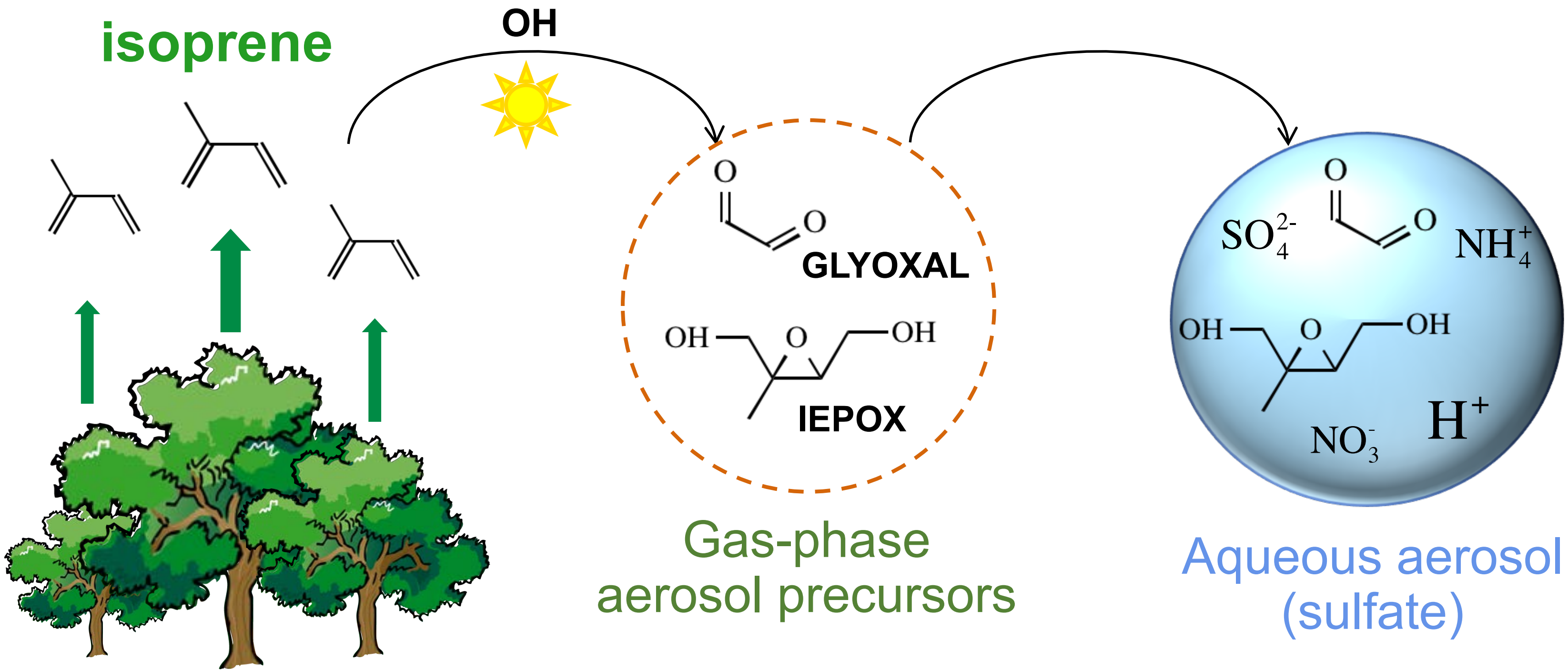
Air quality co-benefit of SO_2 emission controls to decrease biogenic organic aerosol and sulfate



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

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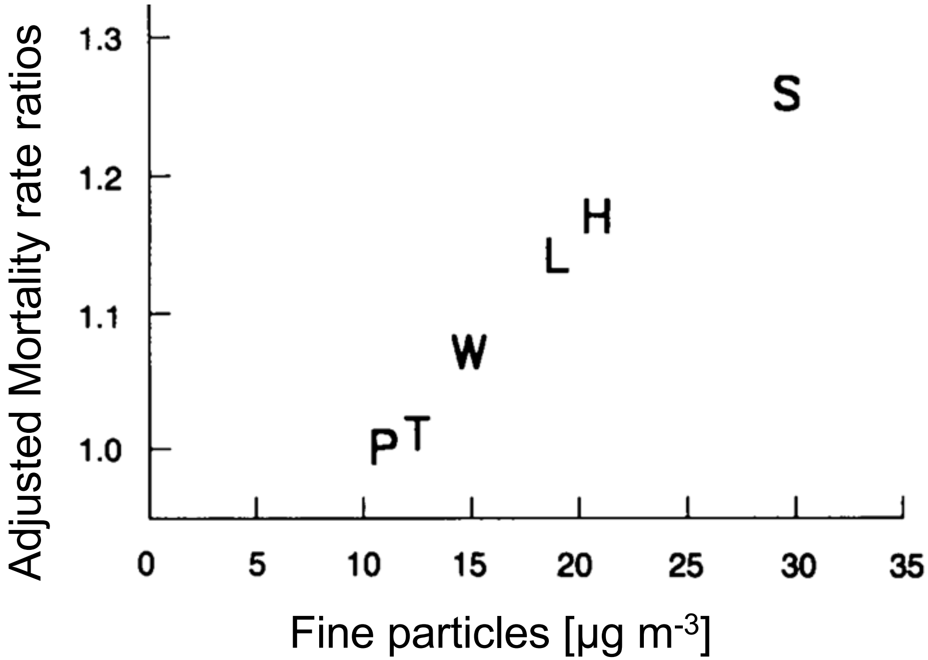
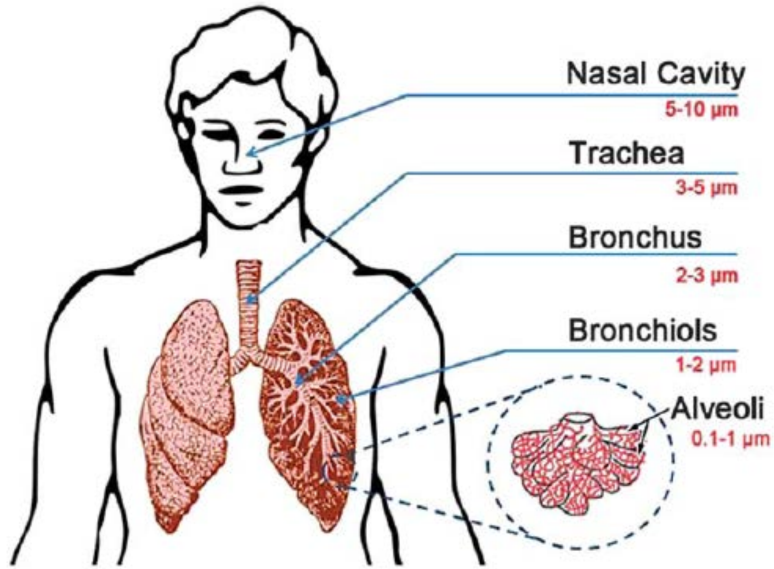
Aerosols Impact Climate, Human Health, and Visibility

Fine particles are associated with **increased mortality**



[Dockery et al., 1993]

