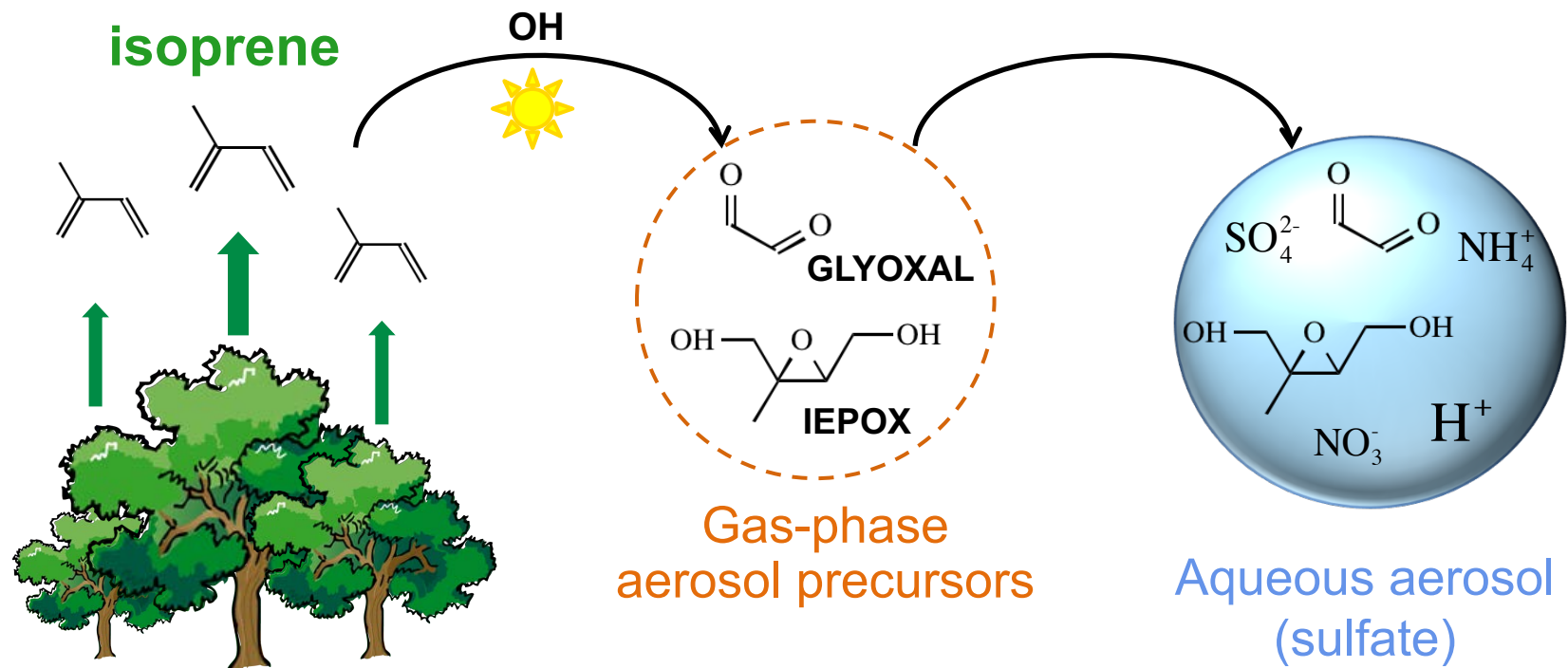


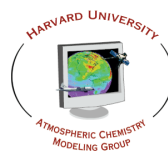
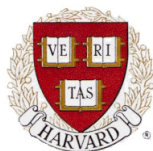
Air quality co-benefit of SO₂ emission controls to decrease biogenic organic aerosol and sulfate



Coauthors: D. J. Jacob, J. L. Jimenez, P. Campuzano-Jost, D. A. Day, W. Hu, J. Krechmer, L. Zhu, P. S. Kim, C. C. Miller, J. A. Fisher, K. Travis, K. Yu, T. F. Hanisco, G. M. Wolfe, H. L. Arkinson, J. R. Turner, L. J. Mickley, H. O. T. Pye, K. D. Froyd, J. Liao, V. F. McNeill



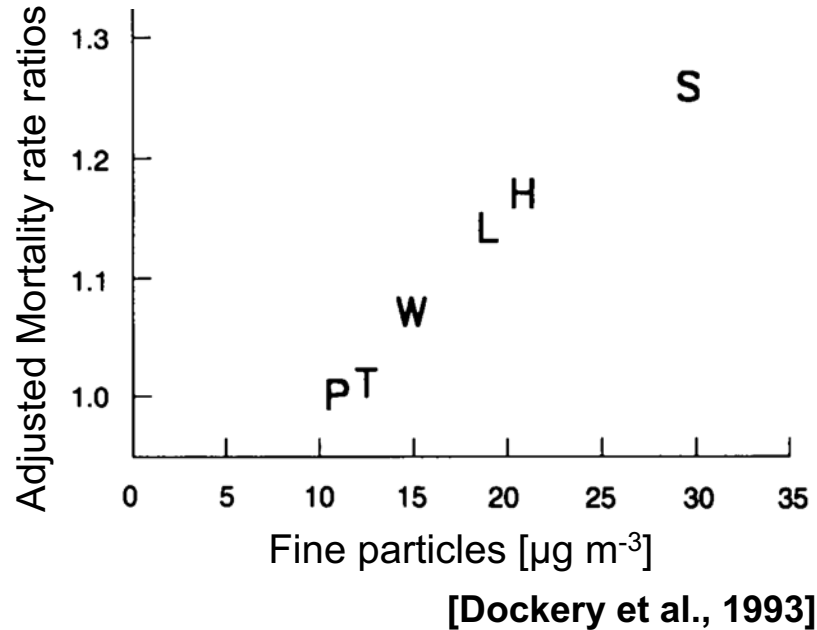
National
Research
Foundation



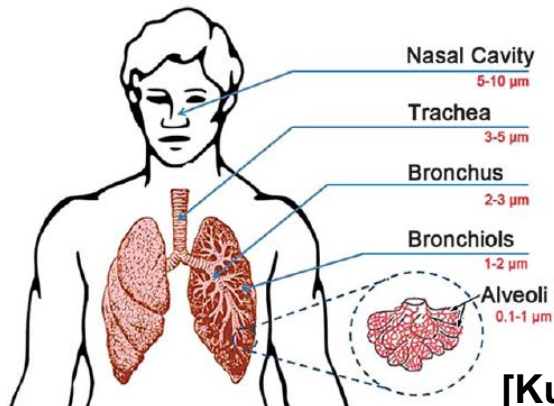
Eloïse A Marais
(e.a.marais@bham.ac.uk)

Aerosols Impact Climate, Human Health, and Visibility

Fine particles are associated with **increased mortality**

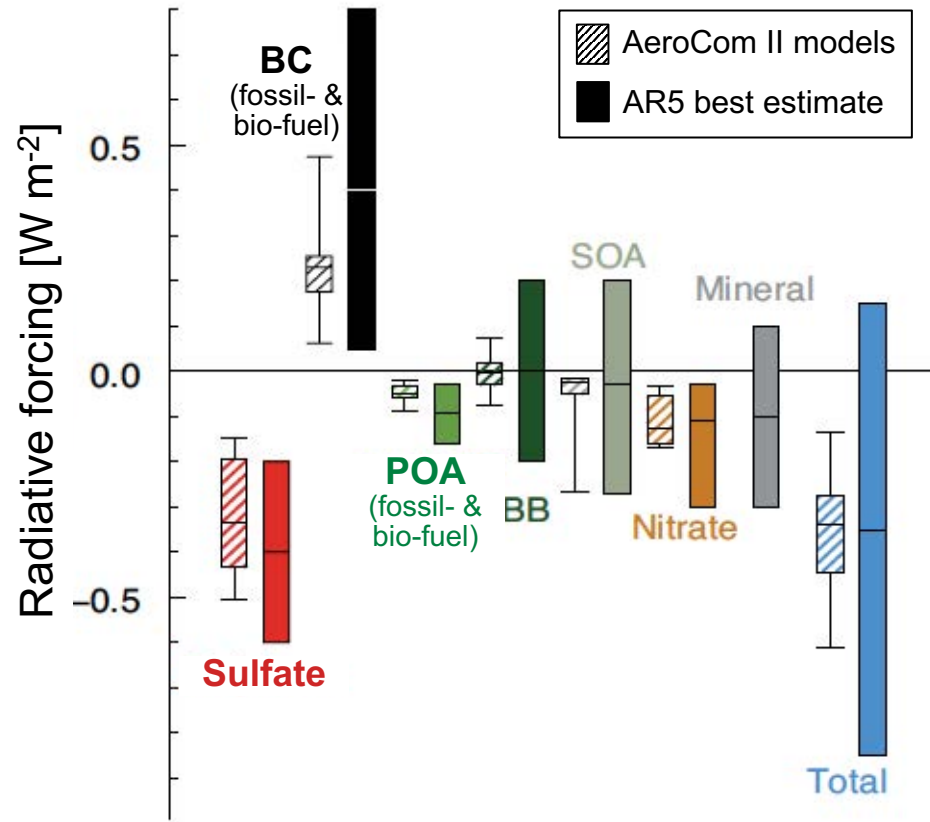


Fine particles travel deep into the lungs



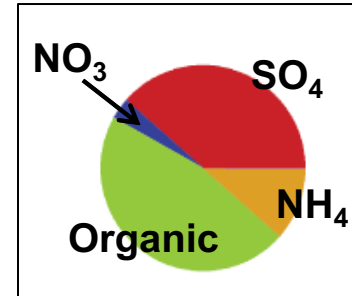
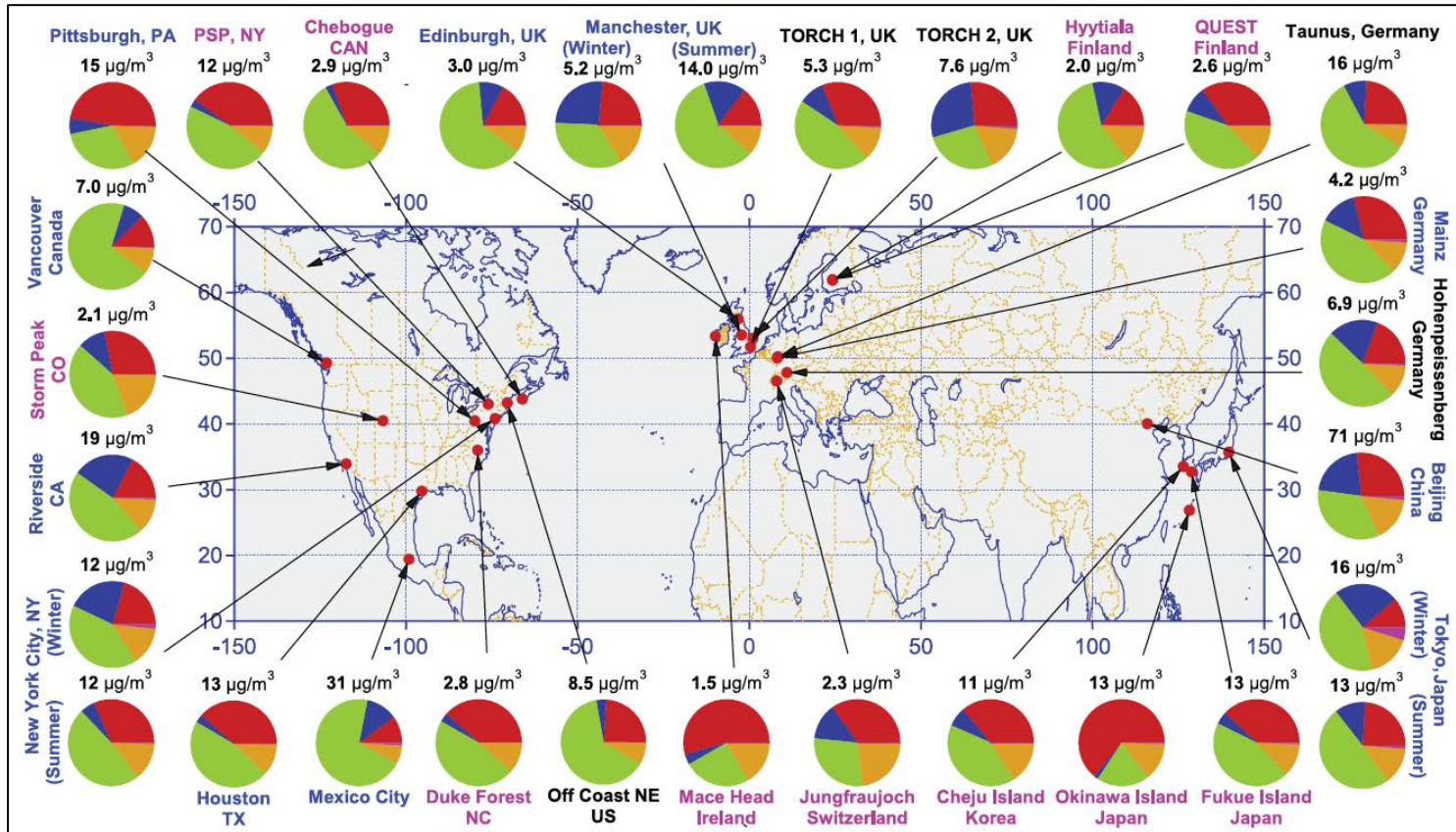
[Kumar et al., 2014]

