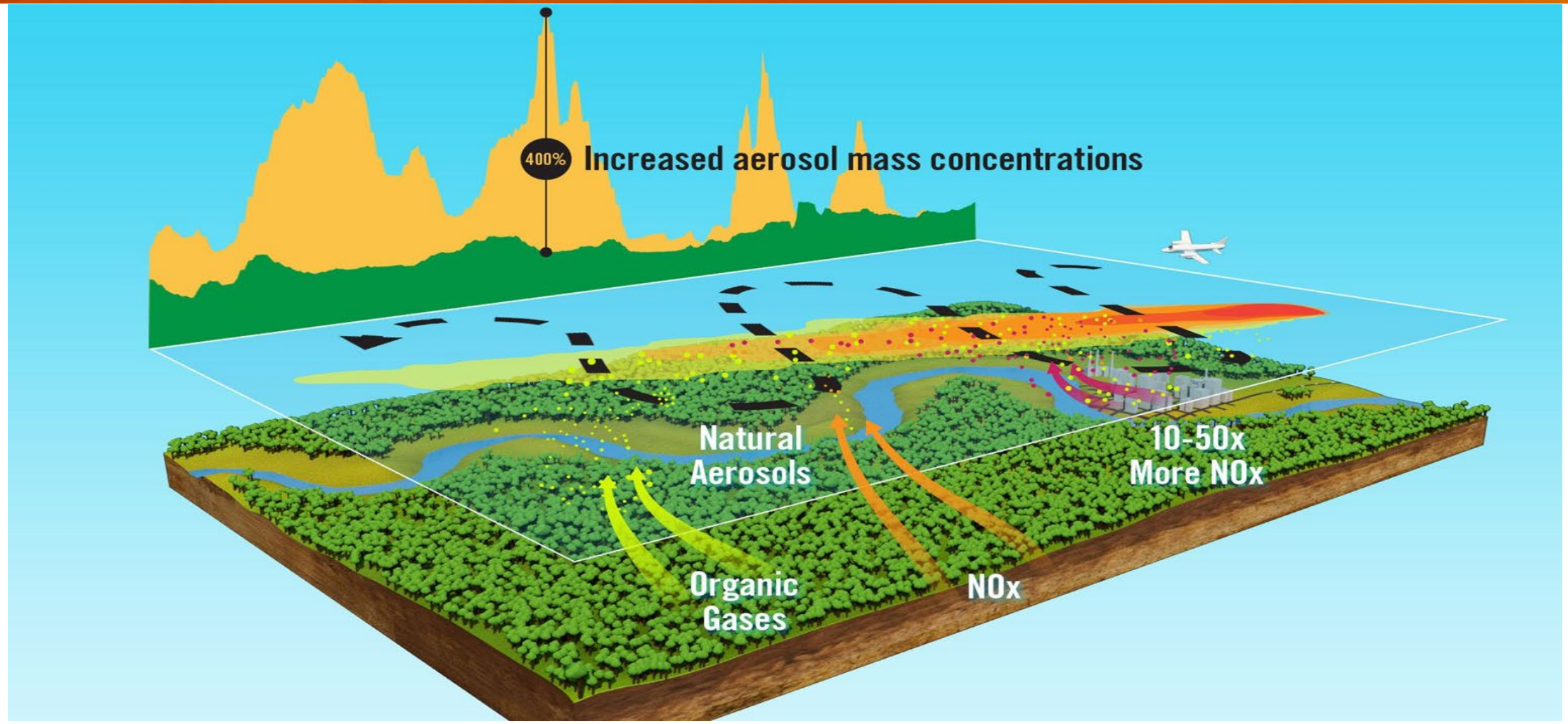
Shrivastava et al. 2022, ACS Earth & Space Chem

- At high altitudes lack of aerosol and cloud liquid water prevents IEPOX-SOA formation
- Previous models incorrectly assumed aerosols are liquid in UT similar to surface
- Treating variations in aerosol phase with T and RH, we identified large model-measurement gaps in UT
- Identified a new process related to 2-MT emissions, which explains UT measurements
- Process-discovery is critical to correctly predict aerosol radiative forcing from preindustrial to present day

A snapshot during GoAmazon2014/5: DOE G-1 aircraft transecting pristine Amazonian forest and the urban plume