Fine particles travel deep into the lungs



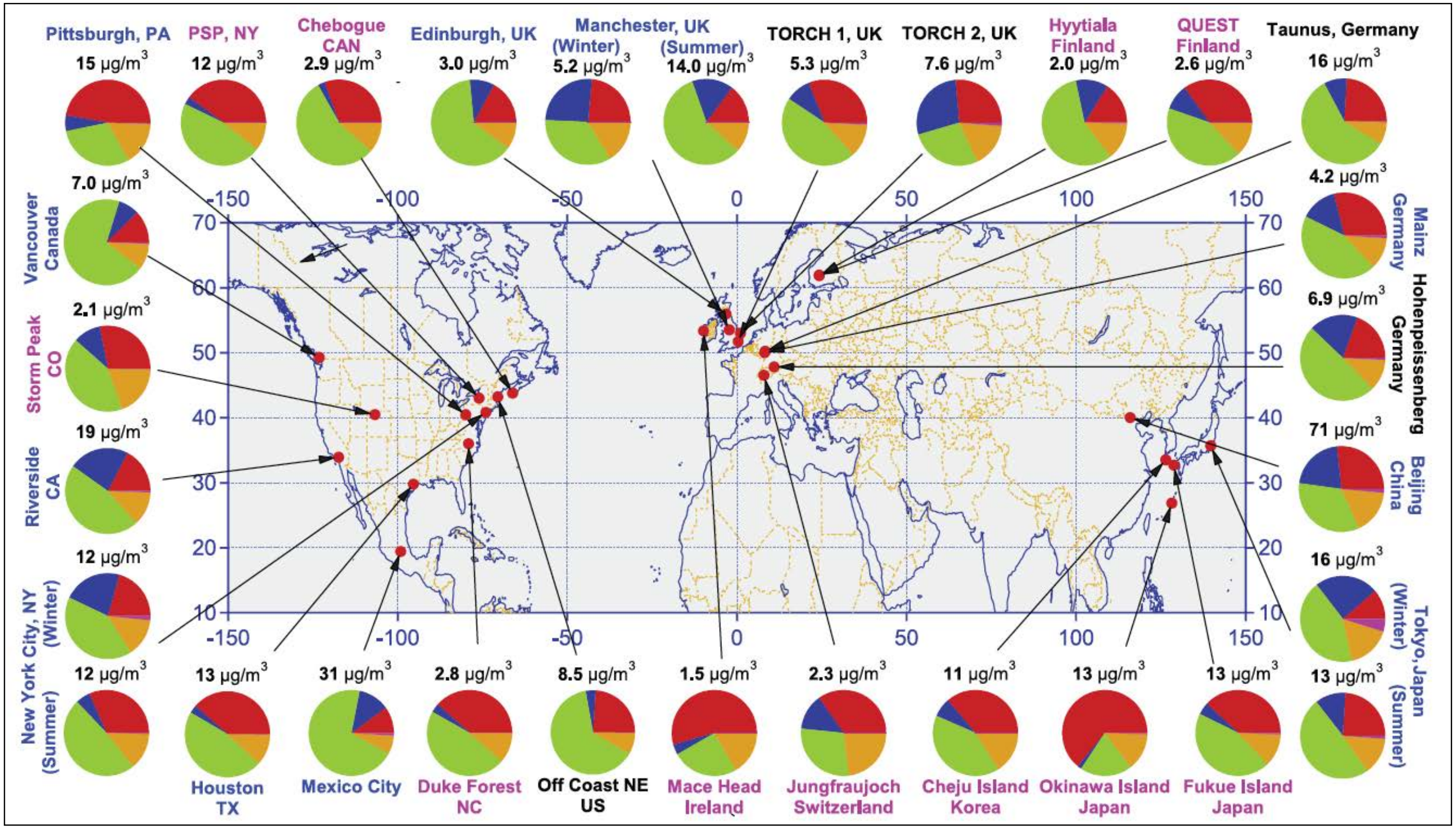
[Kumar et al., 2014]

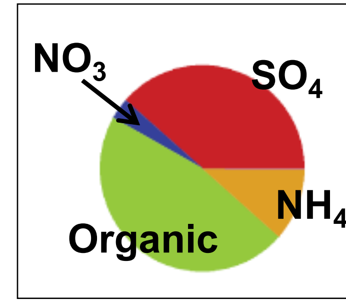
<u>**Comprised on many components:**</u> **sulfate**, nitrate, ammonium, **organics** (**organic aerosol**, **OA**), mineral dust, elemental or black carbon (BC)

Sulfate, nitrate, ammonium → **hygroscopic** (**aqueous aerosol**)

Organic Aerosol is Ubiquitous in the Atmosphere

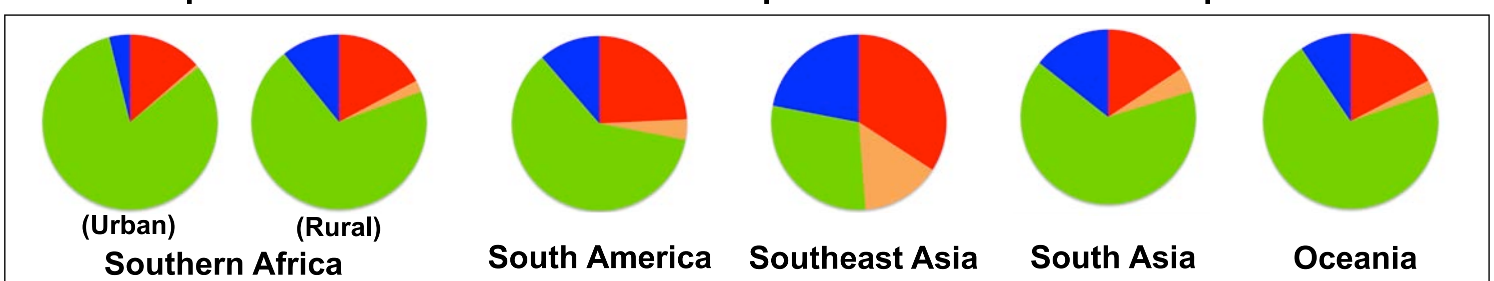
Northern hemisphere aerosol components





[Zhang et al., 2007]

Tropics and southern hemisphere aerosol components

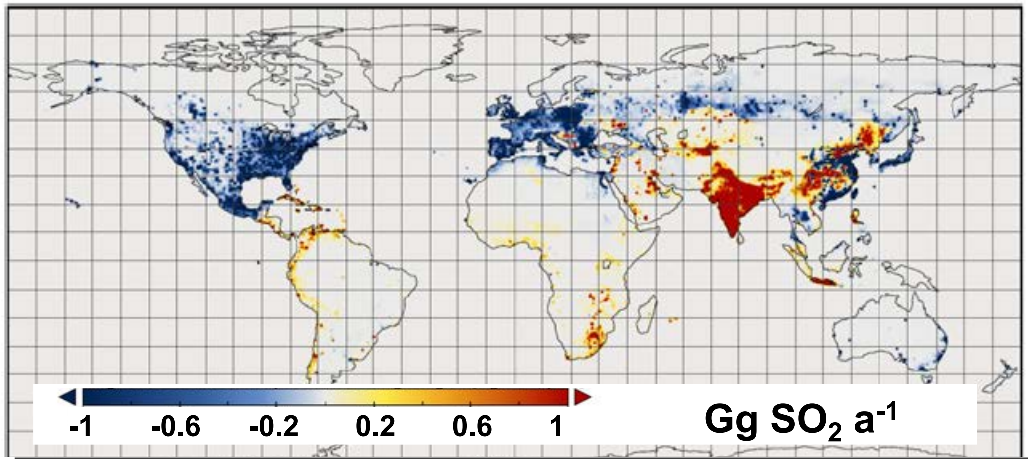


[IPCC, 2013]

Organic Aerosol (OA) Fraction is Increasing

In many parts of the world the OA contribution to $PM_{2.5}$ is increasing as SO_2 emissions (and sulfate) decline

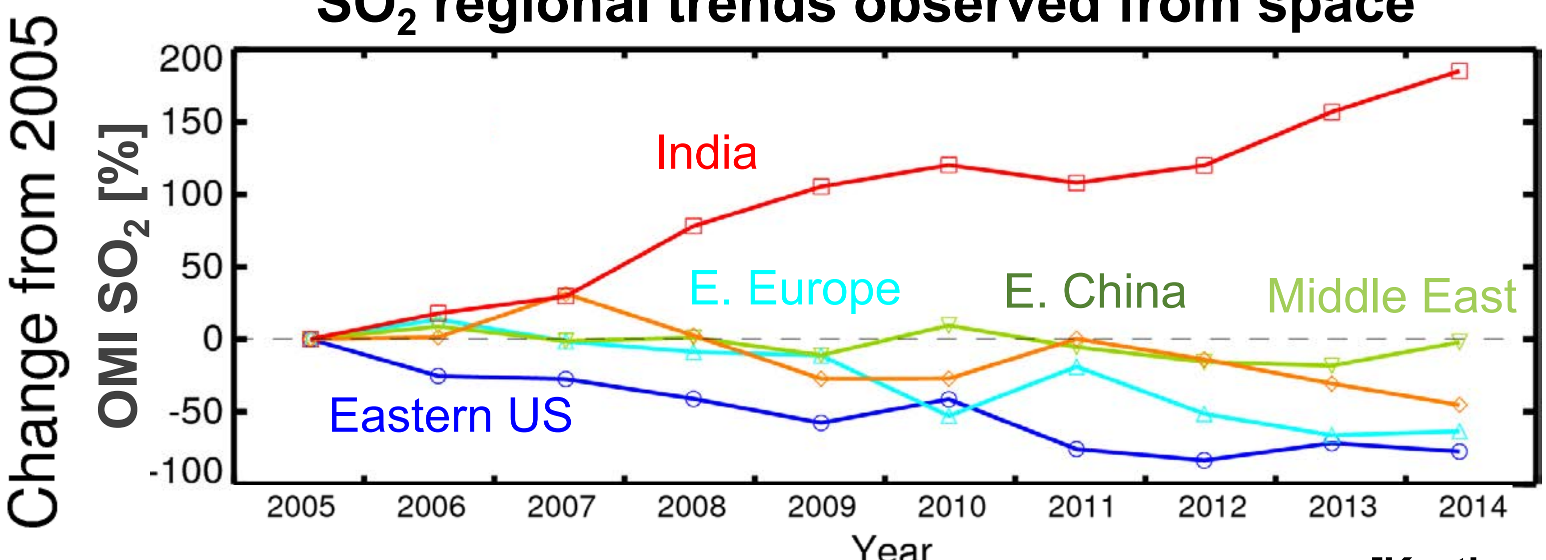
2010 minus 2005 SO_2 emissions



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

[Klimont et al., 2013]