Climate impact of **aerosols** is uncertain



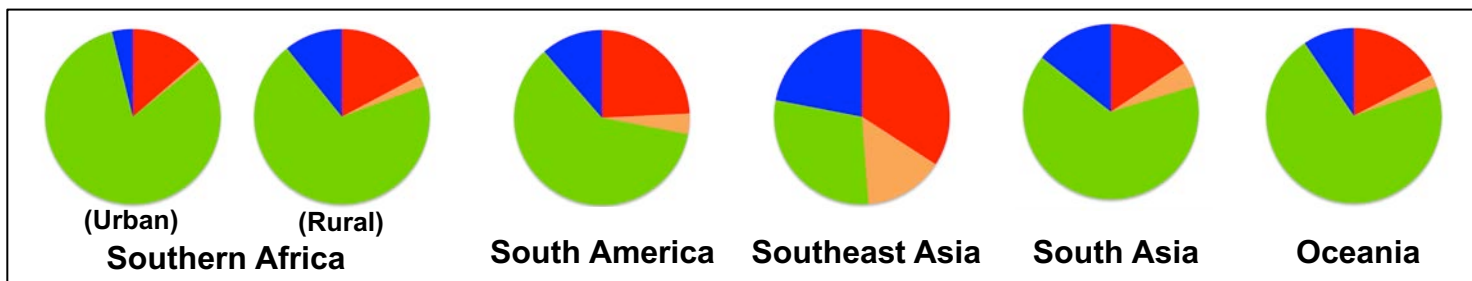
Organic Aerosol is Ubiquitous in the Atmosphere

Northern hemisphere aerosol components



[Zhang et al., 2007]

Tropics and southern hemisphere aerosol components

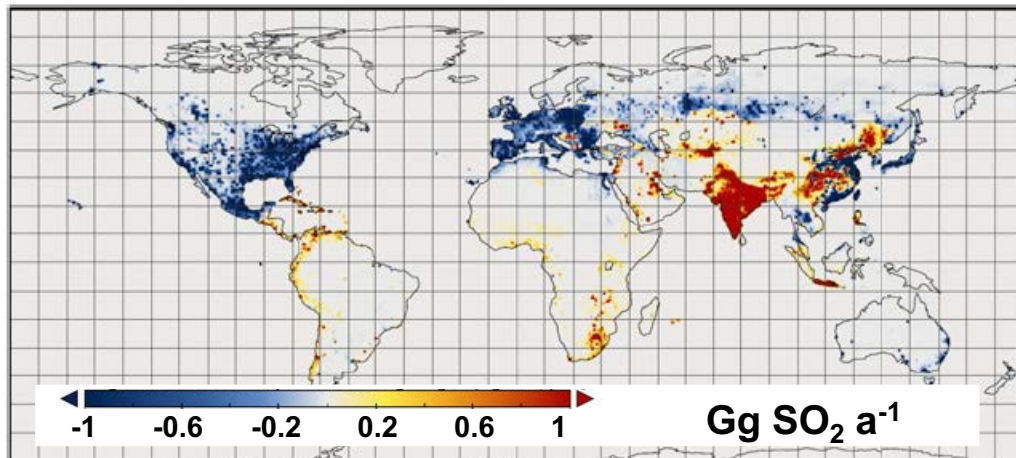


[IPCC, 2013]

Organic Aerosol Fraction is Increasing

In many parts of the world the organic aerosol contribution is increasing as SO₂ emissions (and sulfate) decline

2010 minus 2005 SO₂ emissions

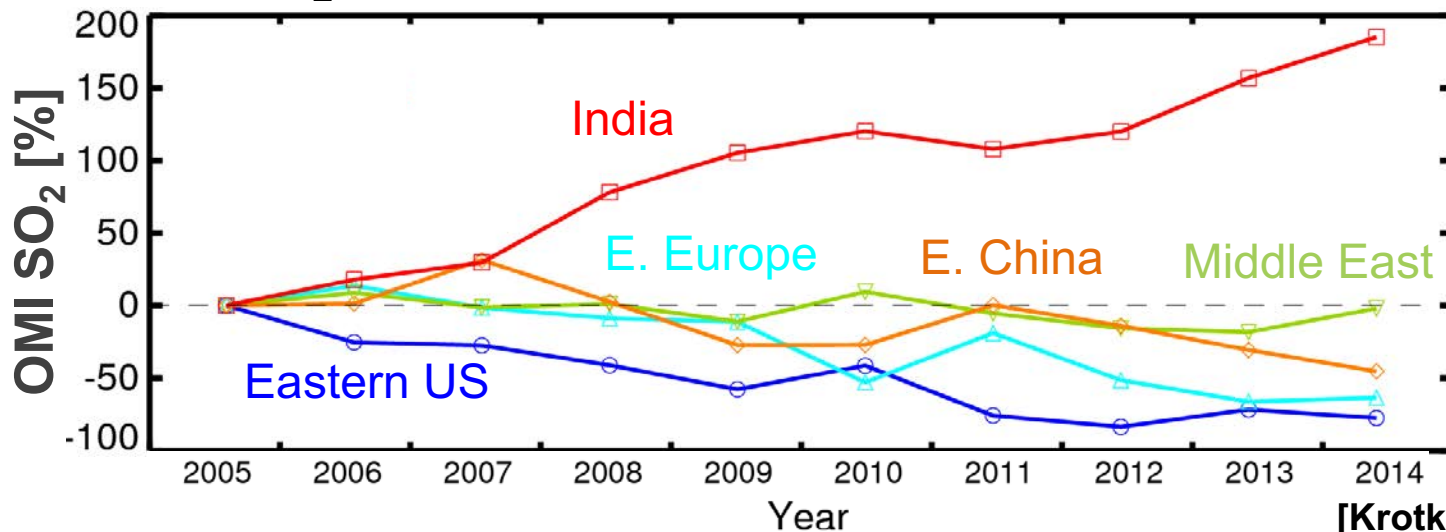


Global bottom-up emission inventory trends (left) corroborated by surface and satellite (see below) observations

[Klimont et al., 2013]

SO₂ regional trends observed from space

Change from 2005

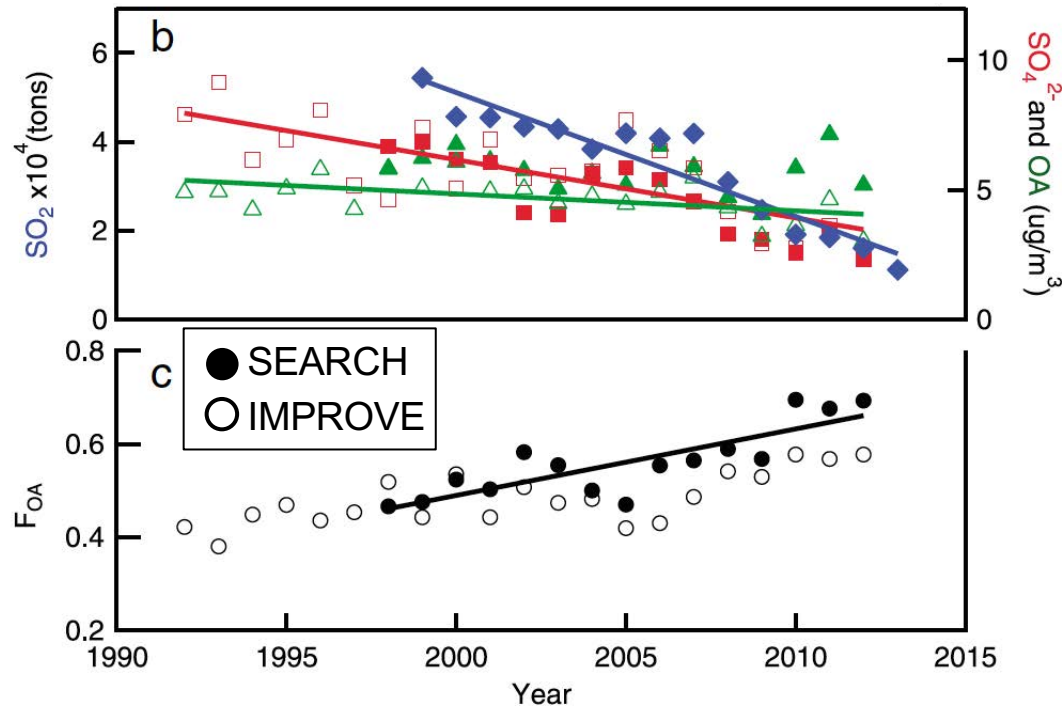


[Krotkov et al., 2015]

Organic Aerosol Fraction is Increasing – Southeast US

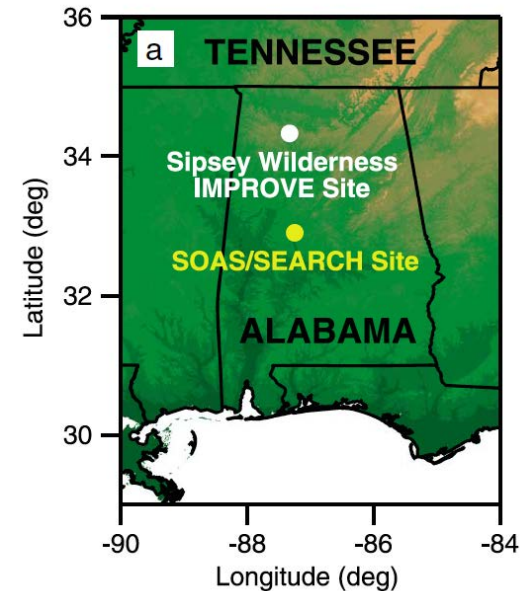
The increasing contribution of organic aerosol is apparent at a rural monitoring site in the Southeast US

SO₂ emissions, and **sulfate aerosol** and **organic aerosol** mass



[Attwood et al., 2014]

Rural Southeast US monitoring site



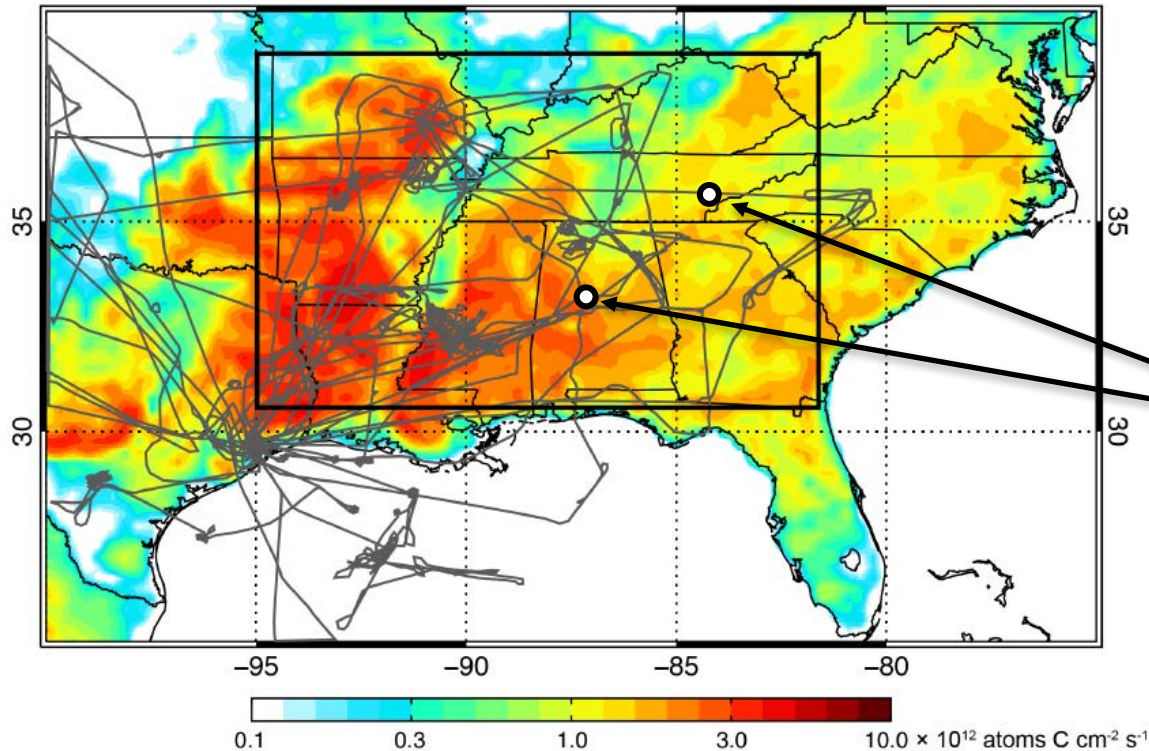
Site impacted by urban, industrial, **biogenic**, and agricultural emissions.

F_{OA} (fraction of organic aerosol) increased from 40% (1992) to 60% (2012).