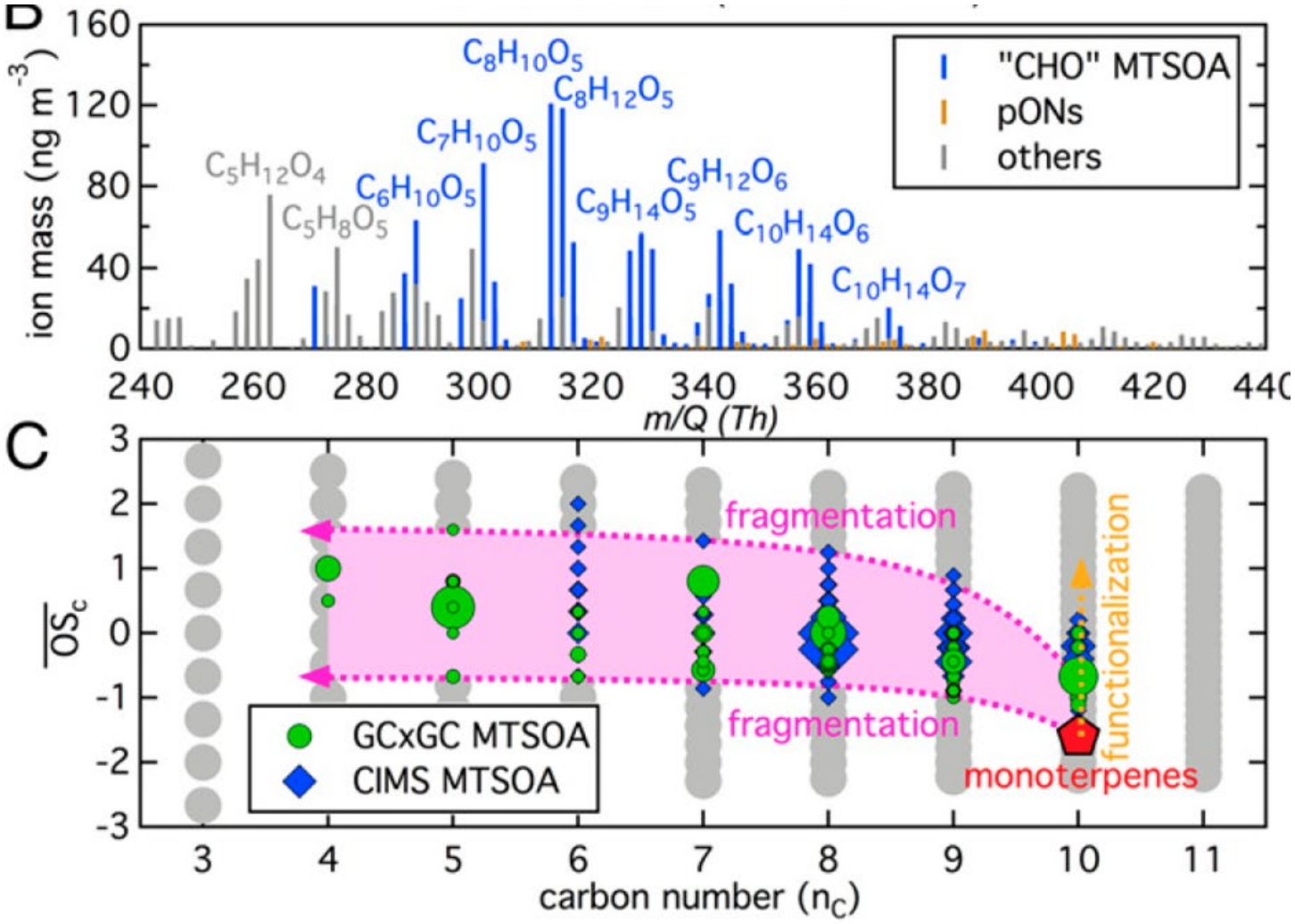


GoAmazon measurements March 13, 2014: G1 aircraft travels between pristine and polluted conditions



- Anthropogenic NO_x causes increase of oxidants that greatly increase biogenic SOA formation in the Manaus city plume compared to the background Amazon

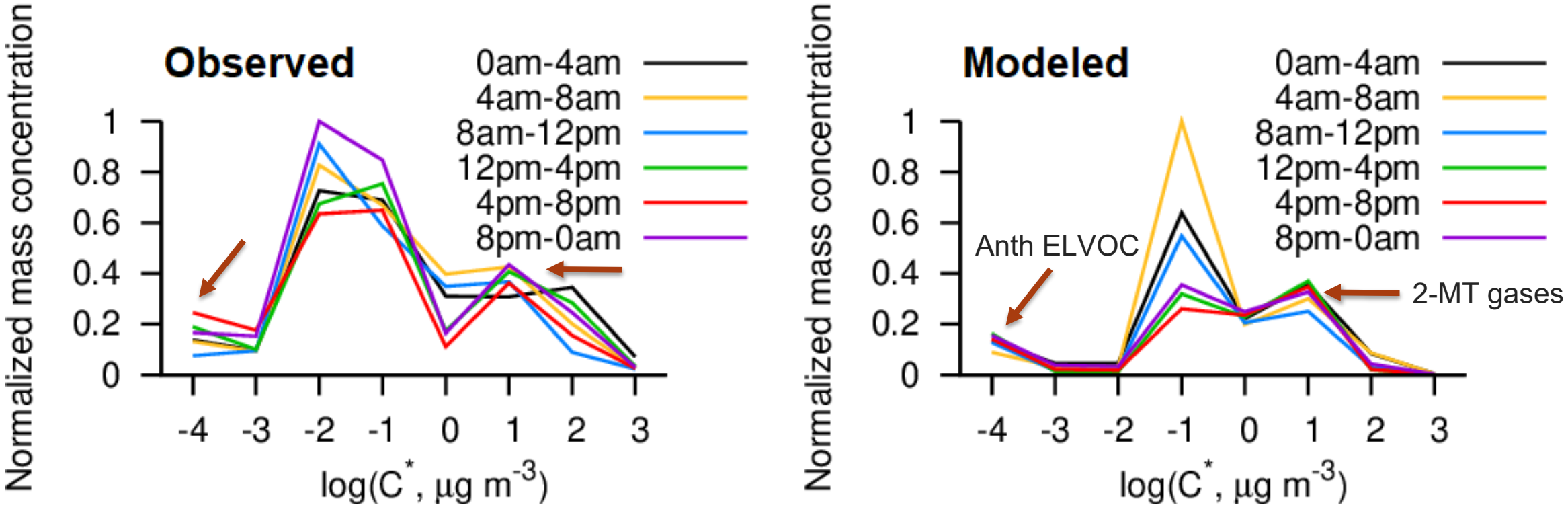
Southeast USA field measurements show monoterpene fragmentation products increase with aging in presence of NOx