SO_2 regional trends observed from space

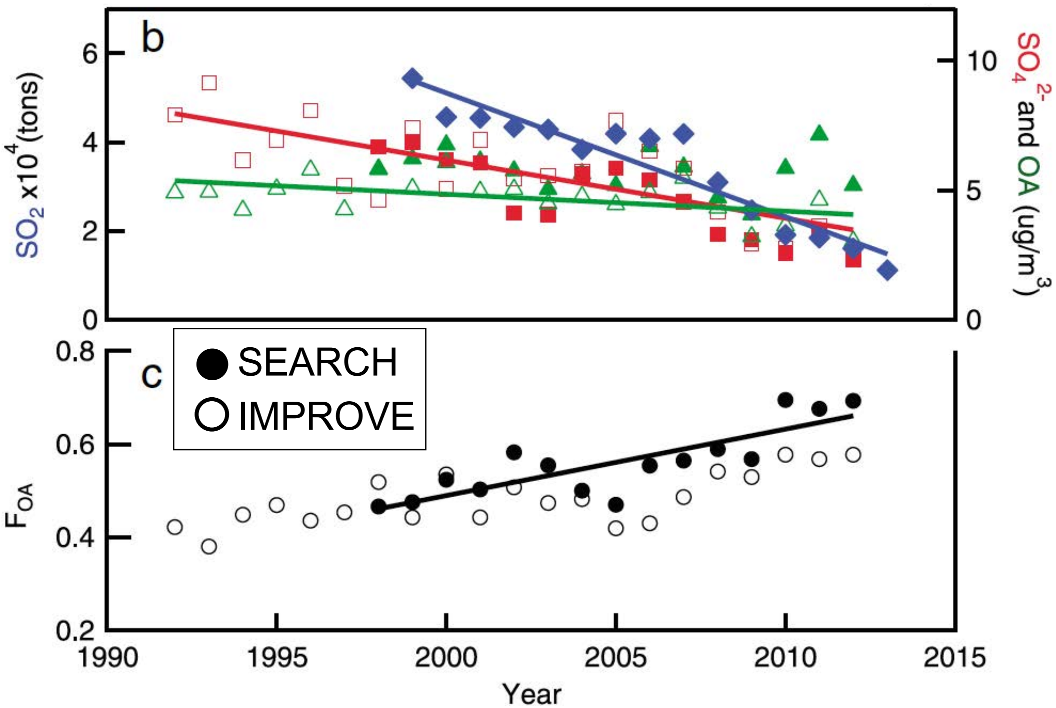


[Krotkov et al., 2015]

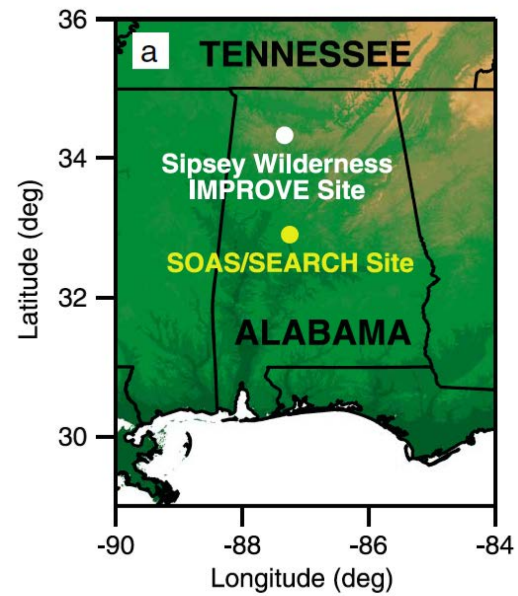
OA Fraction is Increasing – Southeast US

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

SO_2 emissions, and sulfate and organic aerosol mass



Rural Southeast US monitoring sites



[Attwood et al., 2014]

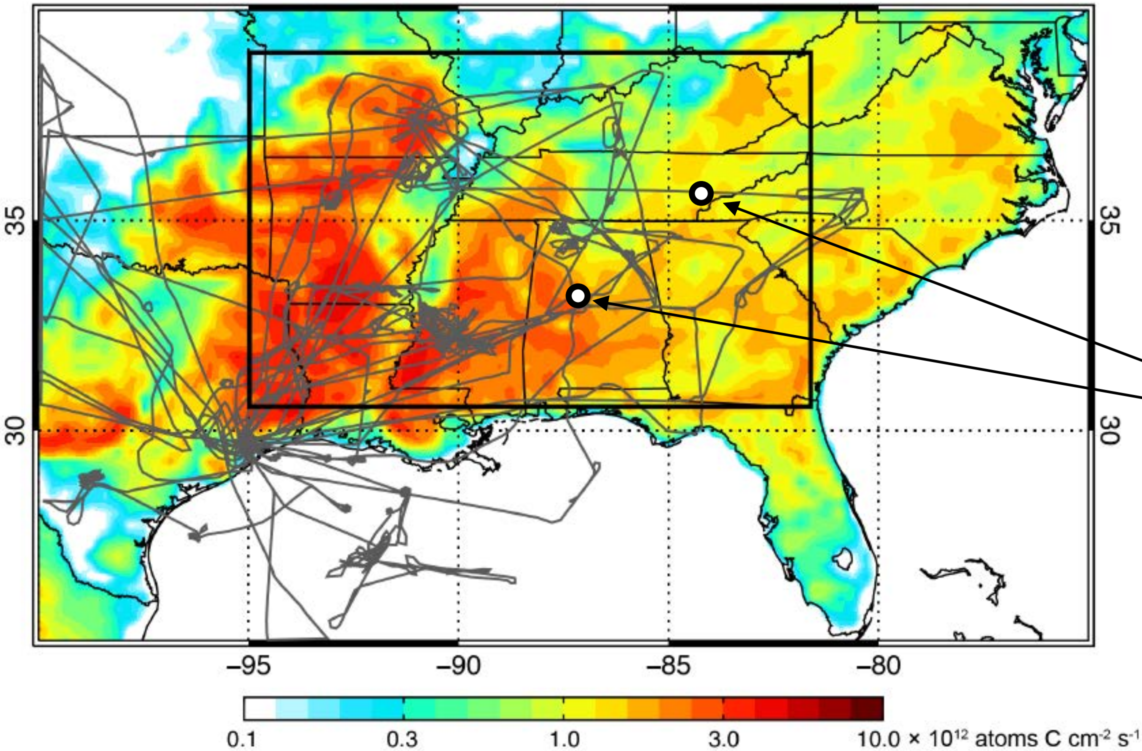
Sites impacted by urban, industrial, **biogenic**, and agricultural emissions.

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

Multiple Campaigns in the Southeast US in 2013

Multiple summer 2013 campaigns to understand biogenic-anthropogenic interactions

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



Aircraft campaign
(Aug-Sep 2013)