The Southeast United States

Multiple summer 2013 campaigns to understand biogenic-anthropogenic interactions

MEGAN isoprene emissions, SEAC⁴RS flight tracks, and SOAS monitoring sites



**Aircraft campaign
(Aug-Sep 2013)**



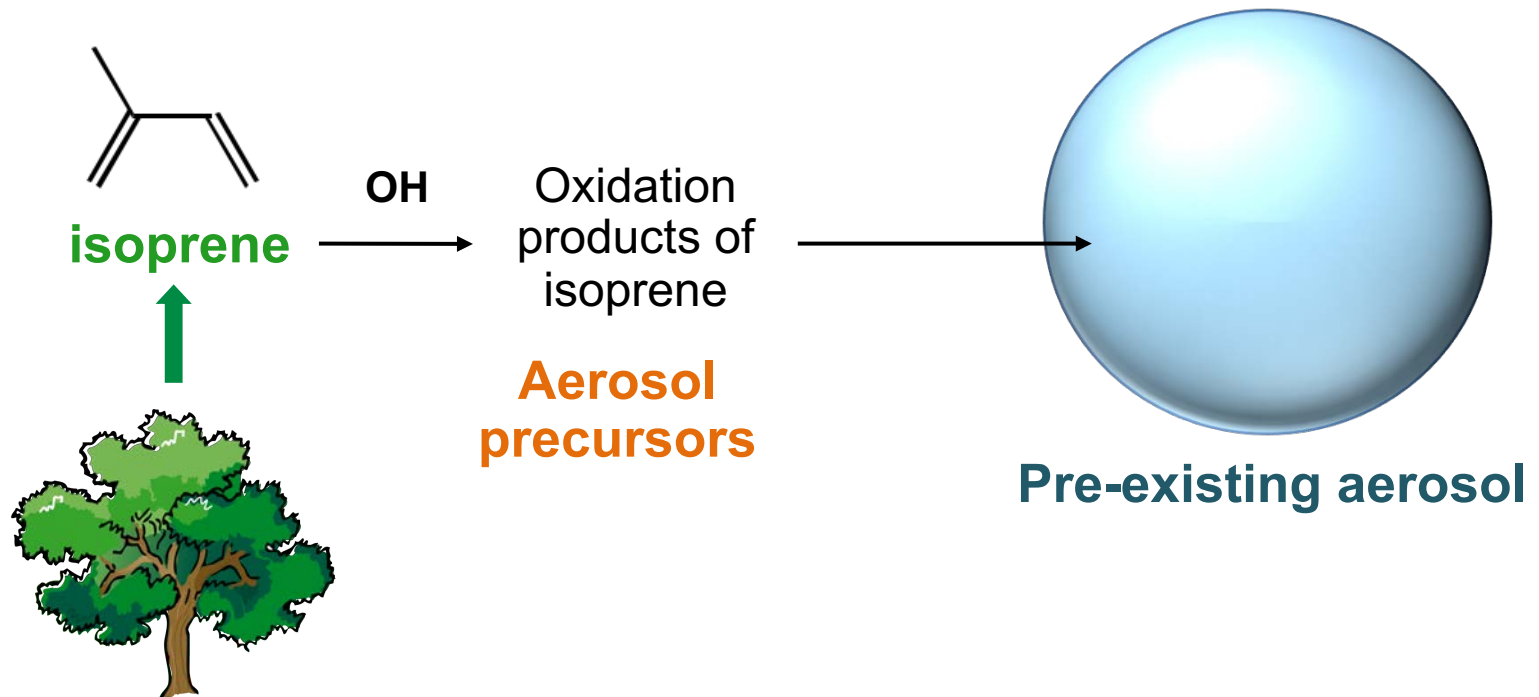
**Surface campaign
(Jun-Jul 2013)**

[Kim, P. et al., 2015]

In summer the Southeast US is a large source of **biogenic isoprene** (high temperatures) and **anthropogenic sulfate** (from oxidation of SO₂)

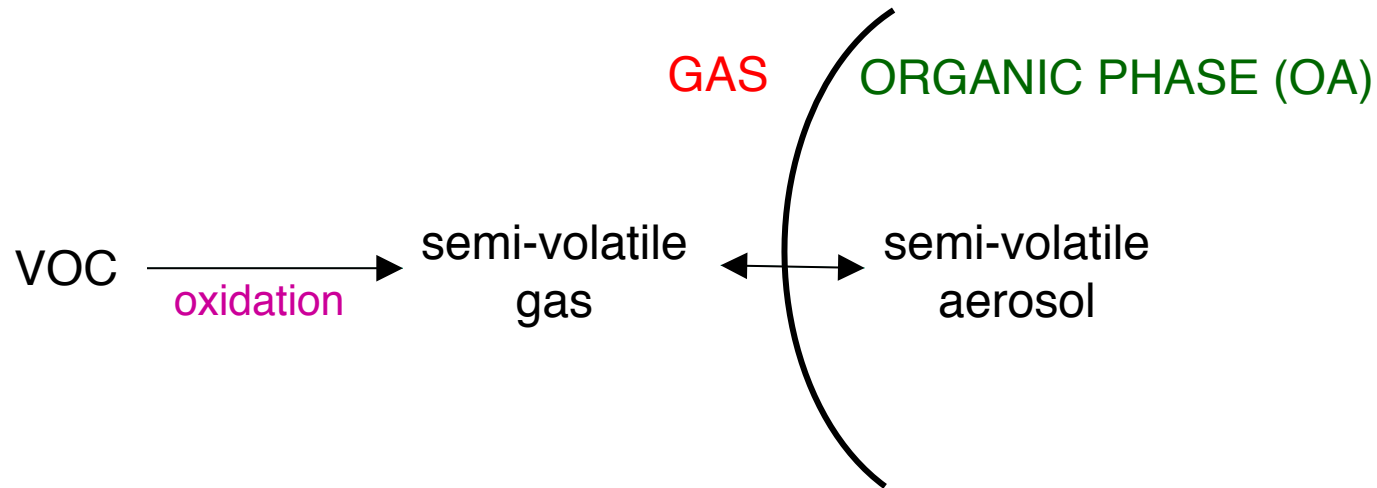
Isoprene oxidizes to form organic aerosol

Isoprene is oxidized to form compounds that then condense to pre-existing aerosol to form secondary organic aerosol (**SOA**)

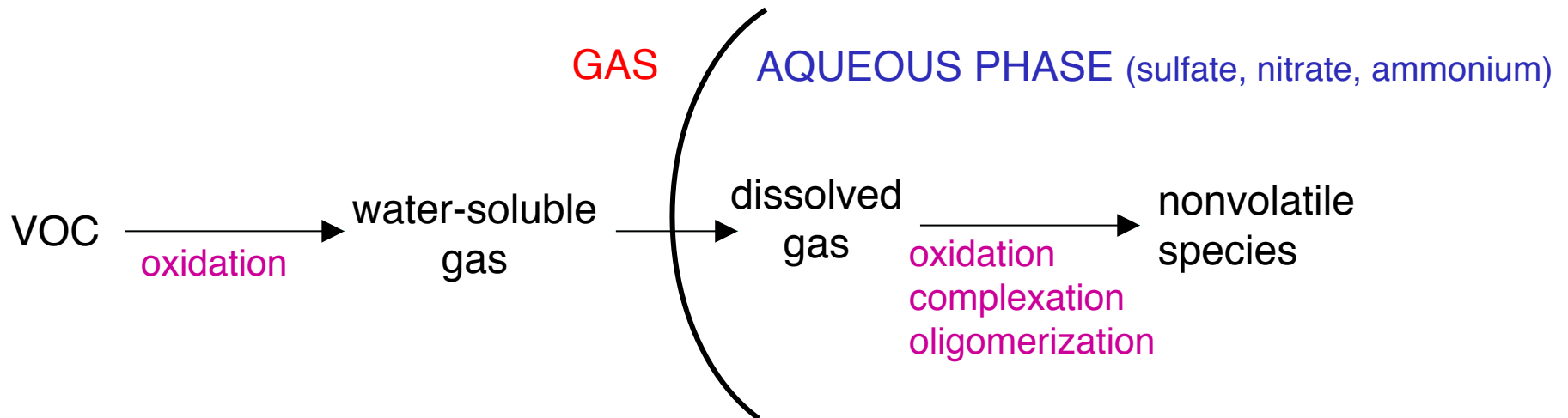


Two approaches to represent secondary organic aerosol

A. Classical model for reversible uptake by pre-existing organic aerosol

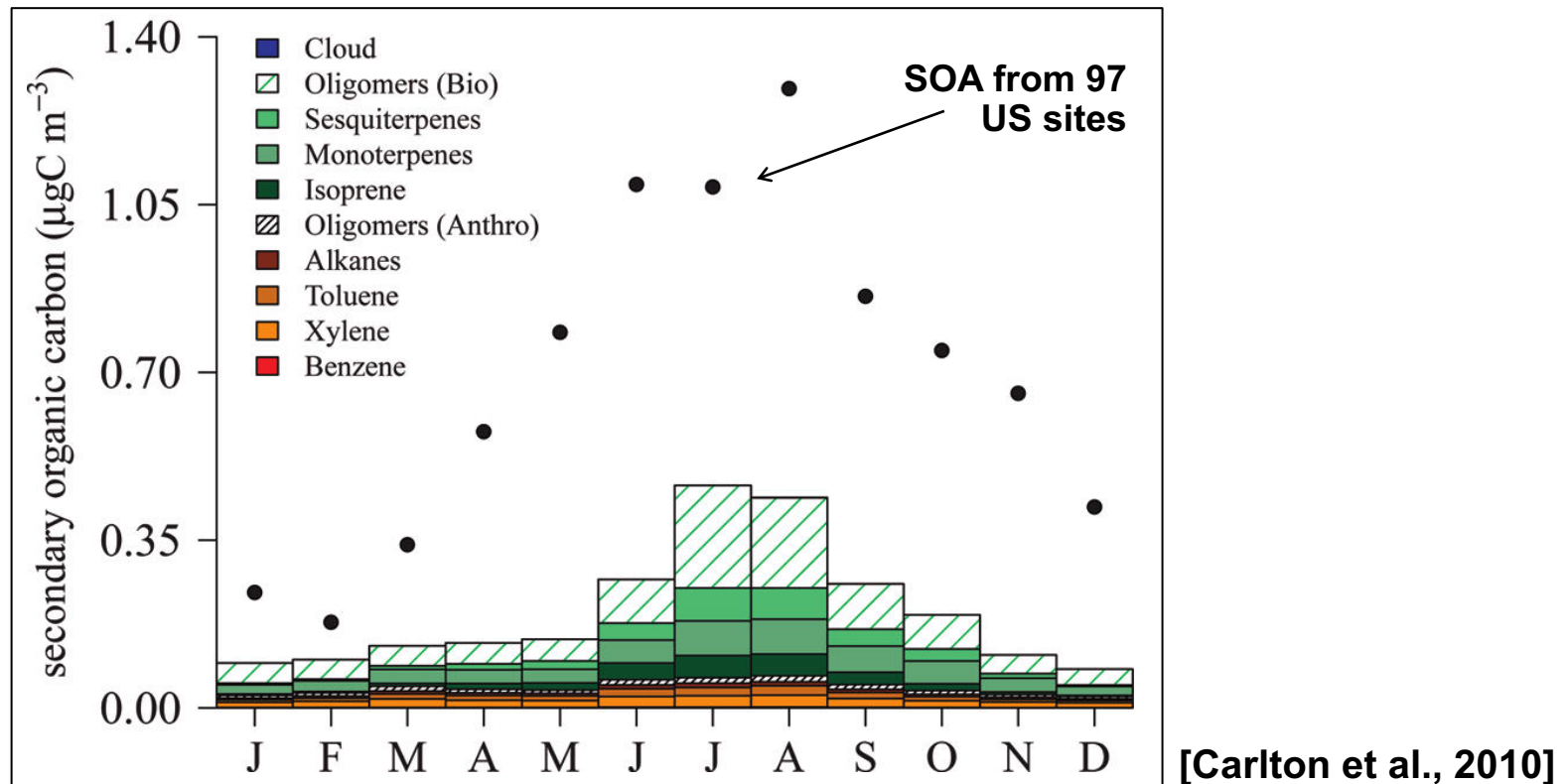


B. Alternate model for irreversible uptake by aqueous aerosol



The classical model routinely Underestimates SOA

Measured vs modeled SOA across the US



Model captures the seasonality (peaks in summer is due to biogenic SOA), but not the magnitude