Zhang et al. 2018, PNAS

Despite multigenerational chemistry GCxGC shows volatility distributions of organics do not vary much during the day

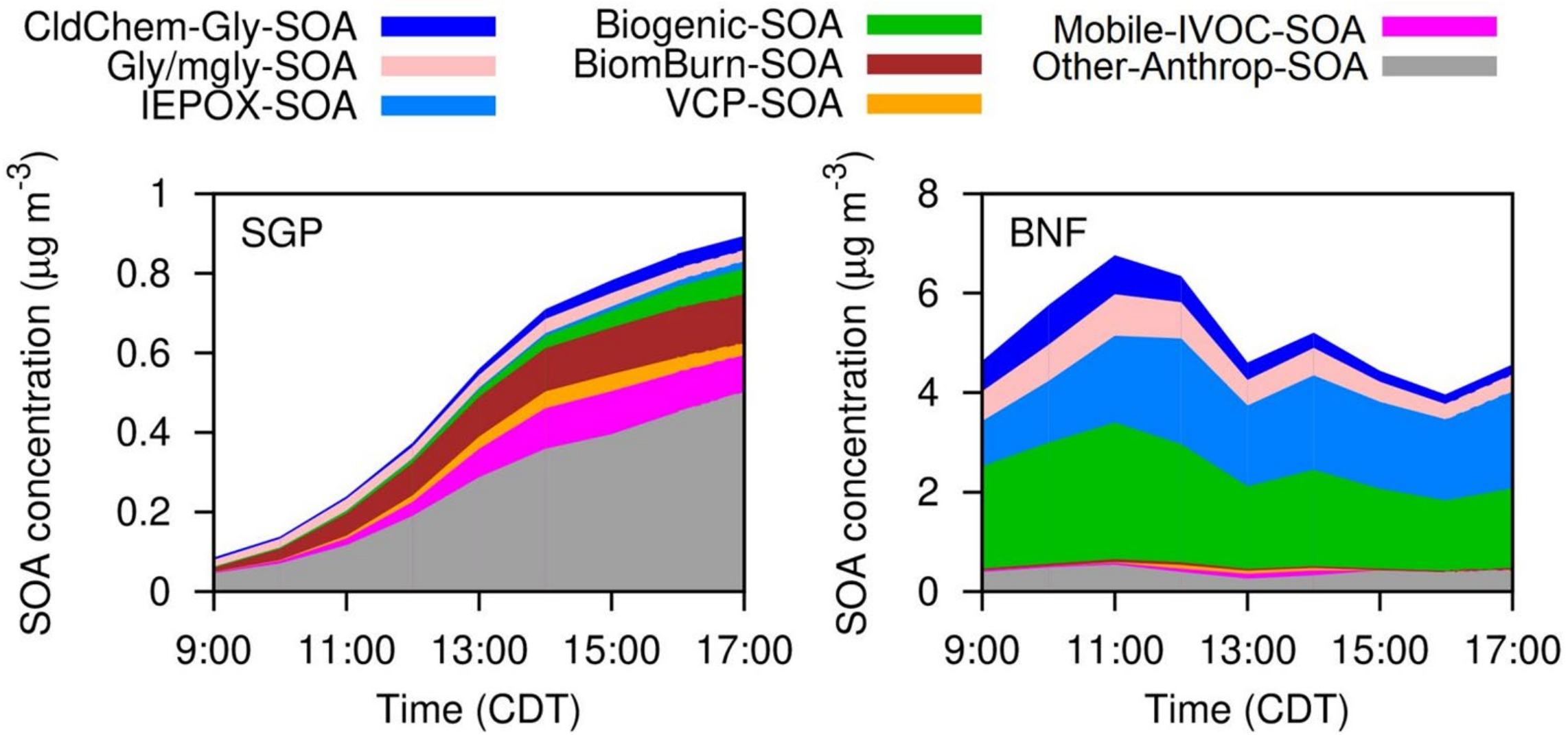
WRF-Chem predicted and GCxGC measured SOA particle volatility distributions at SE USA site