SOAS
Southern Oxidant & Aerosol Study

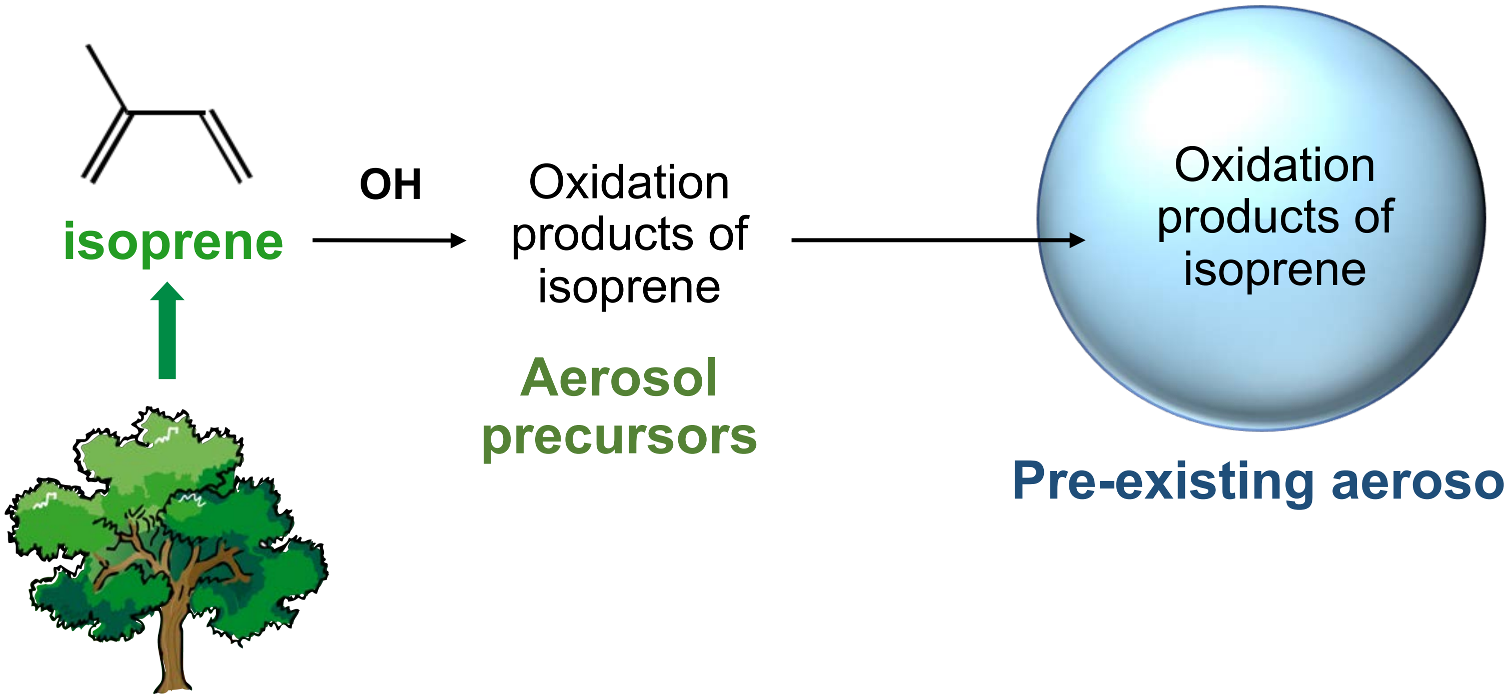
Surface campaign
(Jun-Jul 2013)

[P. Kim et al., 2015]

In summer the Southeast US is a large source of **biogenic isoprene** (high temperatures) and **anthropogenic sulfate** (oxidation of SO_2)

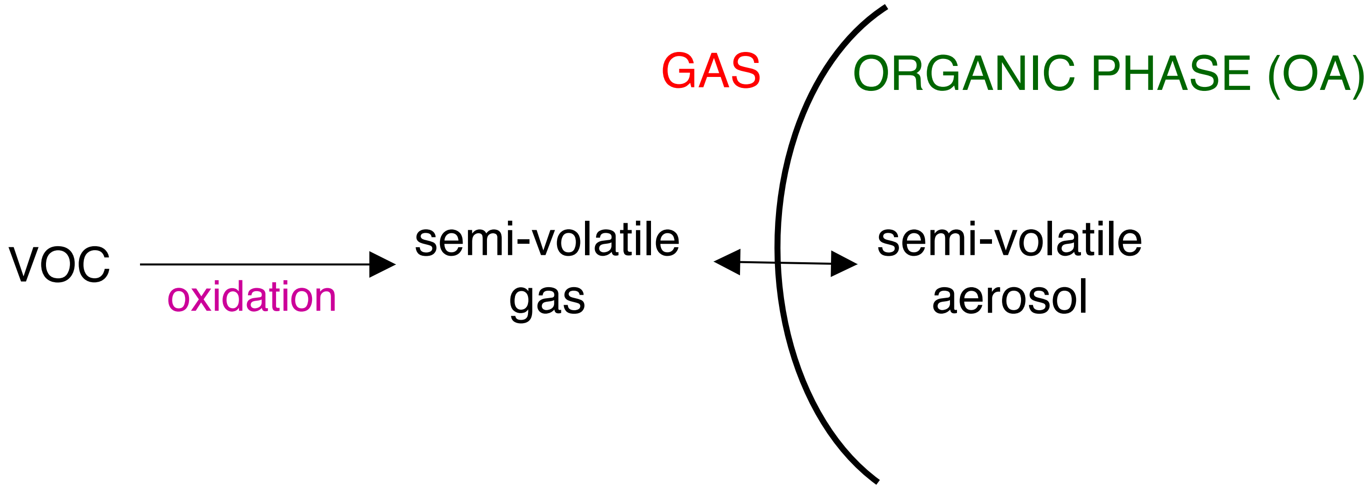
Isoprene oxidizes to form organic aerosol precursors