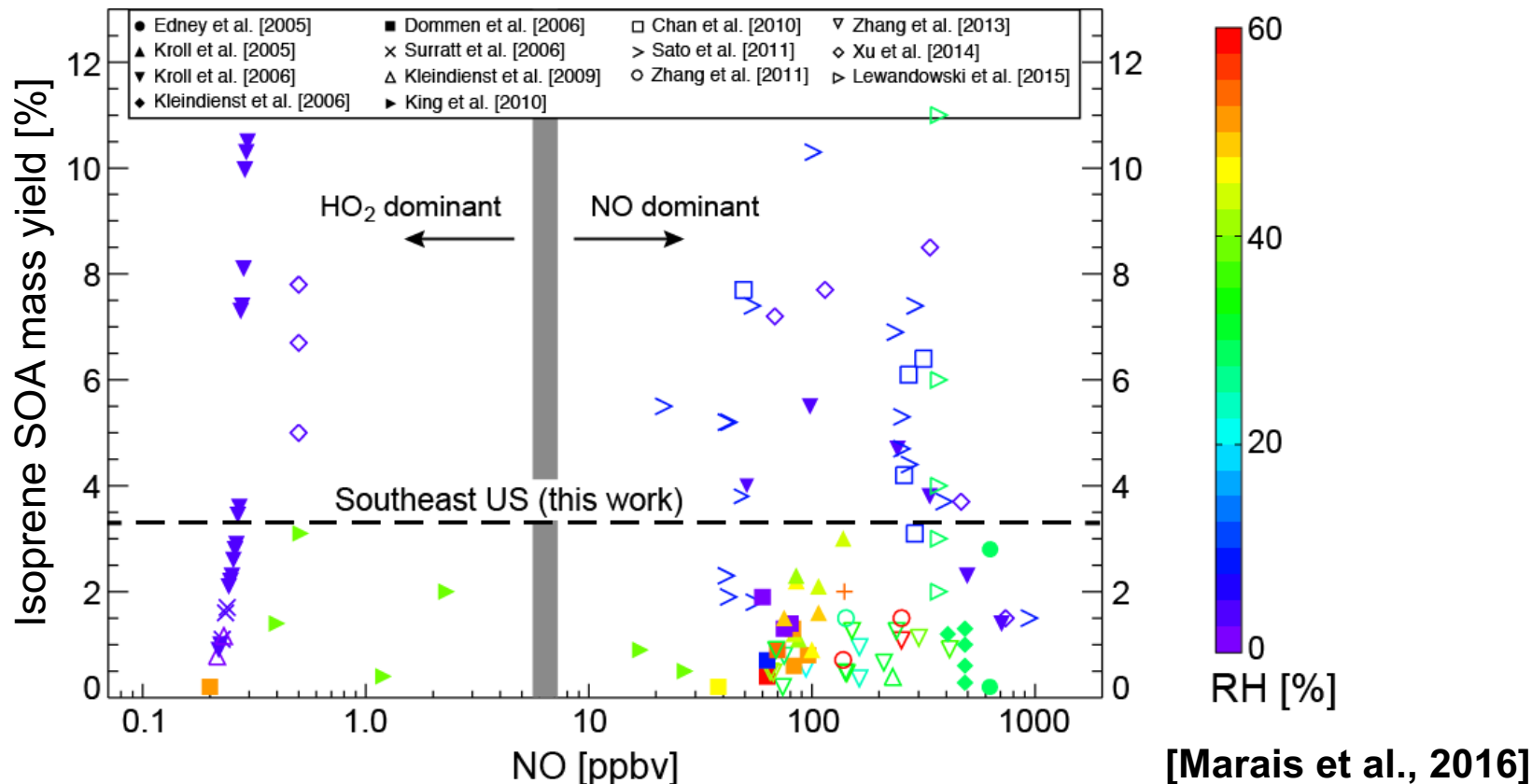
Limits ability to determine impact of isoprene SOA on **climate** and **human health**

Increasing evidence that SOA formation is instead by irreversible uptake to **aqueous aerosol**

Model Parameterizations of Isoprene Organic Aerosol

Traditional model based on chamber studies conducted at conditions very different to the ambient atmosphere

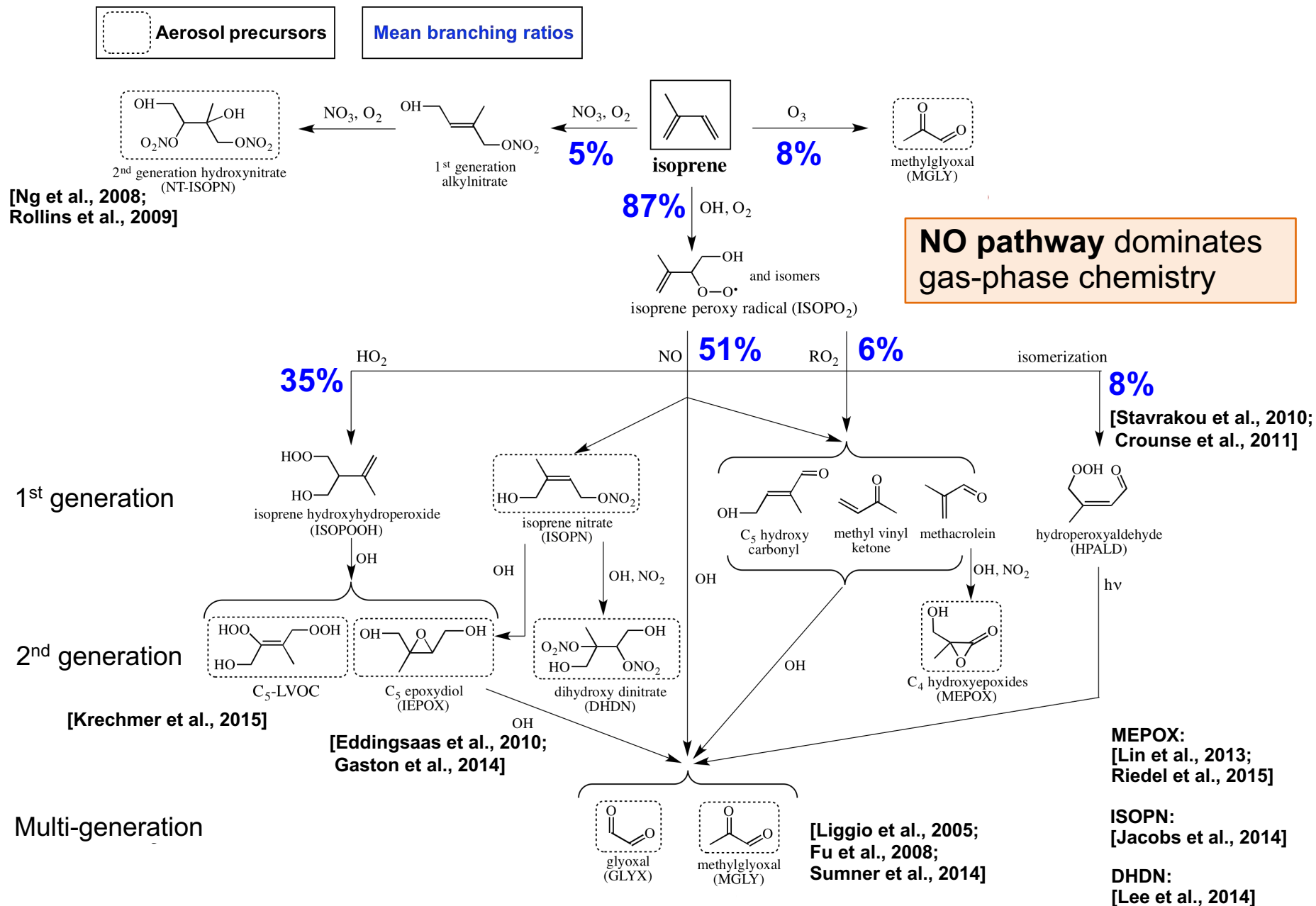
Compilation of chamber study isoprene + OH SOA mass yields



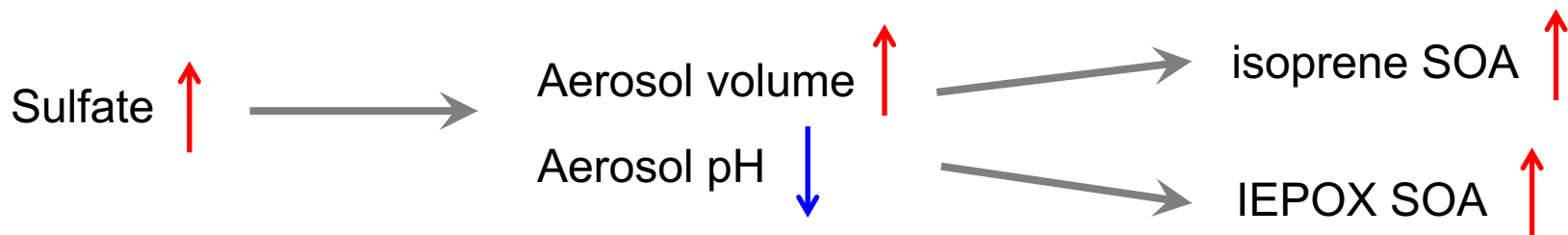
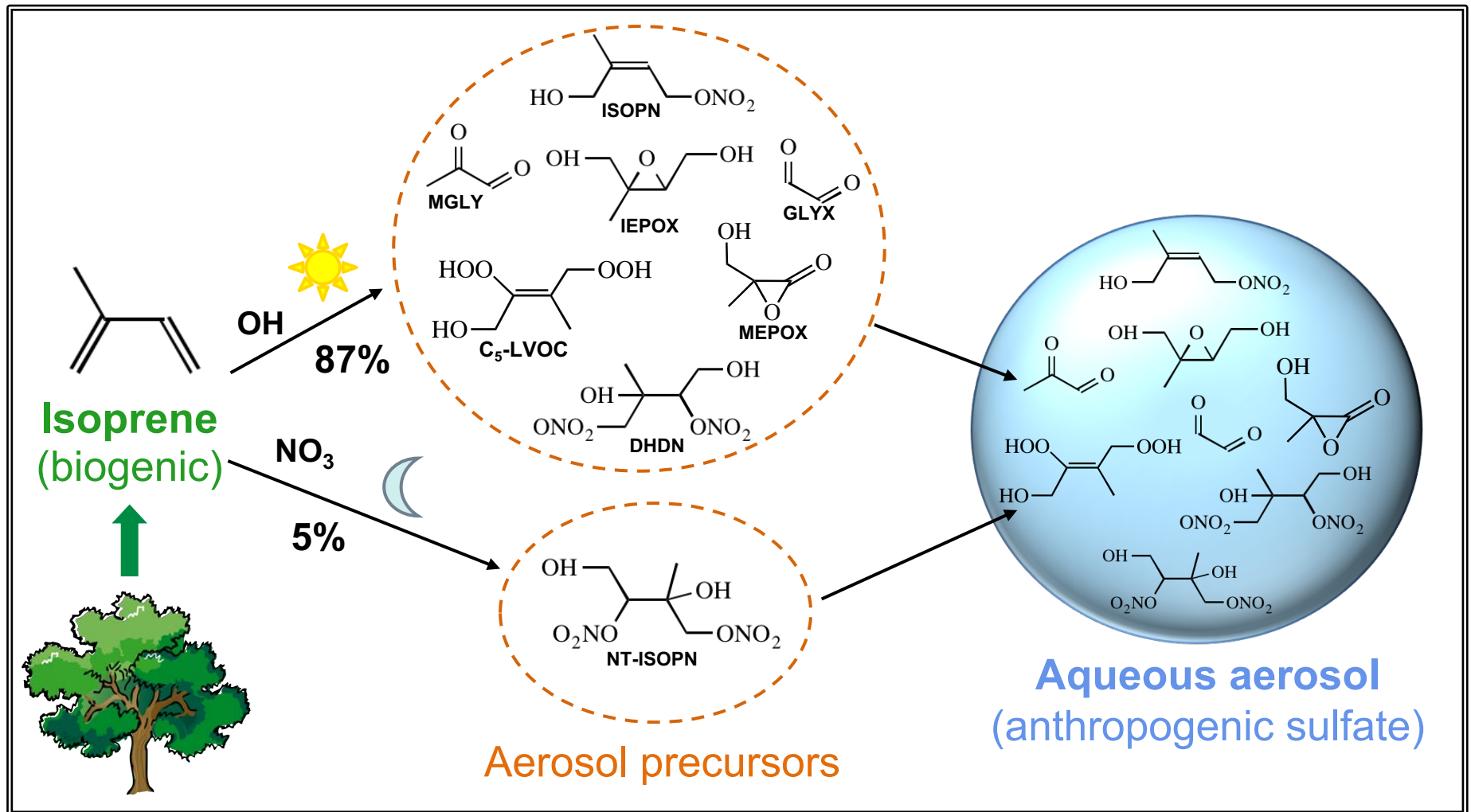
Southeast US Boundary-Layer Summer Conditions

RH = 72 ± 17 %
NO = 0.053 ± 0.140 ppbv
isoprene = 0.78 ± 0.85 ppbv

Gas-phase Isoprene SOA precursors in GEOS-Chem



Aqueous-Phase Mechanism Framework



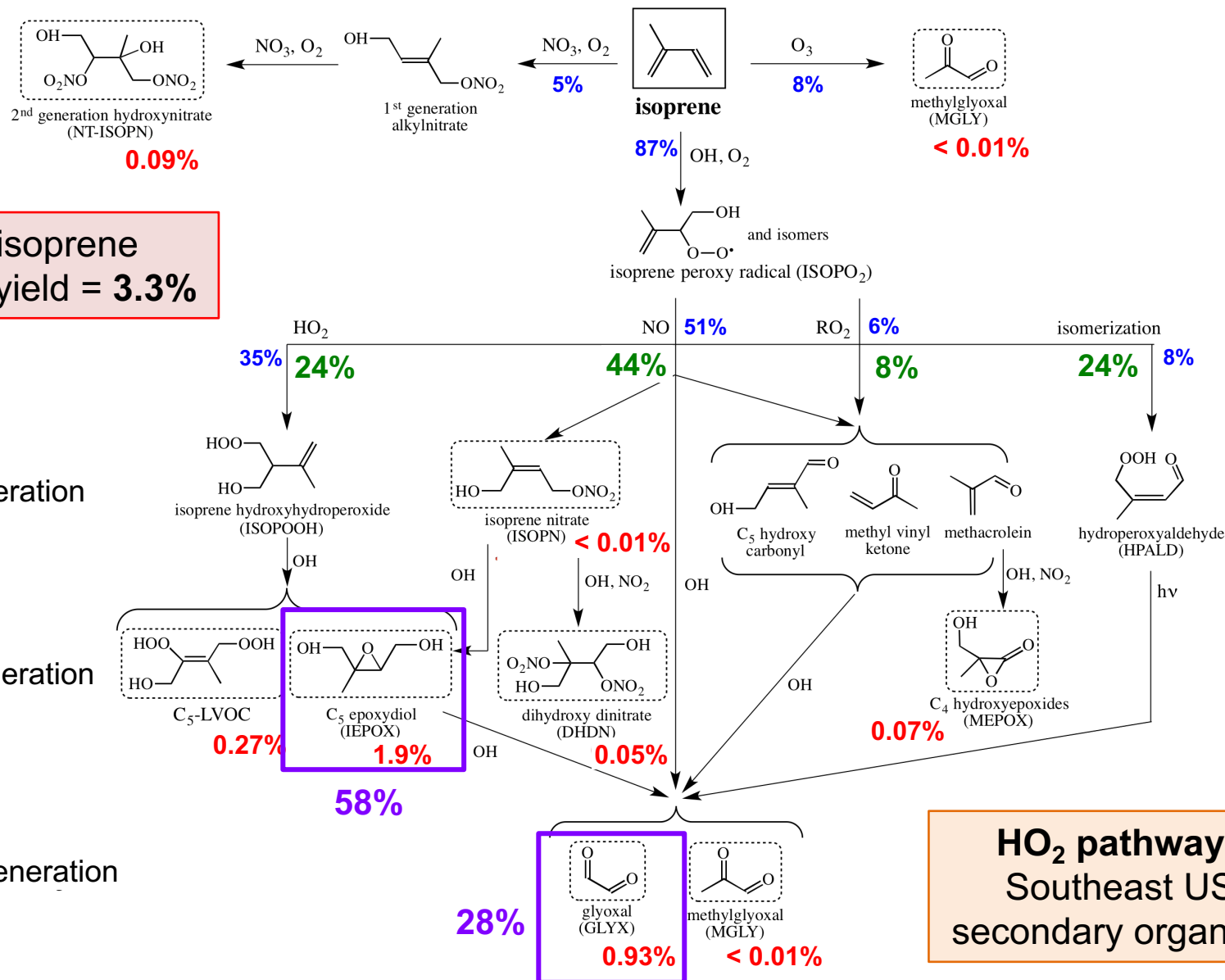
GEOS-Chem Isoprene SOA Yields in the Southeast US