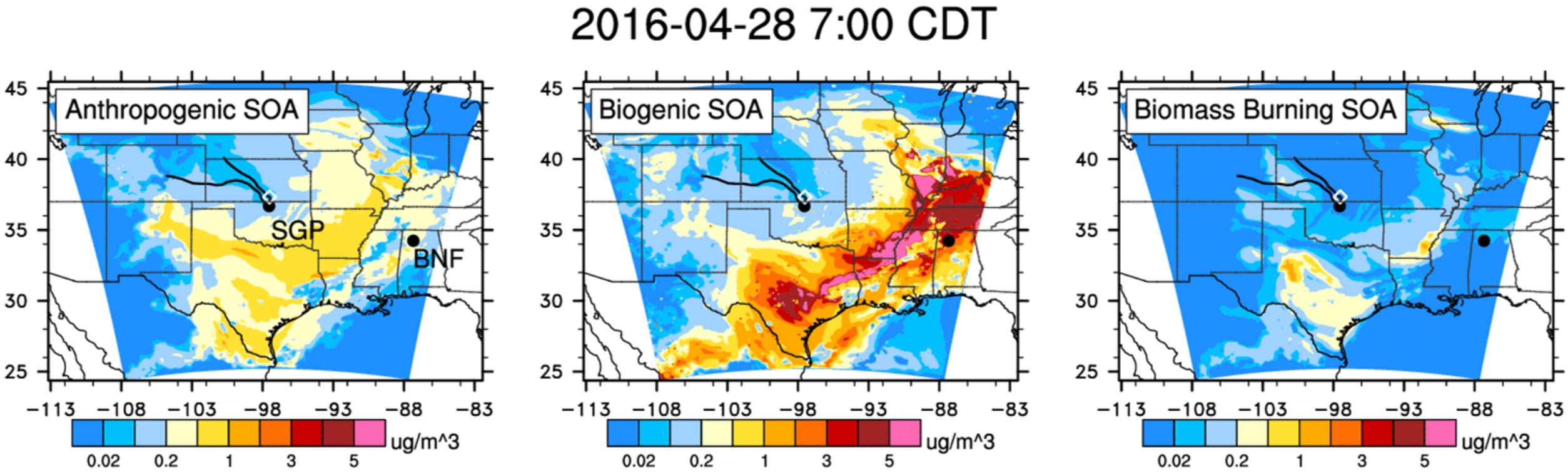
GCxGC measurements from Haofei Zhang & Allen Goldstein in SE USA during SOAS 2013, low volatility species can decompose during measurements, HOMs/organosulfates (OS) not measured

- Anthropogenic ELVOCs from WRF-Chem explain observations at C*= 10^{-4} ug m^{-3} bin
- Need measurements of molecular tracers for oligomers/OS from SE USA for SOA processes

WRF-Chem: IEPOX-SOA and terpene SOA dominate at BNF while anthropogenic SOA dominates at SGP site on April 28, 2016