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

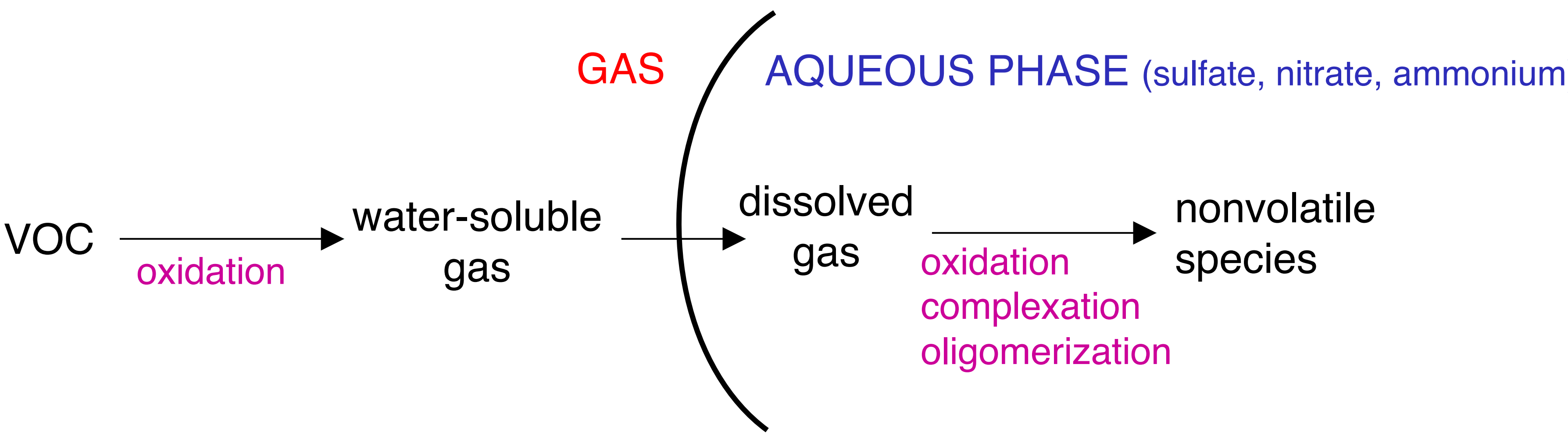


Two approaches to represent secondary organic aerosol

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

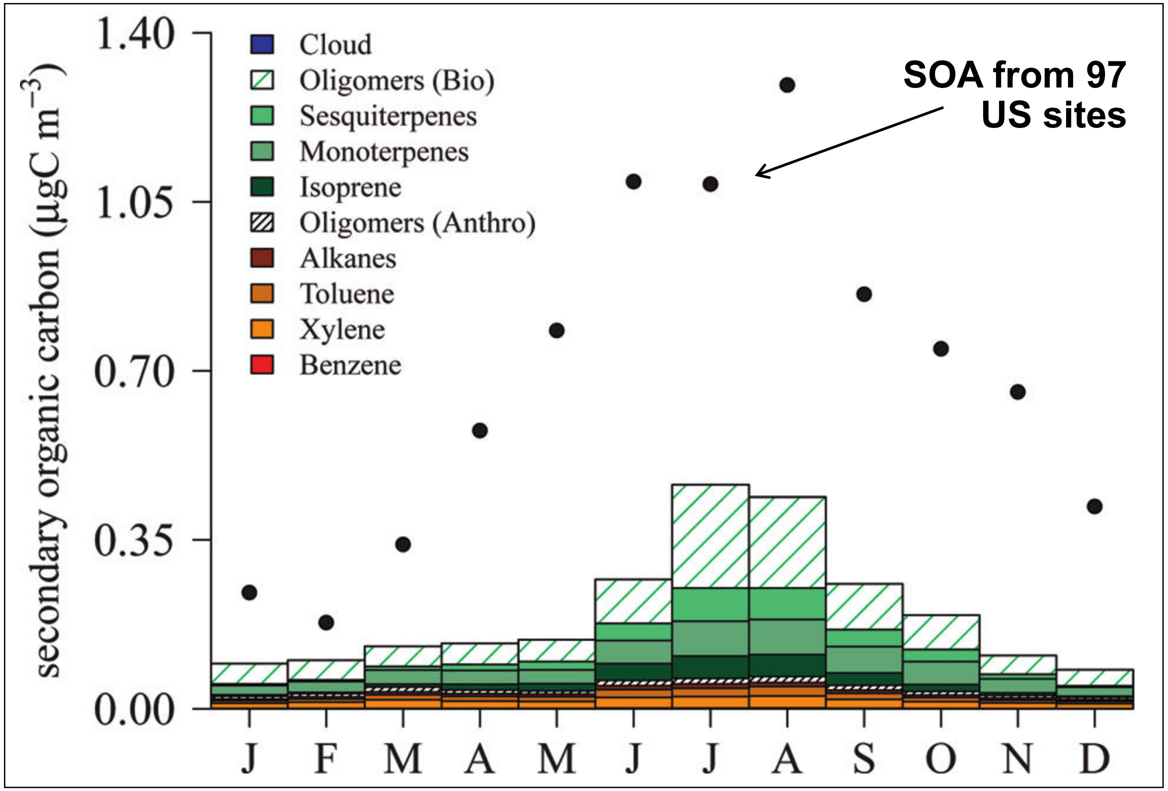


B. **Alternate model** for irreversible uptake to aqueous aerosol



The classical model routinely underestimates SOA

Measured vs modeled SOA across the US



[Carlton et al., 2010]

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

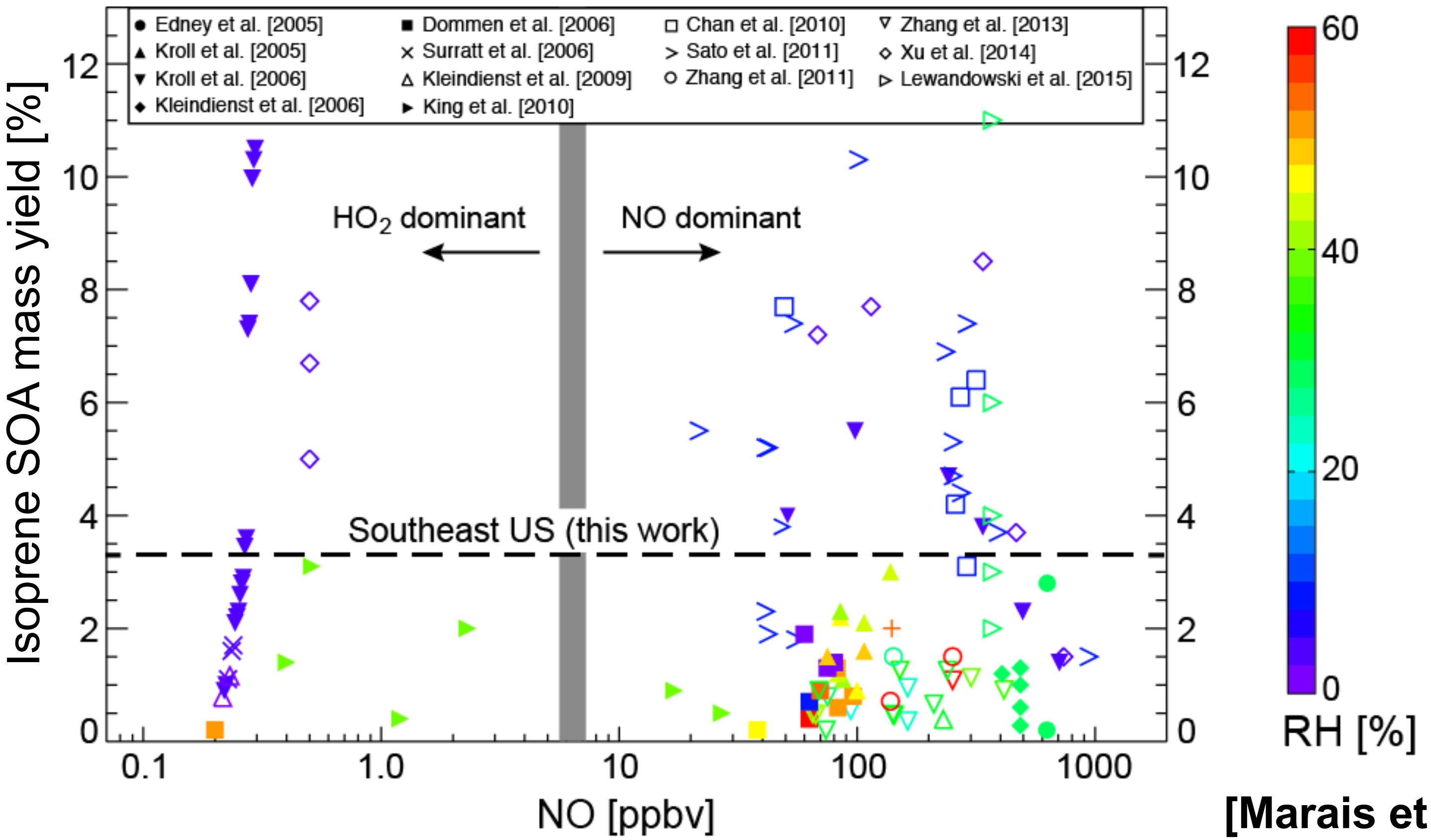
Limits ability to determine impact of isoprene SOA on **human health**

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

Classical model based on chamber experiments

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

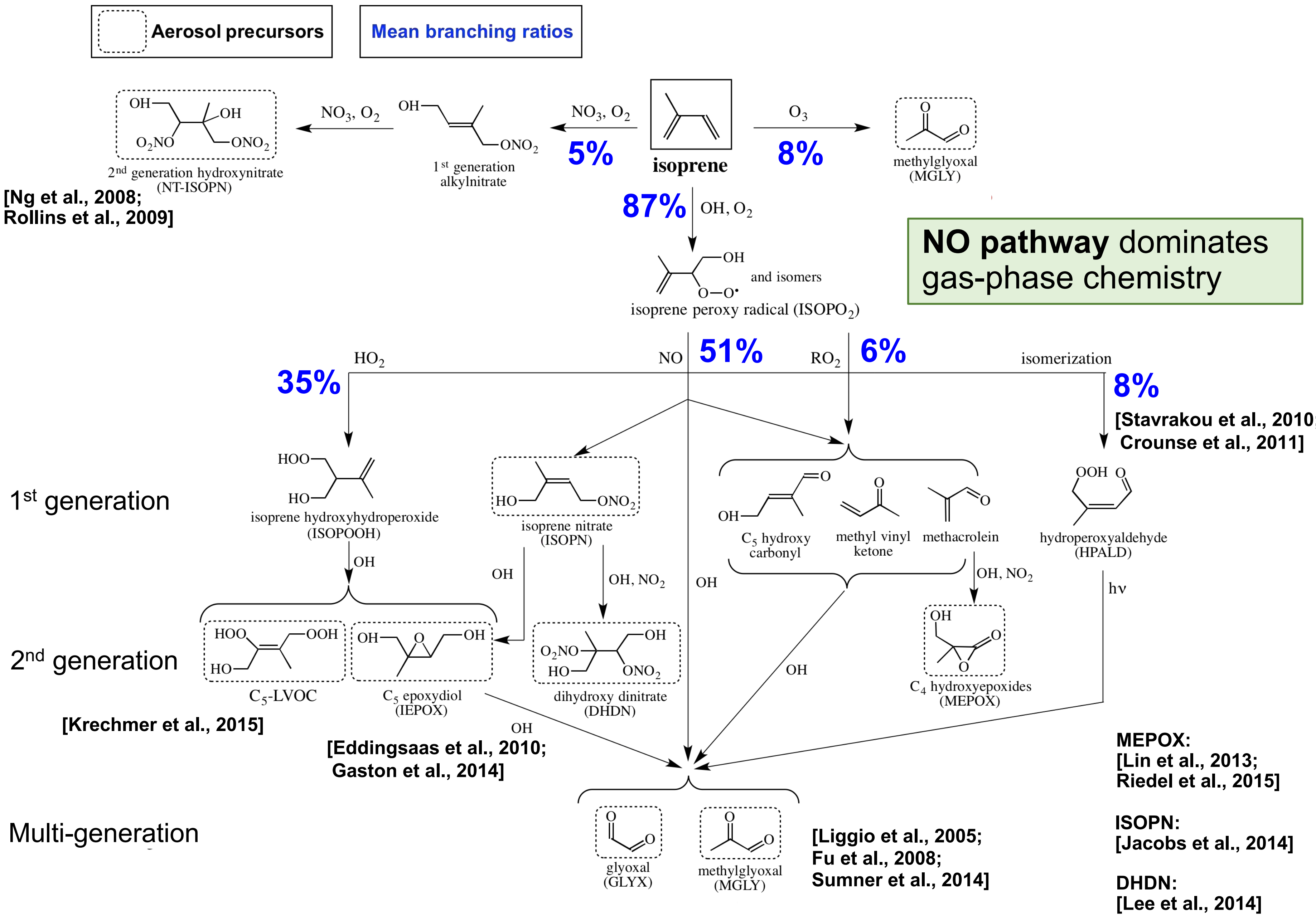
Compilation of chamber study isoprene + OH SOA mass yields