Aerosol precursors

Mean branching ratios

Aerosol yield per unit isoprene

Share of glyoxal formation

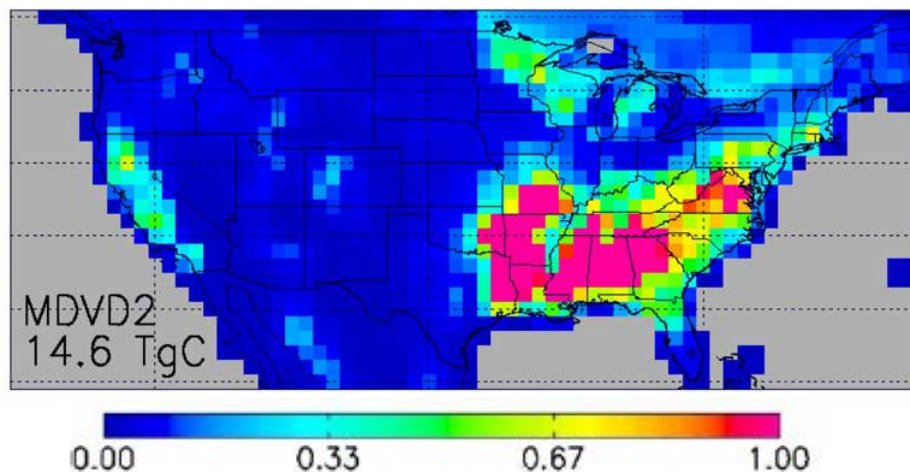


OA-HCHO Relationship Constrains Isoprene SOA Yields

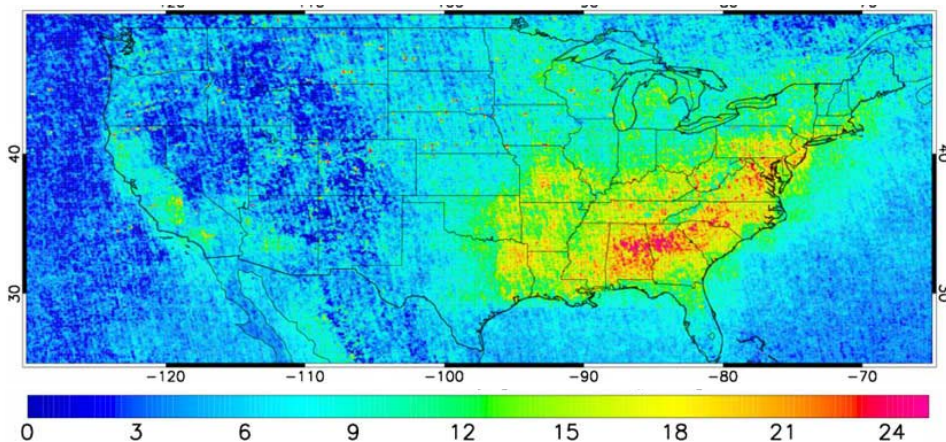
In the Southeast US...

Isoprene is the largest source of HCHO

Isoprene Emissions [10^{13} atoms C cm^{-2} s^{-1}]



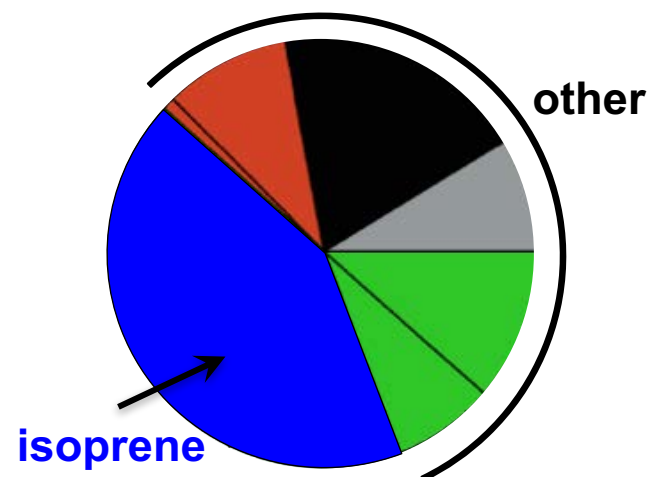
HCHO Column Density [10^{16} molecules cm^{-2}]



[Millet et al., 2008]

Isoprene SOA is 40% of OA

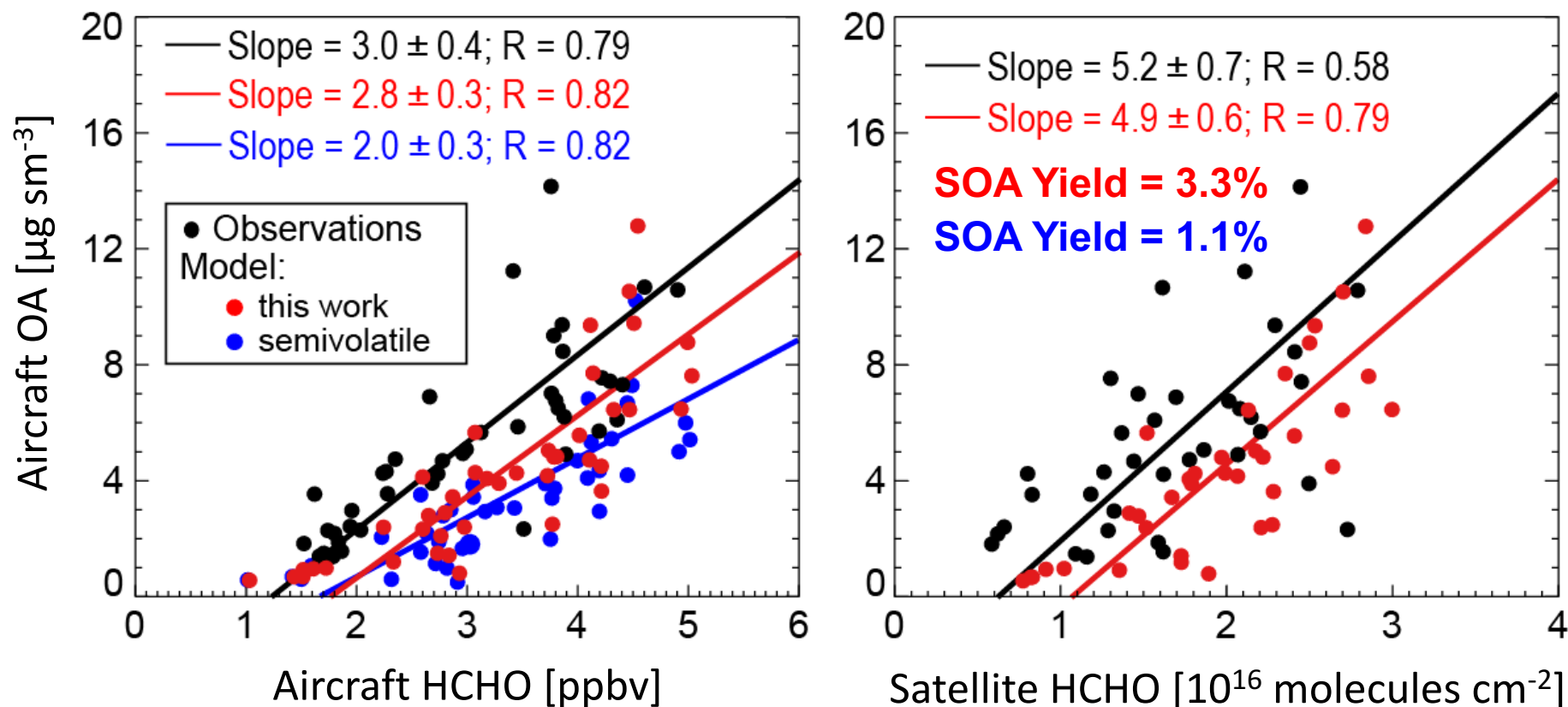
Southeast US OA



Adapted from Kim et al. [2015]

OA-HCHO Relationship Constrains Isoprene SOA Yields

OA-HCHO Relationships during SEAC⁴RS



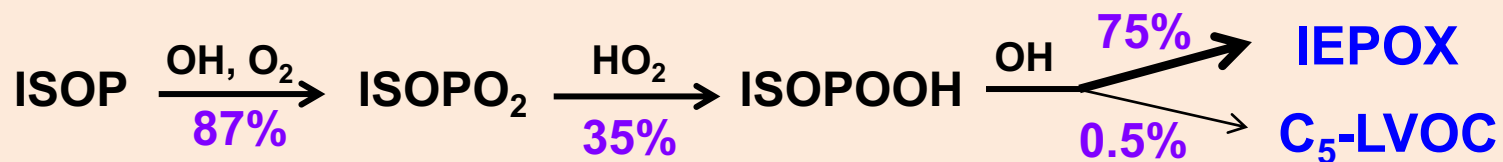
Requirement: Slope is sensitive to the underlying isoprene SOA yields

Traditional scheme underestimates the slope

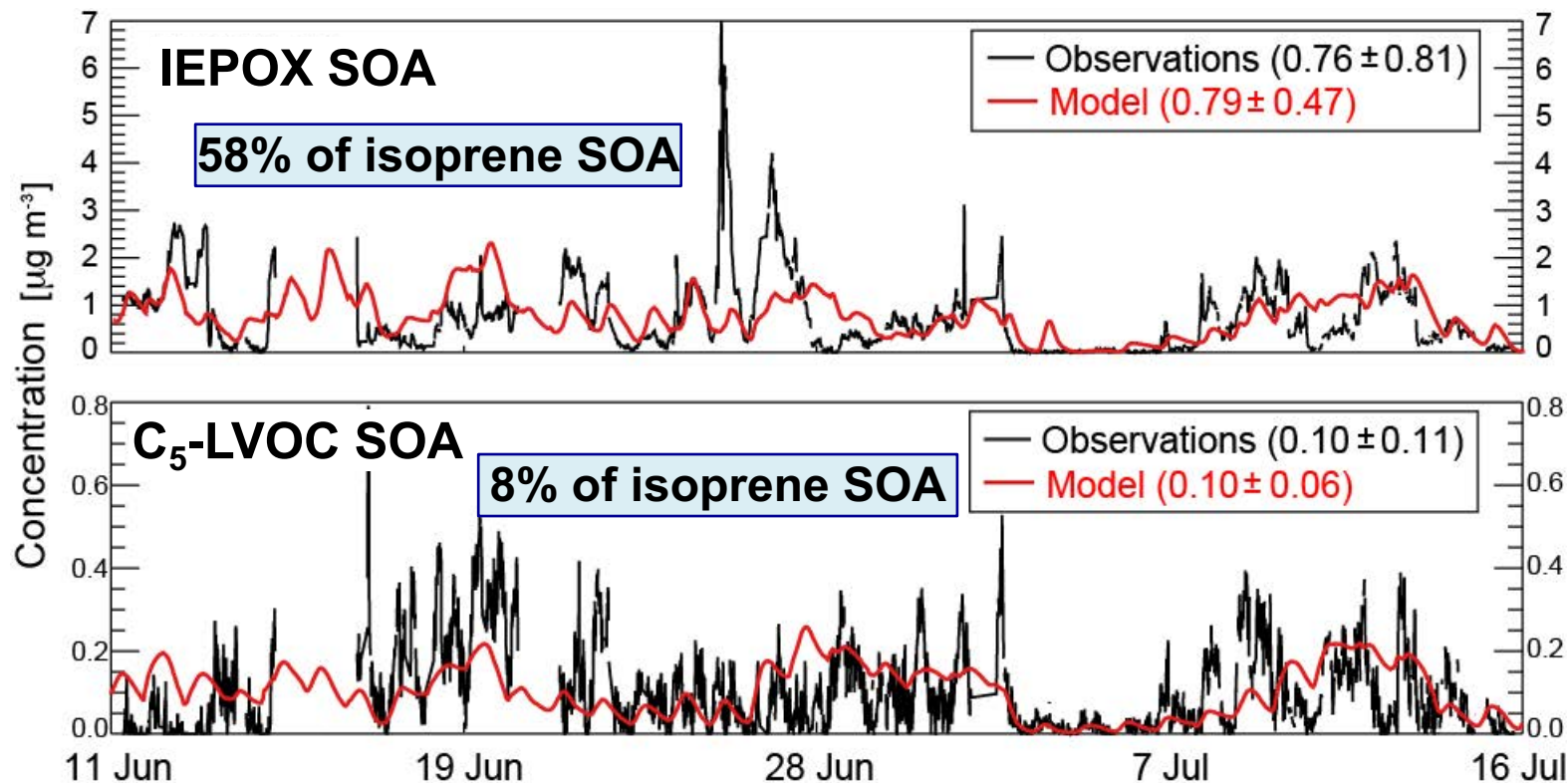
Irreversible uptake scheme slope is consistent with the observations, so **3.3% isoprene SOA yield** in the model is representative of the Southeast US in summer 2013.