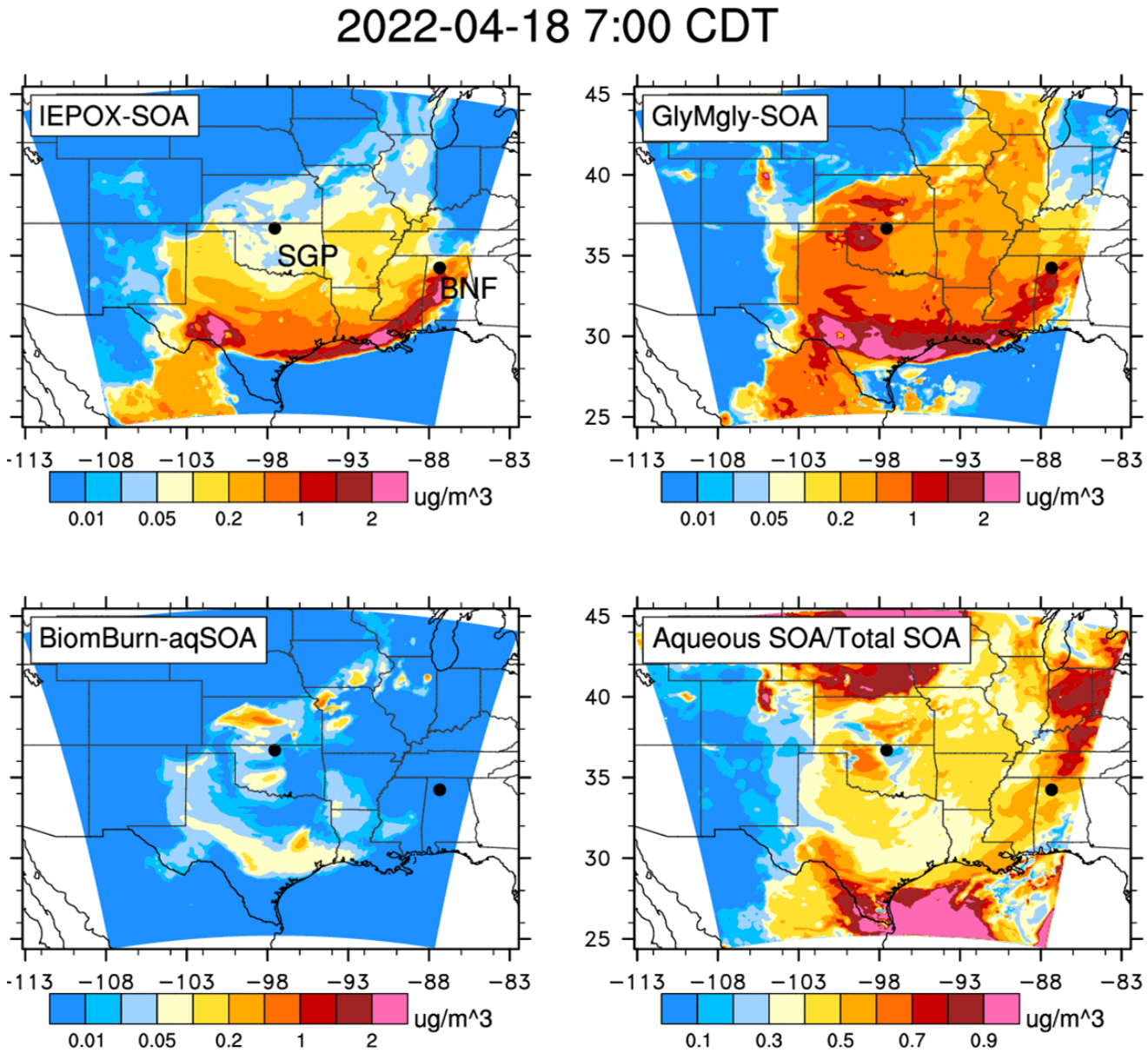


WRF-Chem: Modeling SOA sources during HI-SCALE 2016



- Anthropogenic SOA is prevalent at SGP, biogenic SOA dominates at BNF
- Biomass burning make some contributions to SOA at both sites

WRF-Chem: SOA formed by aqueous aerosol and cloud chemistry



- Aqueous SOA contributes ~40-70% to total SOA at BNF
- IEPOX-SOA, glyoxal/methylglyoxal SOA and biomass burning phenols contribute to aqueous SOA in SE USA
- In addition to gas-phase chemistry, measurements of aqueous SOA are needed at BNF

Integrated Model-Measurement strategies critical for designing measurements at BNF

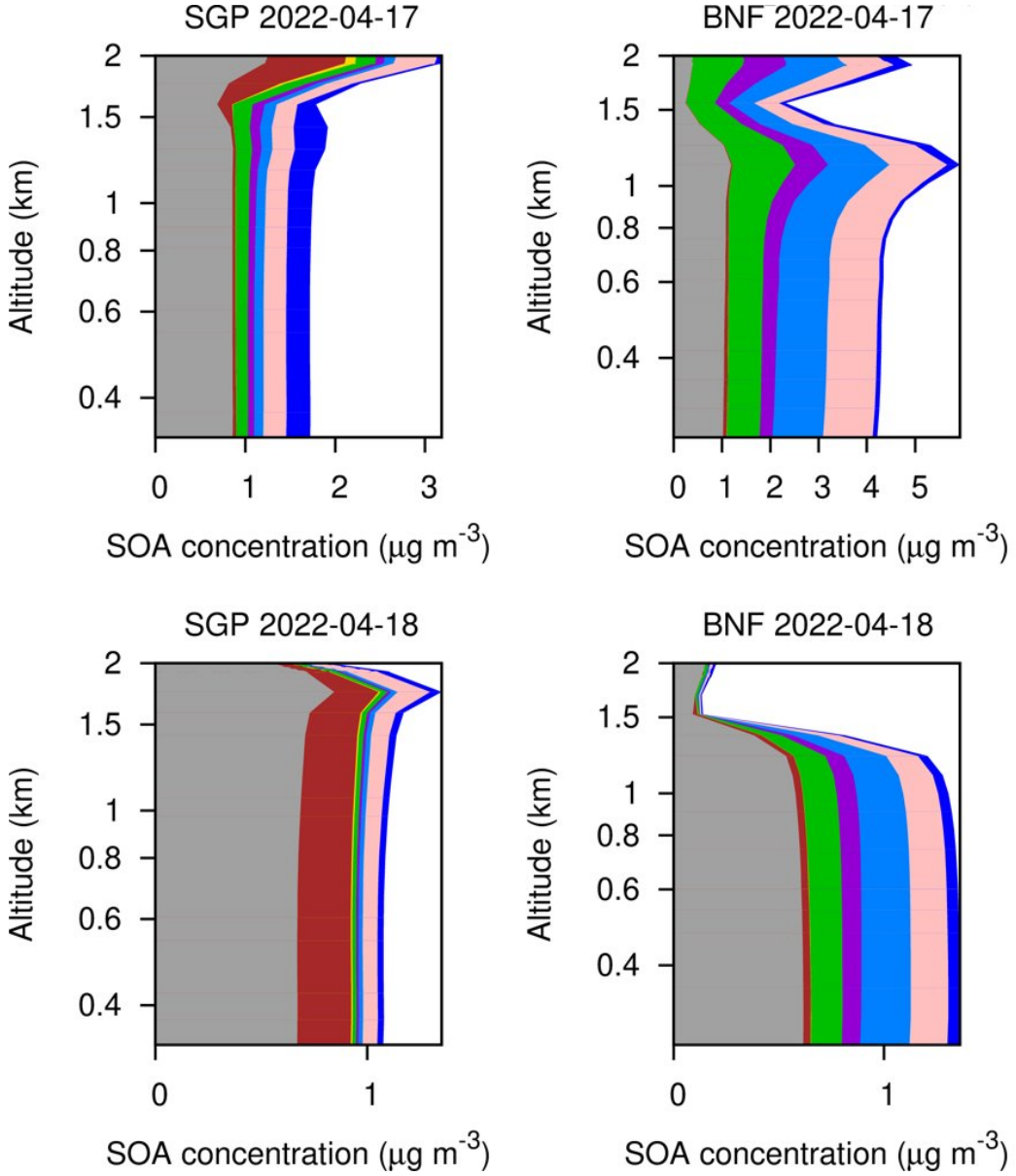
- What are sensitivities of SOA to changes in sulfate and oxides of nitrogen (NOx) in SE USA?
- What is the role of cloud chemistry and aqueous chemistry of SOA in SE USA?
- How do a mix of different VOC sources (anthropogenic, biogenic, biomass burning) affect SOA formation in SE USA?
- How does aging and functionalization/fragmentation as a function of NOx change volatility distributions of organics contributing to SOA at BNF?