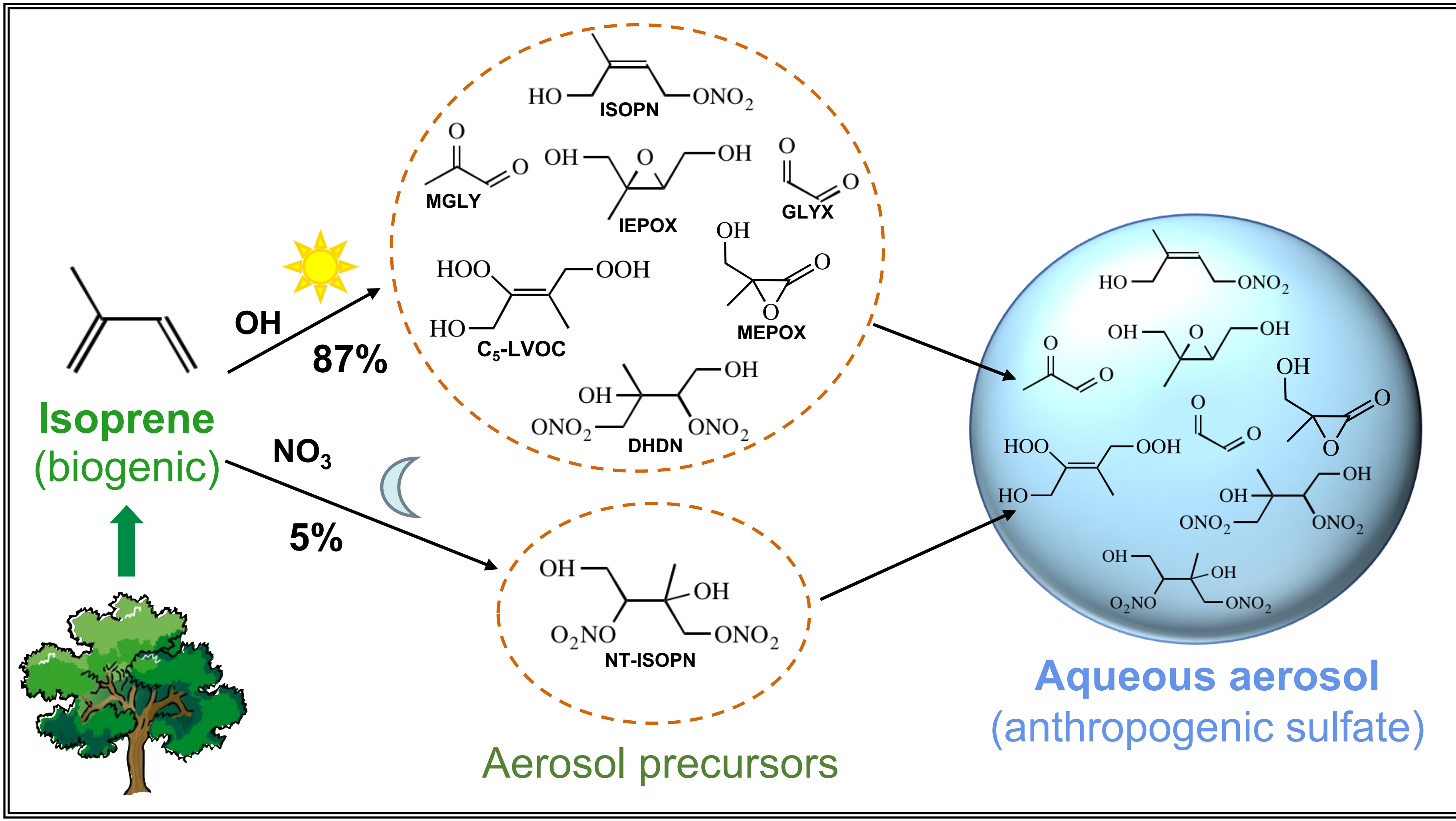
[Marais et al., 2016]

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

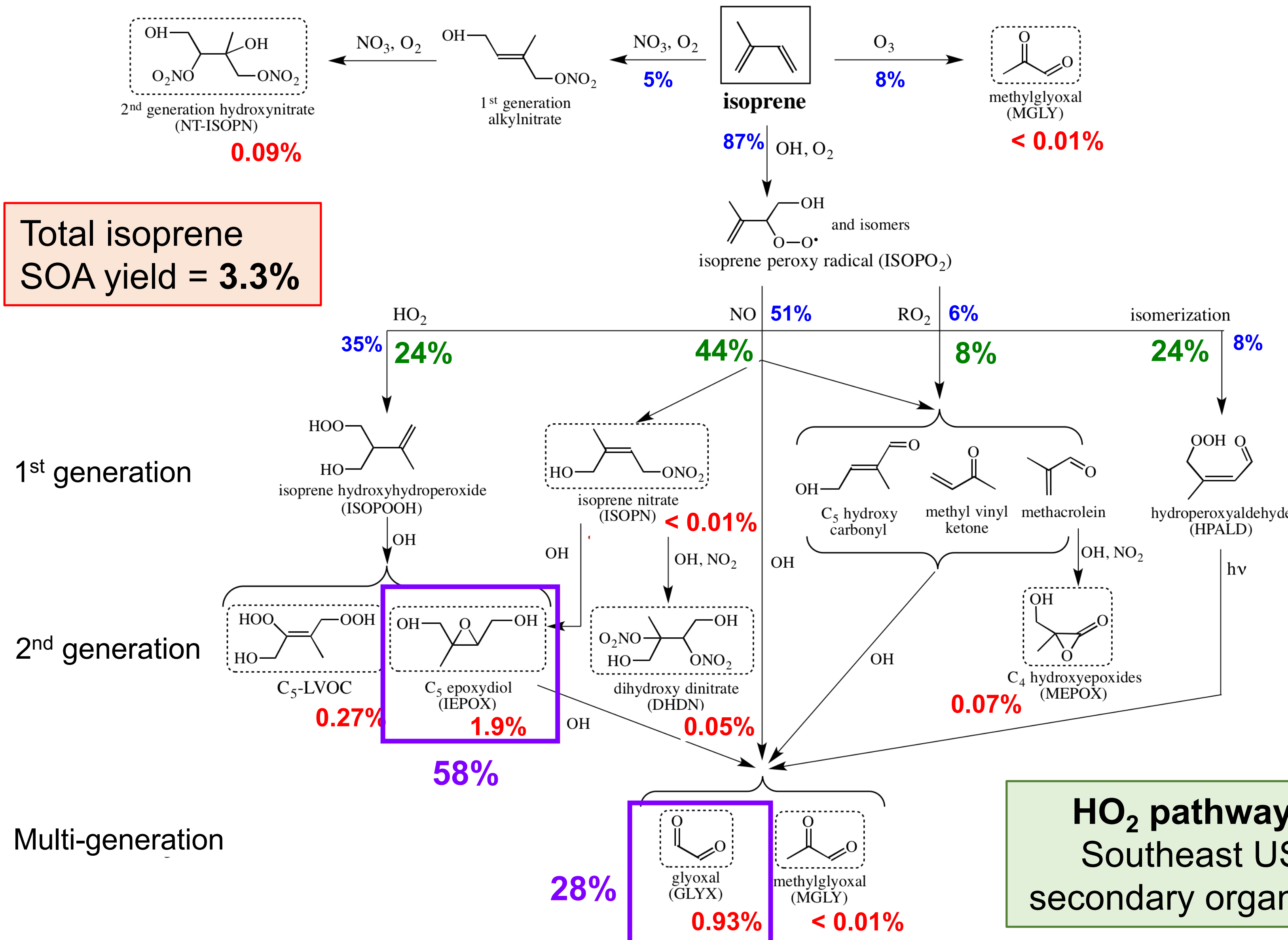


Aqueous-Phase Mechanism Framework



GEOS-Chem Isoprene SOA Yields in the Southeast US

Aerosol precursors | Mean branching ratios | Aerosol yield per unit isoprene | Share of glyoxal formation