[Data from T. Hanisco, G. Wolfe, H. Arkinson, L. Zhu, J. L. Jimenez, P. Campuzano-Jost]

Observational Constraints on Isoprene SOA Components



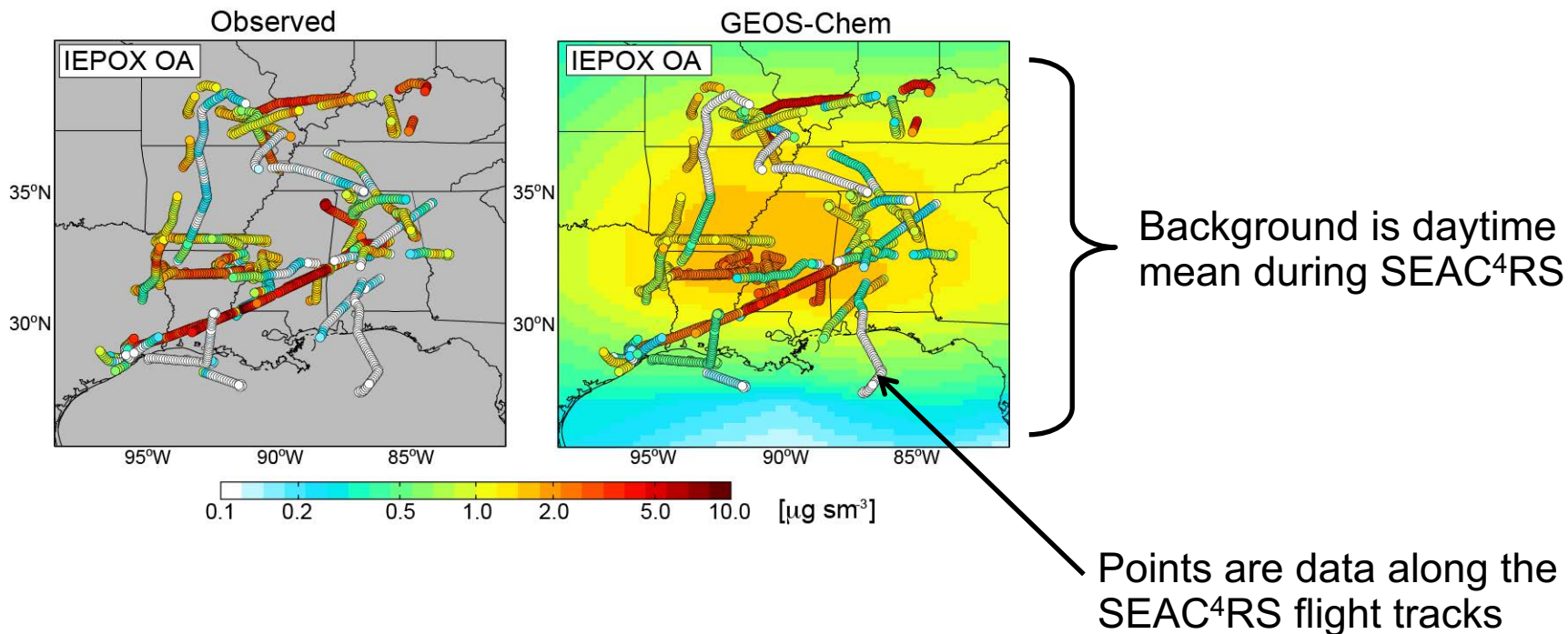
Secondary organic aerosol from IEPOX and C₅-LVOC at Centreville, AL (SOAS campaign; Jun-Jul 2013)



[Data from D. A. Day, W. Hu, J. Krechmer, J. L. Jimenez]

Spatial Distribution of IEPOX SOA

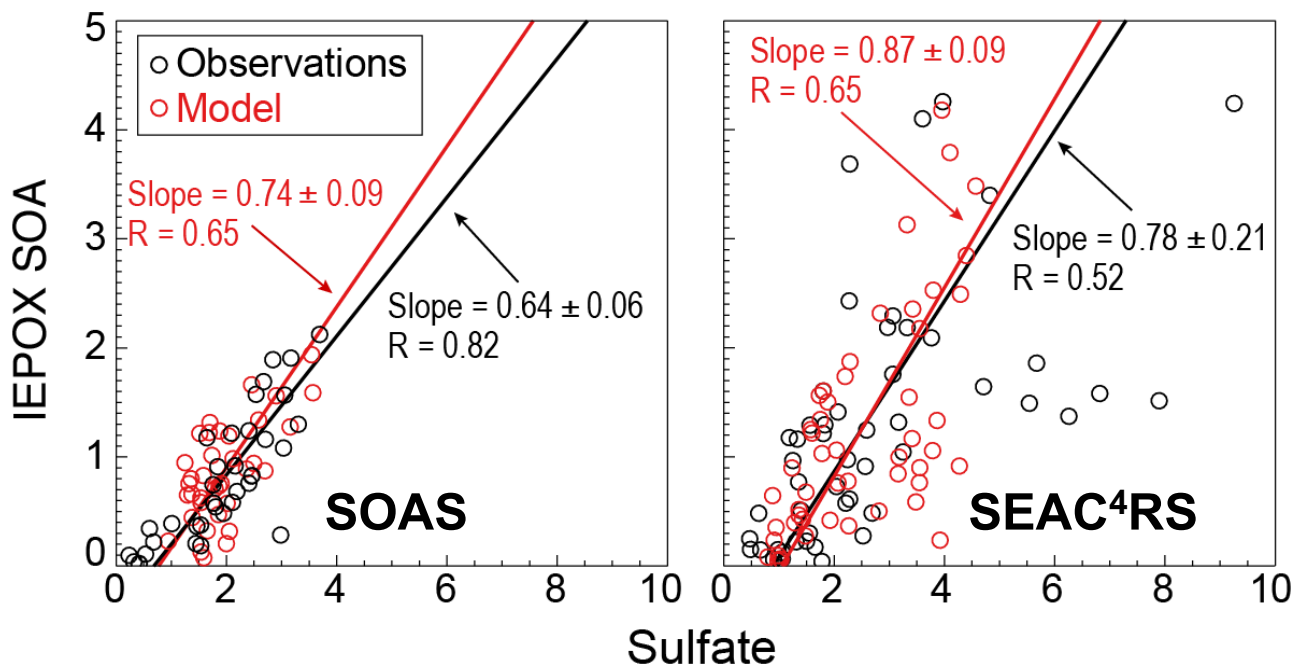
SEAC⁴RS (Aug-Sep 2013) boundary-layer IEPOX SOA



[Data from P. Campuzano-Jost, J. L. Jimenez]

What modulates IEPOX OA in the Southeast US?

IEPOX SOA and Sulfate correlation during SOAS and SEAC⁴RS



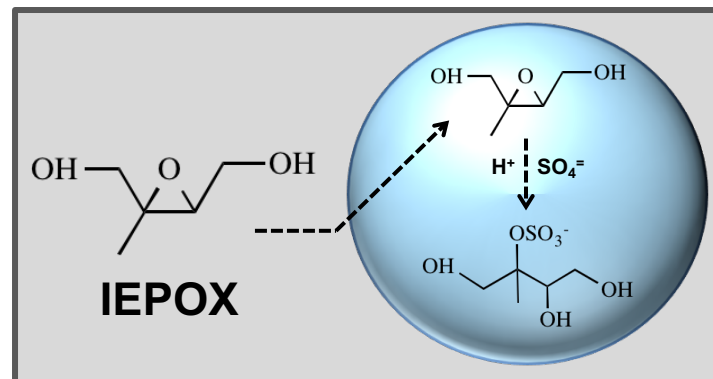
Similar relationship between sulfate and IEPOX OA in the observations and model

Correlation identified throughout the **Southeast US**:

Budisulistiorini et al. [2013, 2015];

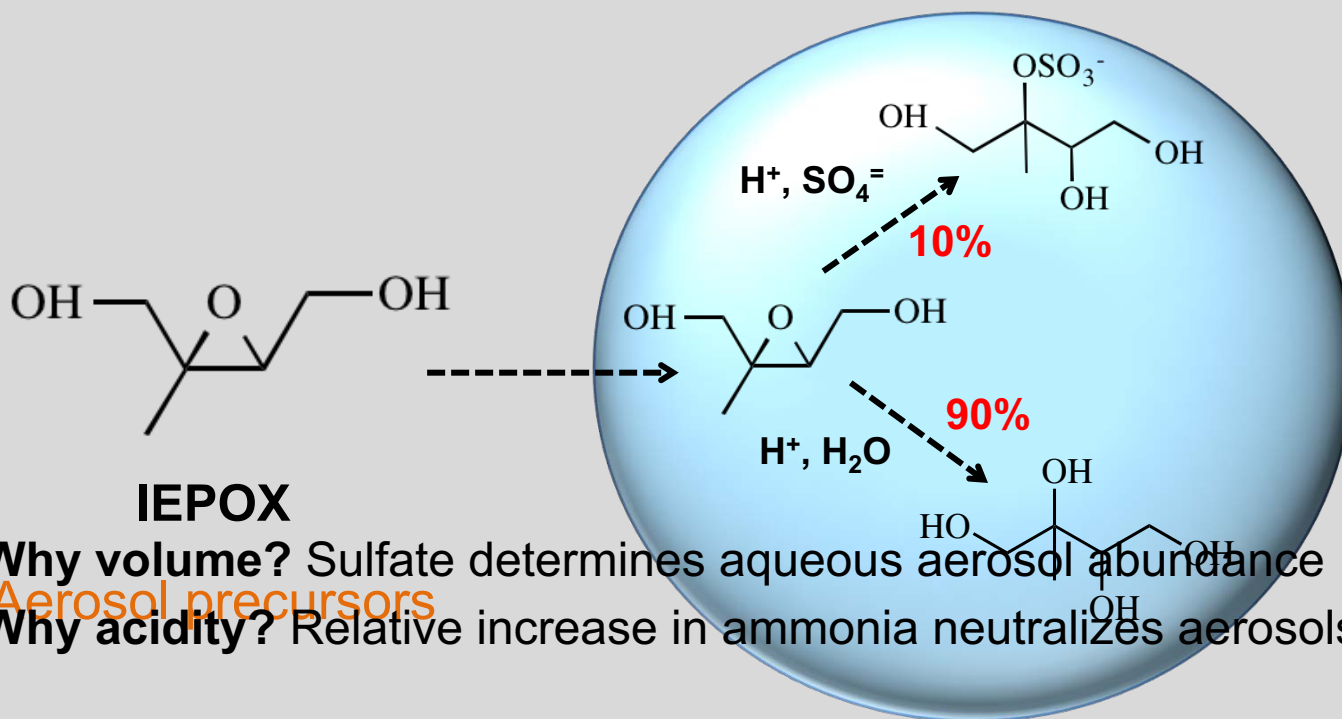
Xu et al., [2015a, 2015b]; Hu et al. [2015]

IEPOX-organosulfate formation



Sulfate correlation not due to nucleophilic addition

Acid-catalyzed ring cleavage to produce non-volatile species

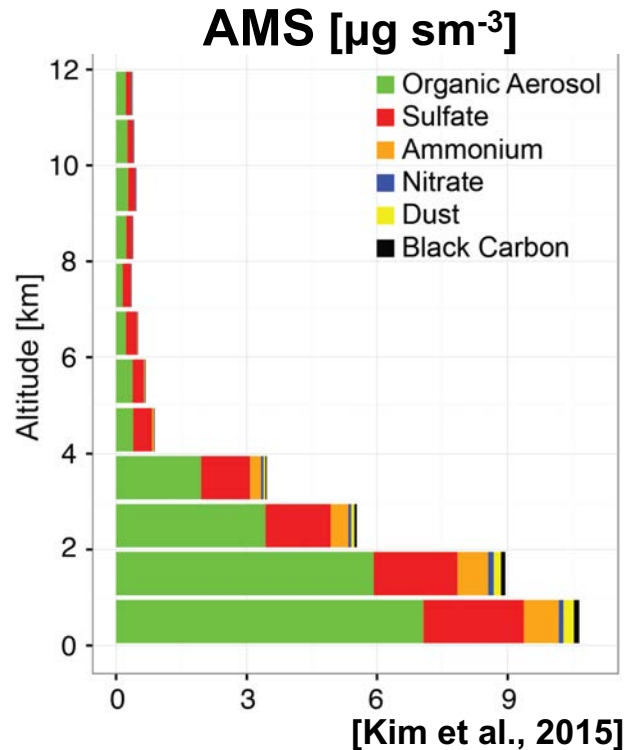
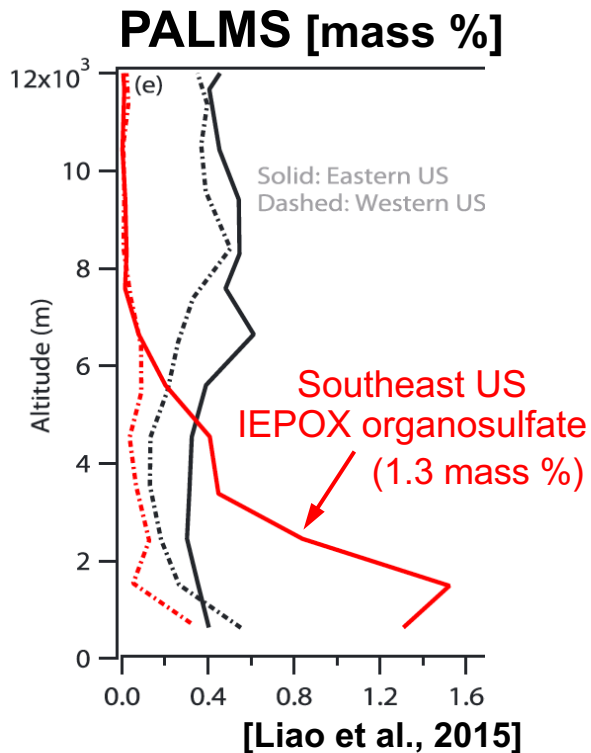