Measurement needs:

- VOC measurements over ground and UAV based platforms are critical to diagnose biogenic emissions and SOA chemistry
- Several aqueous SOA types likely important over BNF: IEPOX-SOA, phenolic SOA etc.
- Measurements of HOMs, ELVOCs and oligomers from SE USA
- TBS systems with ultra high resolution mass spectrometry measurements
- Co-located measurements of speciated VOCs with NOx, oxidants and particle chemical composition
- Diurnal variations of SVOC/IVOCs

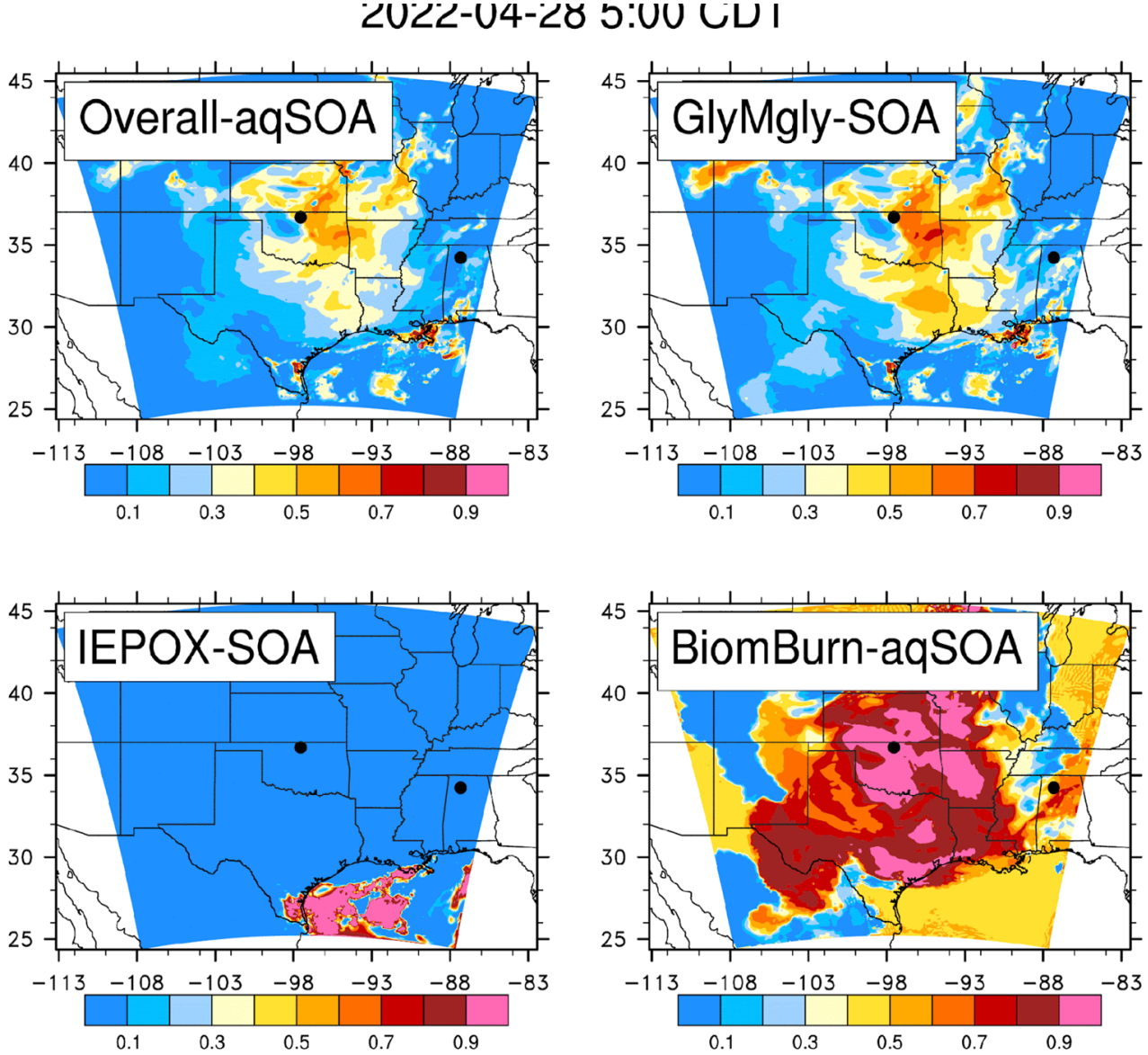
Backup slide