Total isoprene SOA yield = **3.3%**

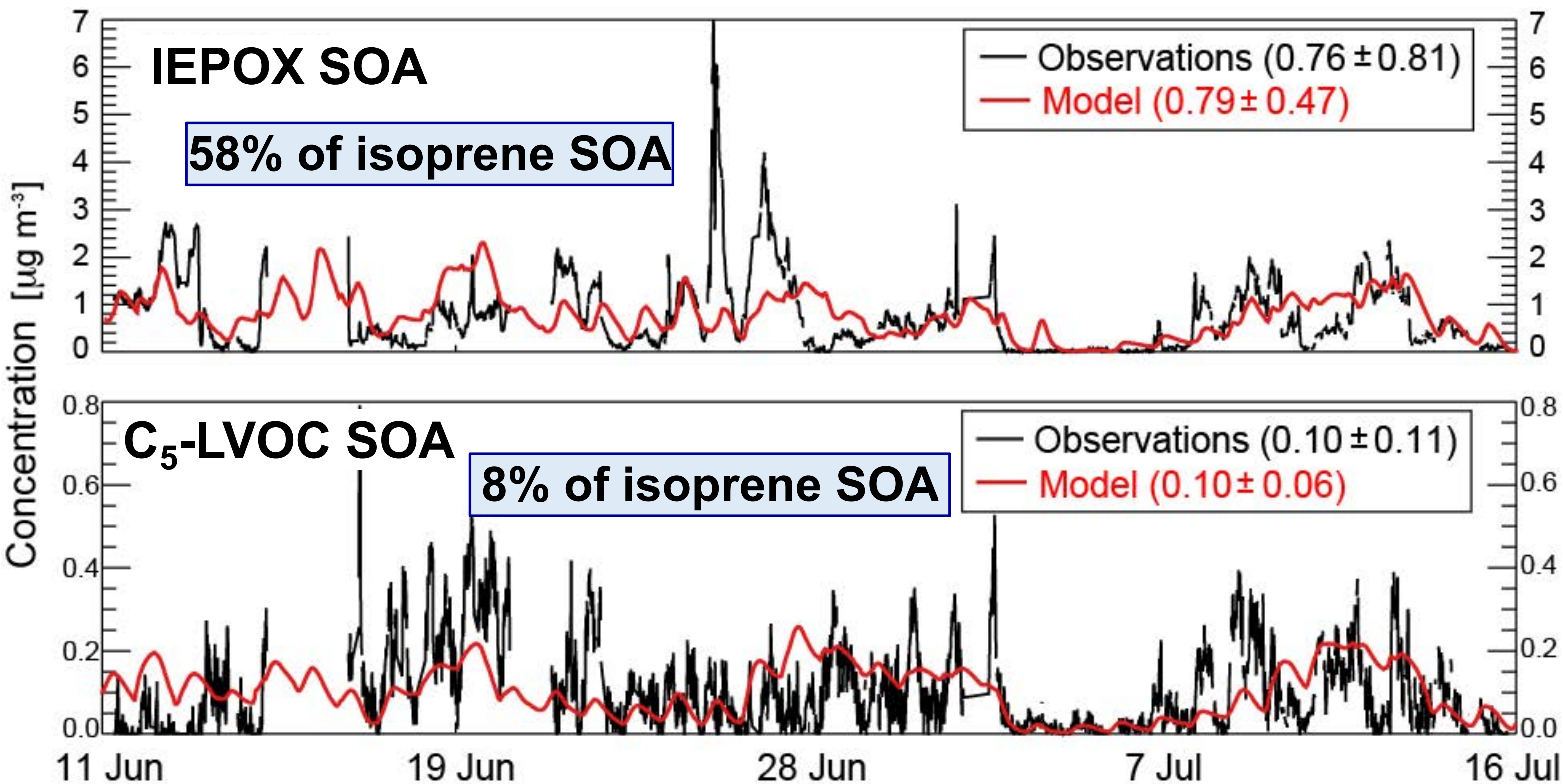
HO_2 pathway is **73%** of Southeast US isoprene secondary organic aerosol

Observational Constraints on Isoprene SOA Components

$$\mathrm{ISOP} \xrightarrow[87\%]{\mathrm{OH,\ O_2}} \mathrm{ISOPO_2} \xrightarrow[35\%]{\mathrm{HO_2}} \mathrm{ISOPOOH} \xrightarrow[75\%]{\mathrm{OH}} \mathrm{IEPOX}$$

$$\mathrm{ISOPOOH} \xrightarrow[0.5\%]{\mathrm{OH}} \mathrm{C_5\text{-}LVOC}$$

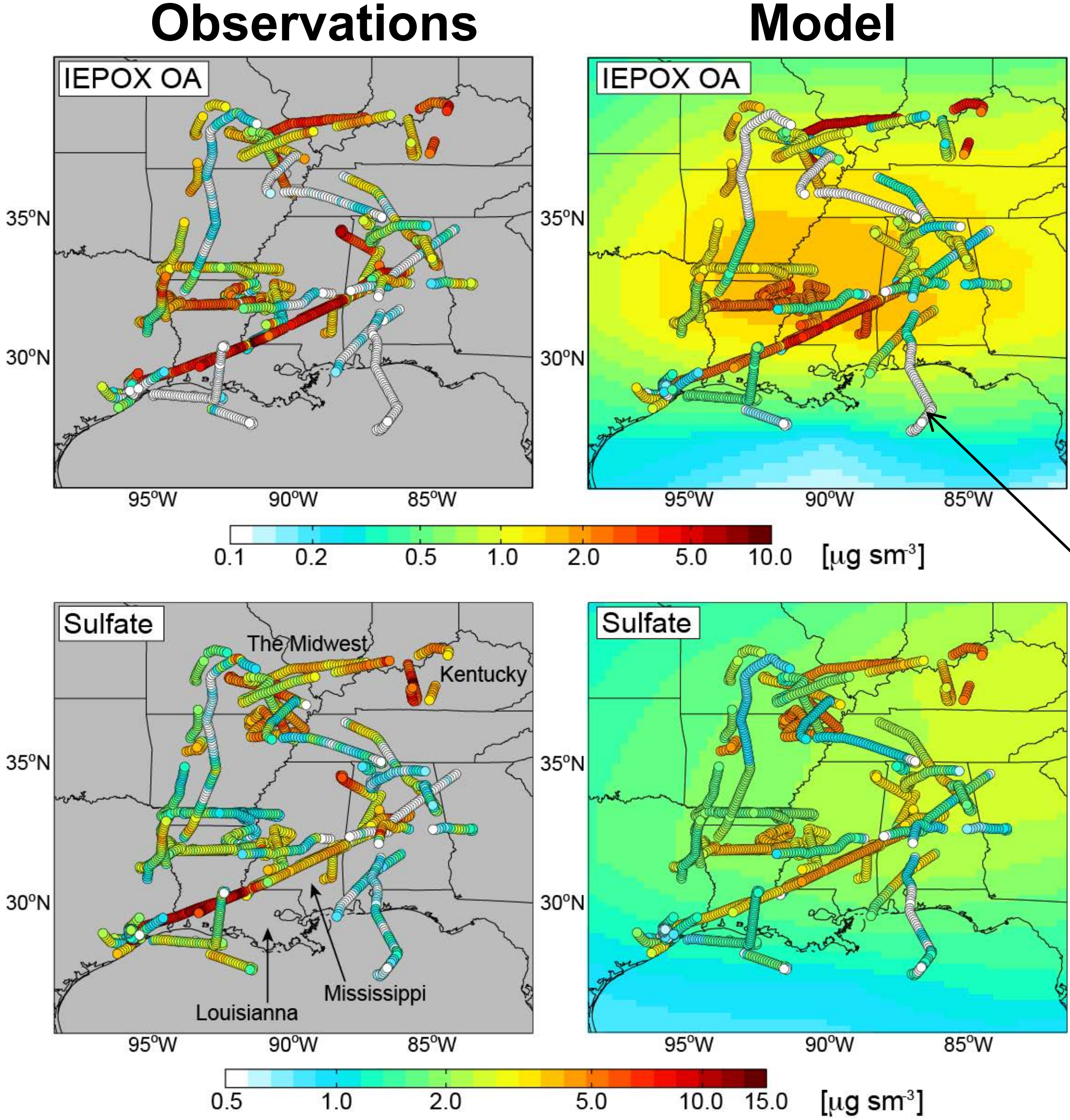
Secondary organic aerosol from IEPOX and non-volatile C_5-LVOC at Centreville, AL (SOAS campaign; Jun-Jul 2013)