IEPOX secondary organic aerosol
(IEPOX SOA)

In our mechanism acid-catalyzed **sulfate addition is 10%** and acid-catalyzed **H₂O addition is 90%** of the fate of IEPOX

Aircraft observations constrain organosulfate formation

Additional support for limited role of sulfate channel from SEAC⁴RS
PALMS **IEPOX-organosulfate observations:**

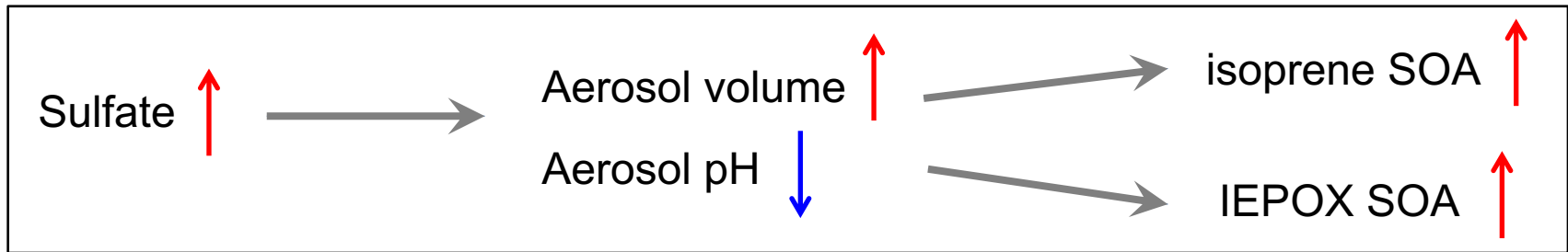


Boundary-layer IEPOX-organosulfate: **$0.14 \mu\text{g sm}^{-3}$**
(10% of IEPOX SOA)

Isoprene-derived organosulfates are **stable** during the aerosol lifetime
[Darer et al., 2011;
Hu et al., 2011]

Organosulfates from IEPOX are long-lived, so remain intact throughout the lifetime of the aerosol

Sulfate impacts aerosol acidity and volume



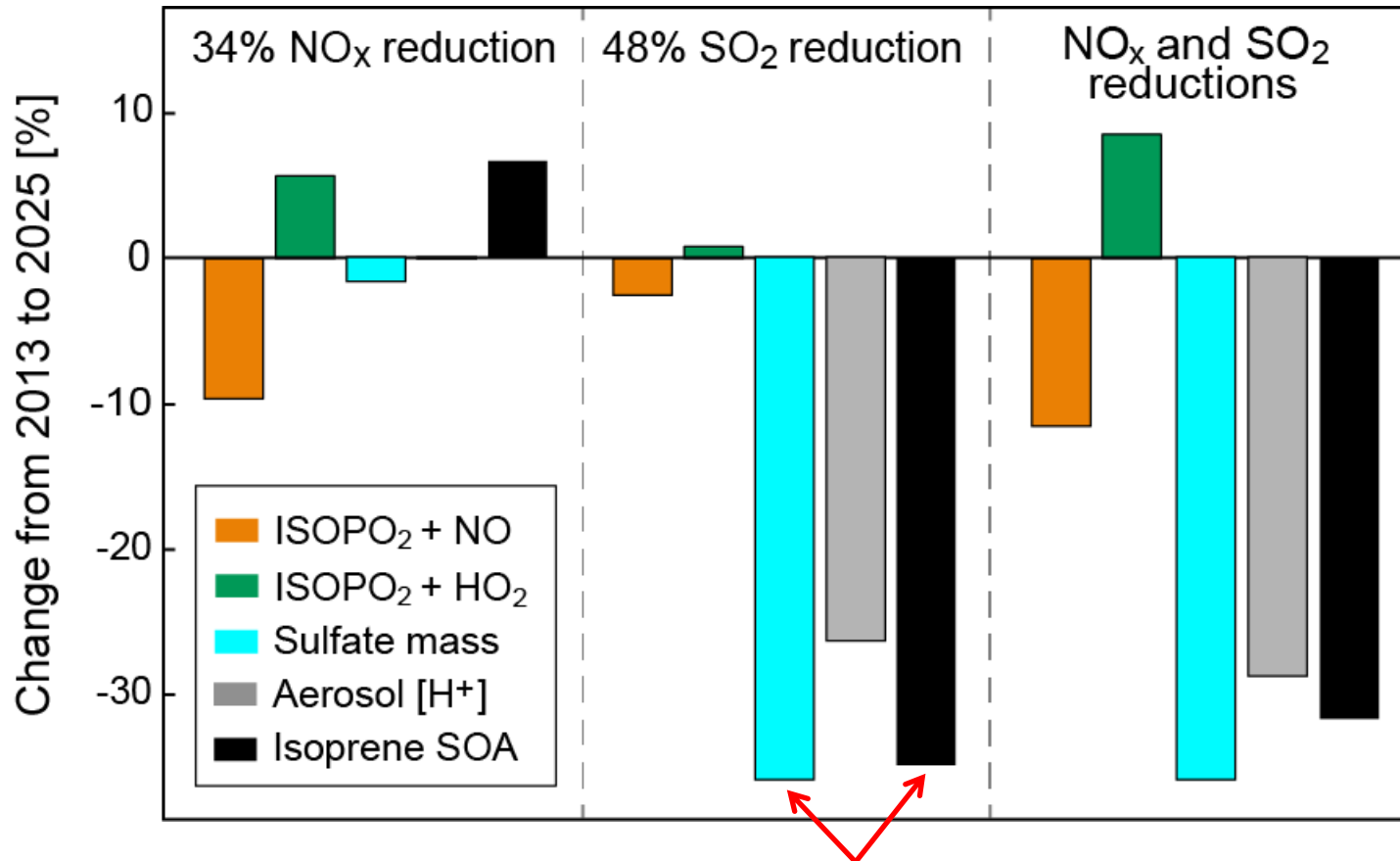
Why volume? Sulfate determines aqueous aerosol abundance

Why acidity? Relative increase in ammonia neutralizes aerosols

Effect of Anthropogenic Emission Reductions

USEPA projects emissions decline by **48% for SO₂** and **34% for NO_x** from 2013 to 2015

Test the impact on isoprene SOA using GEOS-Chem sensitivity simulations

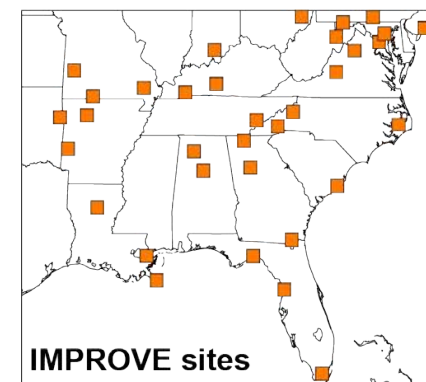
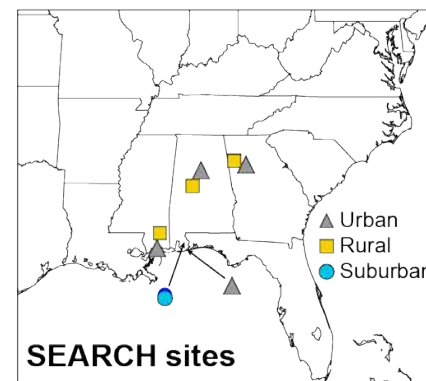
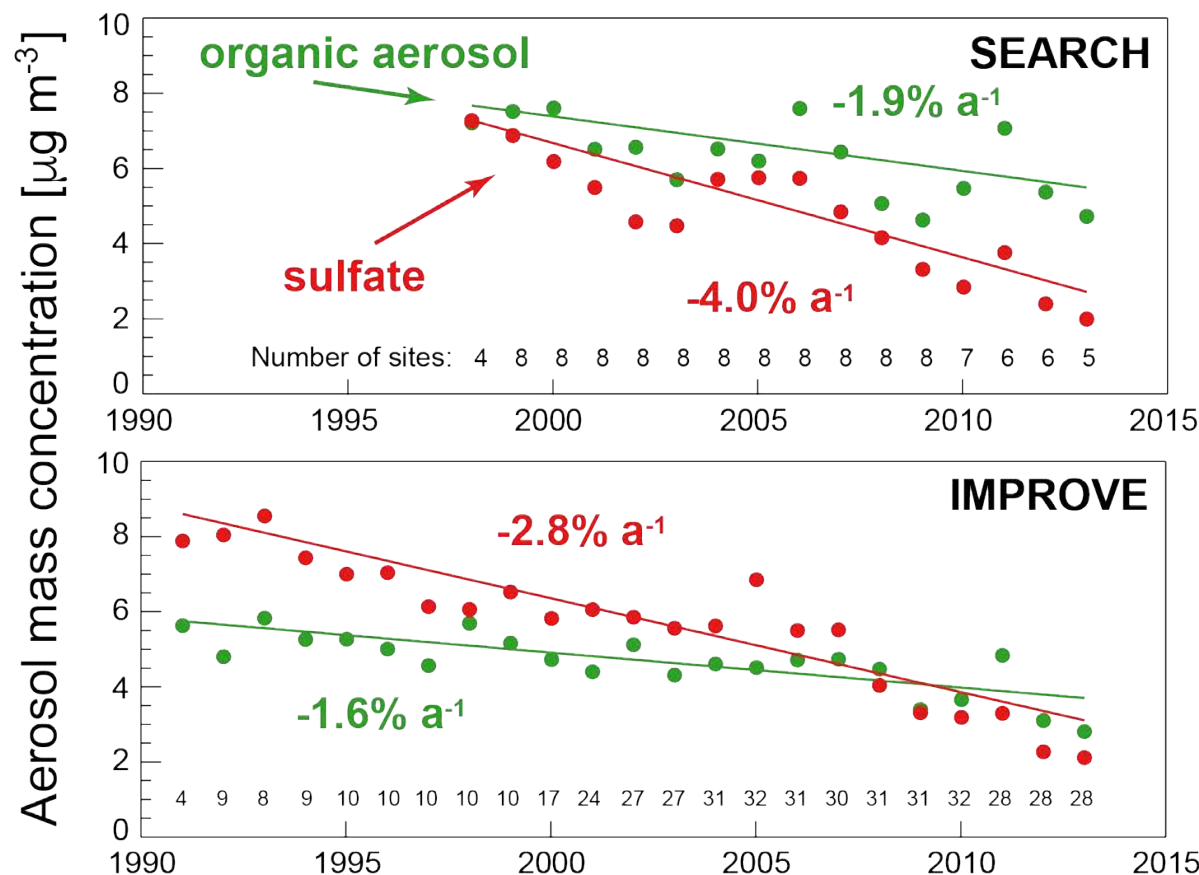