WRF-Chem: Veritcal profile of SOA at SGP and BNF in April 2022



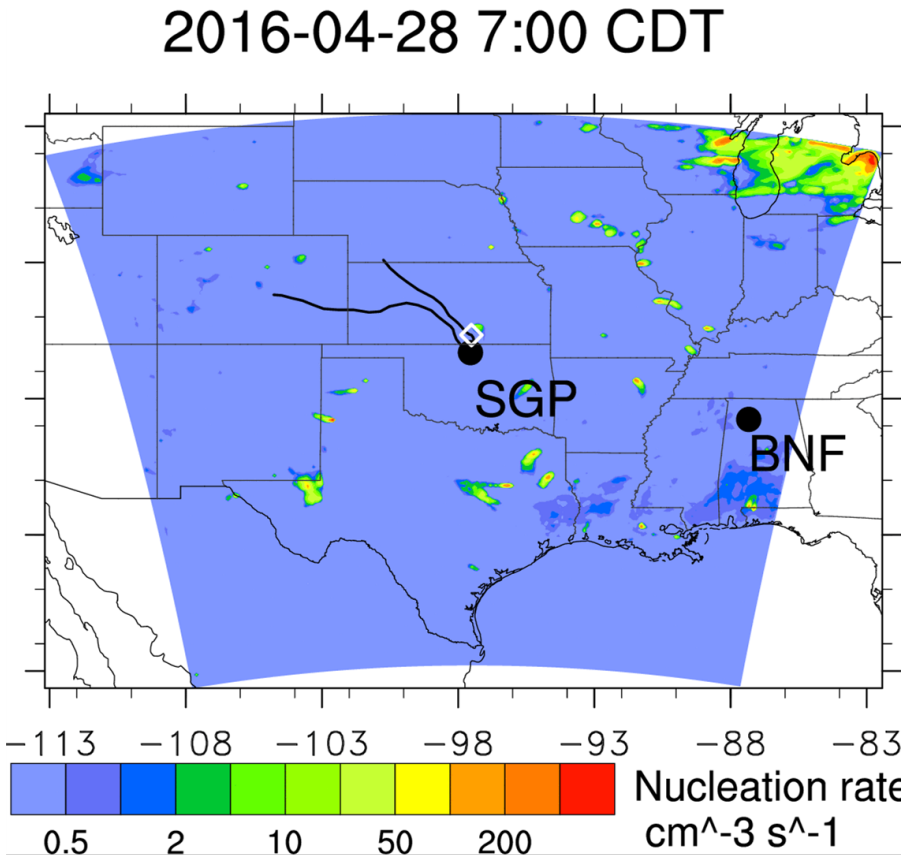
- Biogenic SOA is much higher at BNF compared to SGP
- But Anthropogenic SOA is similar at both sites

WRF-Chem: Cloud chemistry/(sum of cloud chemistry and aqueous aerosol chemistry) at surface

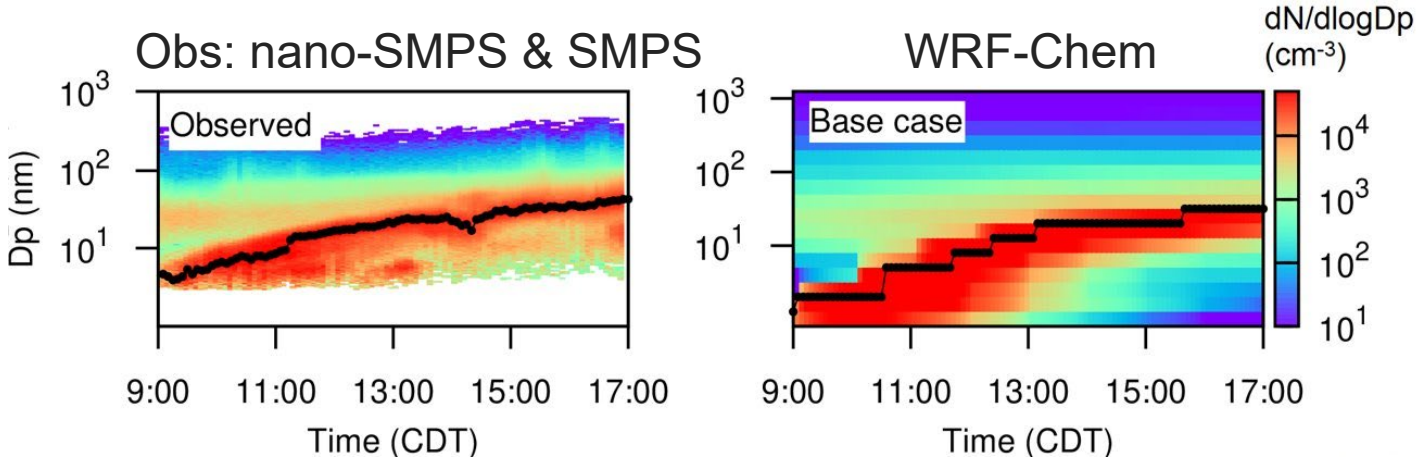


- Cloud chemistry contributes 50-90% of aqueous SOA
- Cloud chemistry is major contributor to aqueous SOA from biomass burning
- In SE USA aqueous chemistry from IEPOX-SOA, glyoxal/methylglyoxal and biomass burning are all important

Nucleation rate



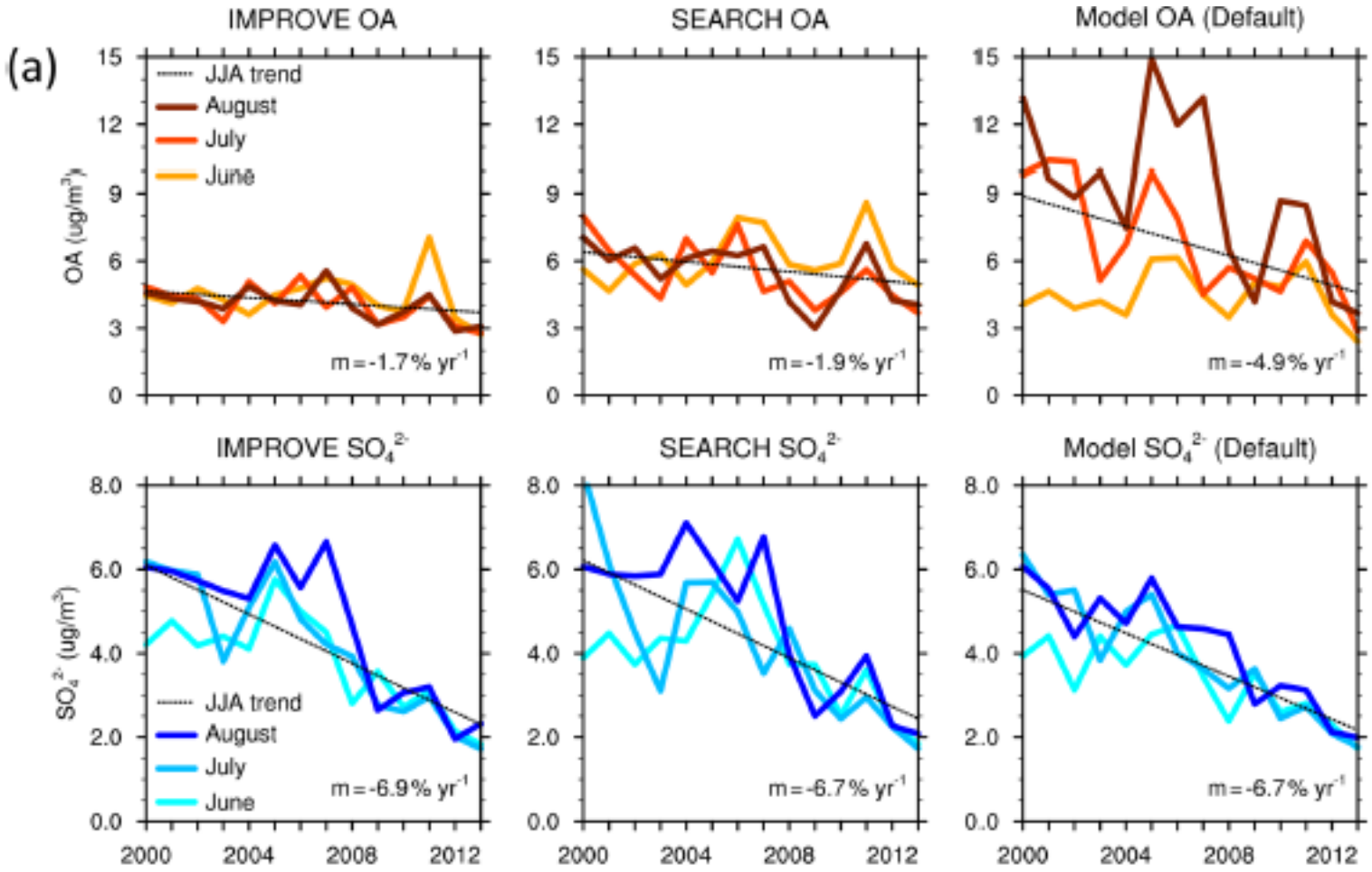
Nucleation and particle growth at SGP



Shrivastava et al. 2023, In preparation

- Nucleation rate at surface SGP site shows strong diurnal variation
- HYSPLIT Backtrajectory: Air masses encounter nucleation at 9 CDT and grow when they reach SGP

IEPOX-SOA in a global model: Modeled long term reduction in OA inconsistent with measurements in SE USA



(Zheng et al., 2020, ACP)

- Modeled IEPOX-SOA dependence on sulfate is too high
- Previous proposed explanation: Viscous SOA coatings limit IEPOX-SOA formation in SE USA
- But In SE USA, high RH at surface causes OA to be liquid-like: Above explanation less likely