Near-equivalent response in **sulfate** and **isoprene SOA**

Factor of 2 co-benefit for PM_{2.5} from SO₂ emission controls

Observed decline in sulfate and OA in the Southeast US

Observed 1991-2013 trends in summertime (Jun-Aug) **sulfate** and **OA**

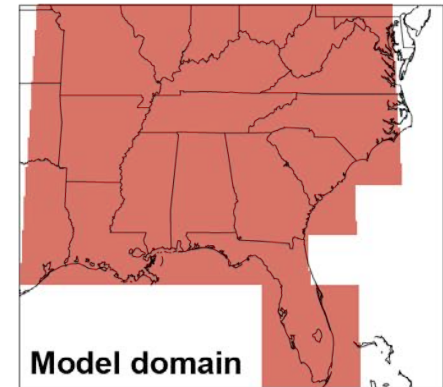
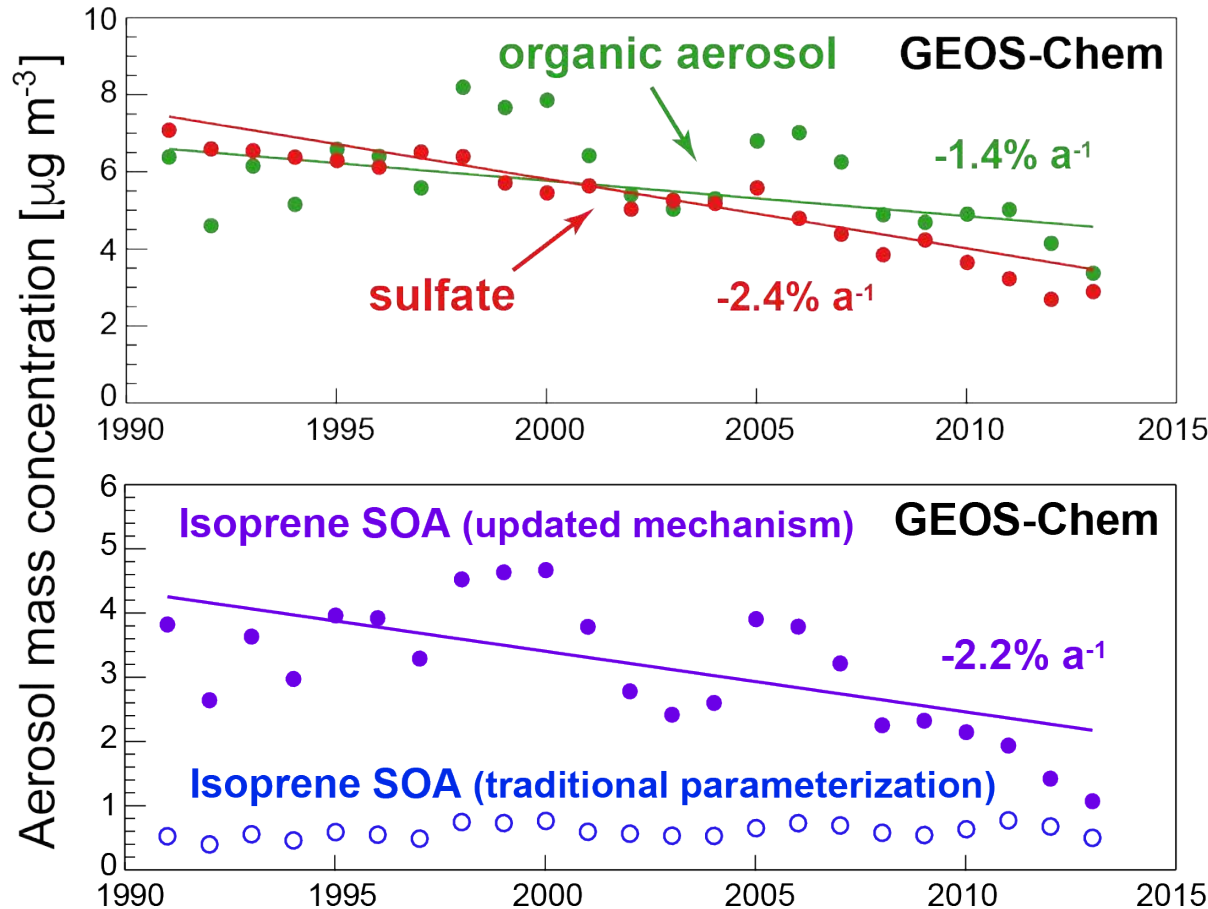


Steeper decline in sulfate at SEARCH than IMPROVE sites – greater urban influence.
Similar OA trends supports **biogenic SOA driving the trend**

OA instead of sulfate is now the dominant $\text{PM}_{2.5}$ component in the Southeast US

Modelled OA decreases due to decline in isoprene SOA

Model 1991-2013 trends in summertime **sulfate** and **OA**, and isoprene SOA (**traditional** and **updated** schemes)



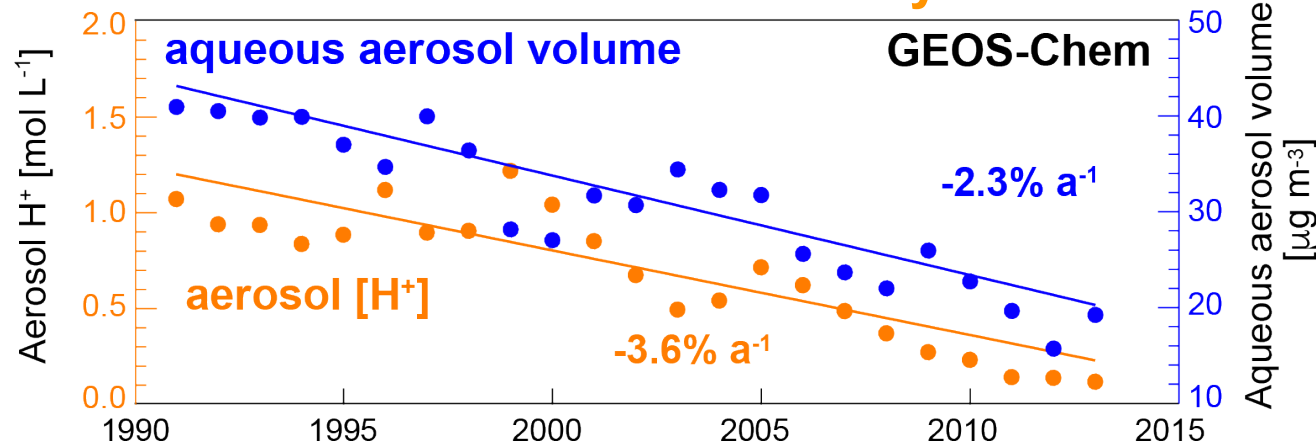
No significant trend in the traditional parameterization. Would underestimate OA for much of the record.

Model includes annual trends in anthropogenic emissions of SO_2 , NO_x , and VOCs. Isoprene emissions exhibit large interannual variability driven by temperature.

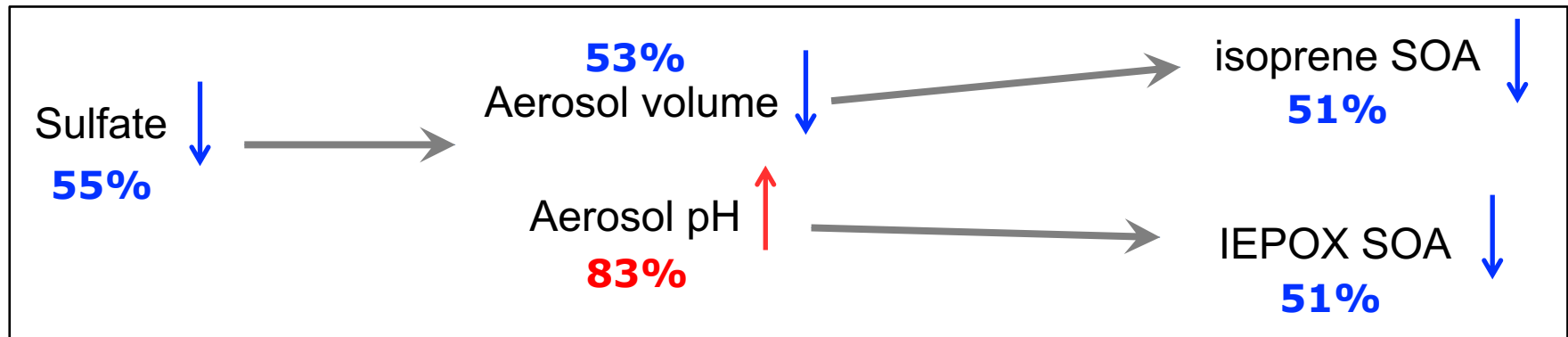
Majority of decline in modelled OA is due to isoprene SOA

Modelled isoprene SOA decreases due to decline in sulfate

Model 1991-2013 trends in summertime aqueous aerosol
volume and **acidity**

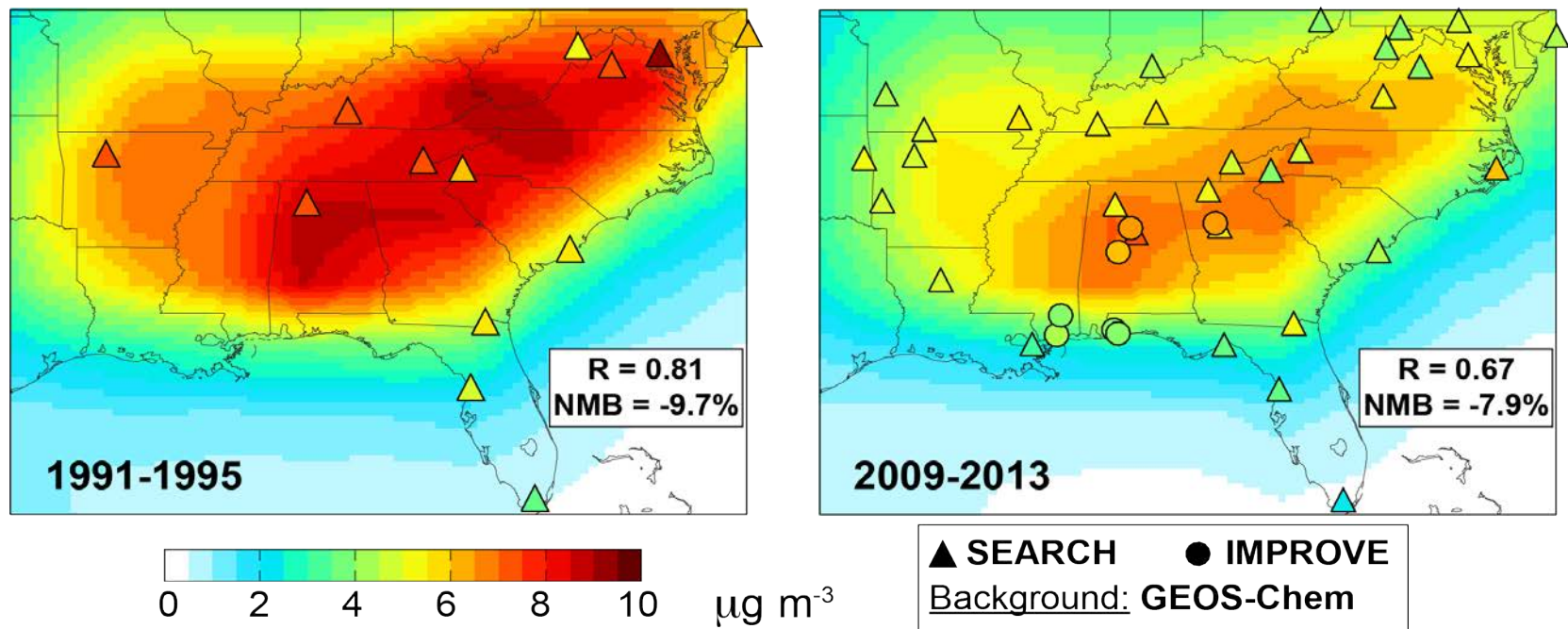


Decline in sulfate (dominant aqueous aerosol component) **decreases aqueous aerosol volume** and **increases aqueous aerosol pH**



Spatial distribution of organic aerosol trends

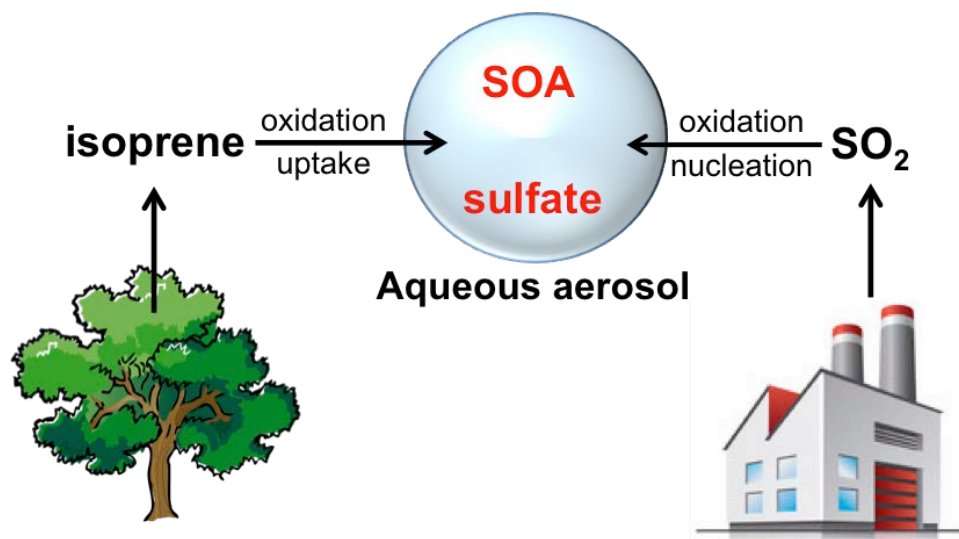
Spatial distribution of five-year mean summertime OA from the model and observations at the start and end of the record



No significant change in OA spatial distribution in the observations or model supports biogenic SOA driving the OA trend.

Small model normalized mean bias (NMB) and similar change in OA in the model and observations

Concluding Remarks



- Biogenic isoprene secondary organic aerosol (SOA) formation by reactive uptake to aqueous aerosol is modulated by sulfate that in turn drives changes in aqueous aerosol volume and acidity.
- Observations in the Southeast US show a large long-term (1991-2013) decline in summertime (Jun-Aug) OA, but the cause of this trend is uncertain.
- The GEOS-Chem model, updated to include aqueous-phase isoprene SOA formation, reproduces the observed trend.
- The model attributes decreases in OA to decline in the isoprene SOA yield as sulfate decreases (driving lower aqueous aerosol volume and acidity).
- This SO₂ emission controls to decrease sulfate have had a large air quality co-benefit in the Southeast US by also decreasing organic aerosol (OA).