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

Spatial Distribution of IEPOX SOA

SEAC^{4}RS (Aug-Sep 2013) boundary-layer IEPOX SOA and sulfate



Mean IEPOX SOA:
AMS: **1.4** ± 1.4 μg sm^{-3}
GC: 1.3 ± 1.2 μg sm^{-3}

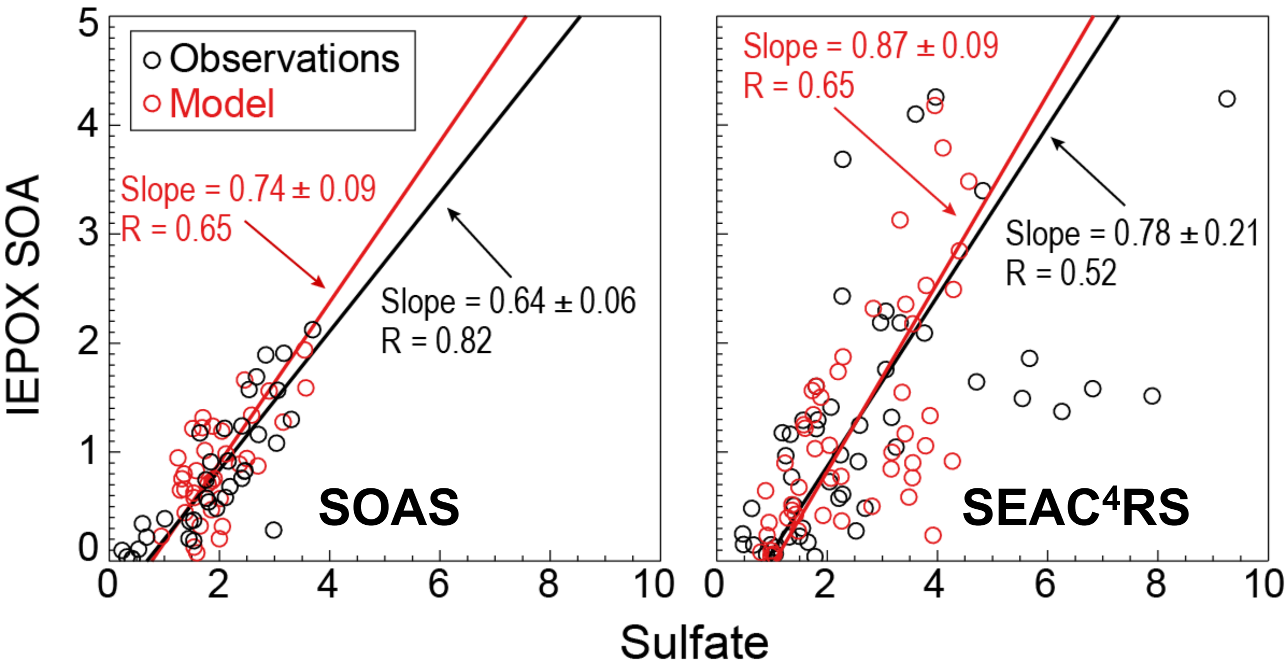
Background is daytime mean during SEAC^{4}RS

Points are data along the SEAC^{4}RS flight tracks

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

What modulates IEPOX OA in the Southeast US?

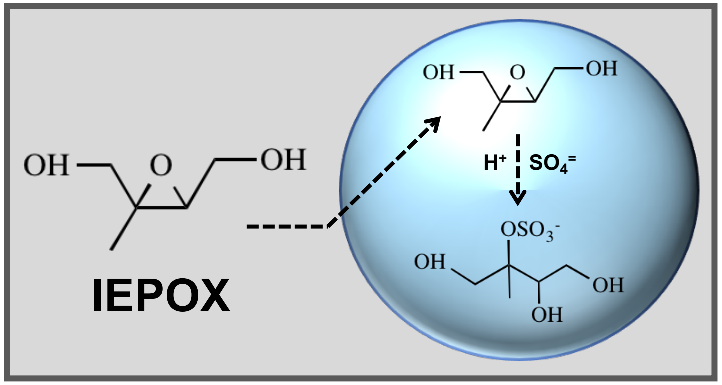
IEPOX SOA and Sulfate correlation during SOAS and SEAC⁴RS



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

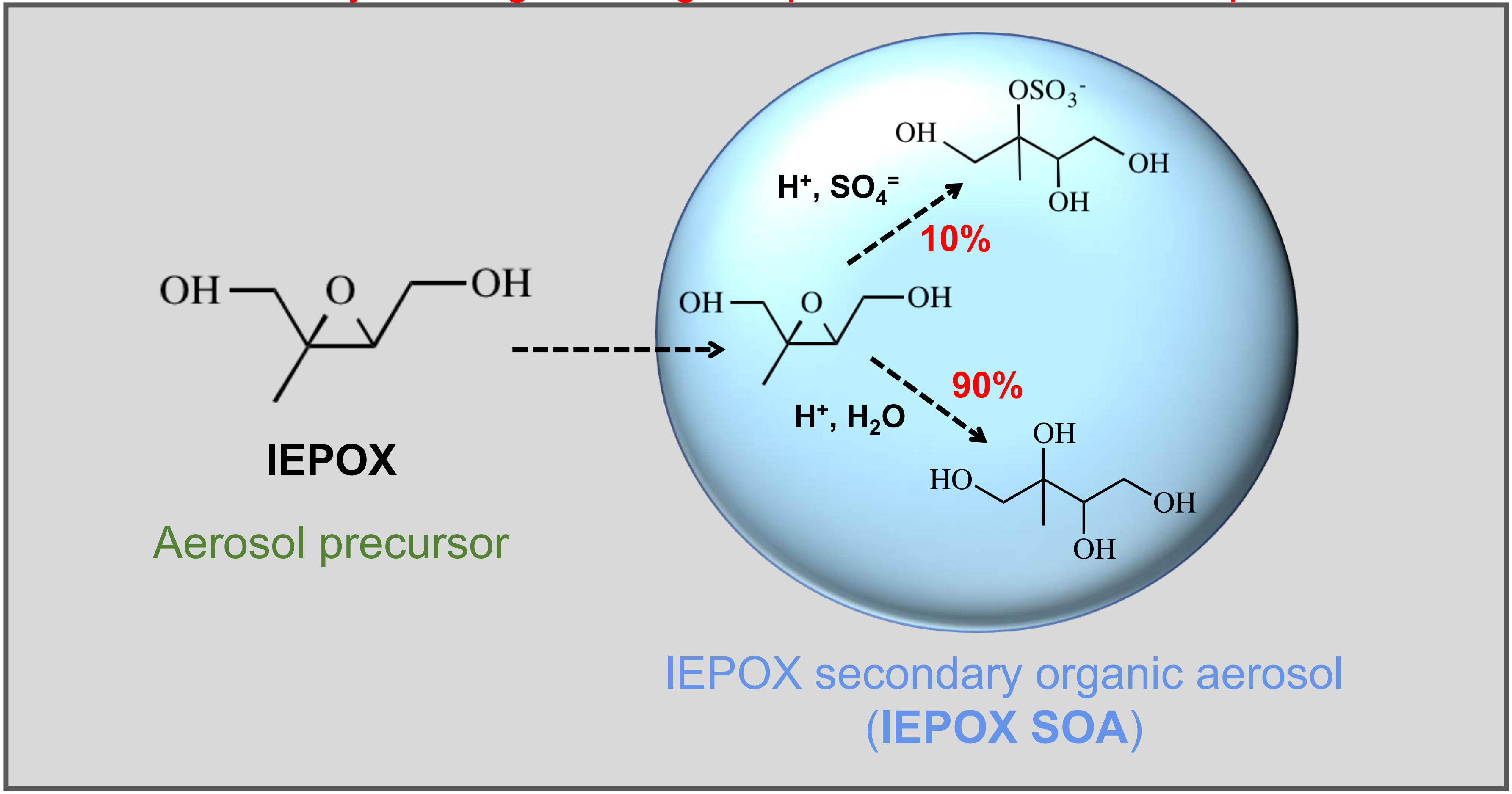
Correlation identified throughout the **Southeast US**:
Budisulistiorini et al. [2013, 2015];
Xu et al., [**2015a**, 2015b]; Hu et al. [2015]

IEPOX-organosulfate formation



Sulfate correlation not due to nucleophillic addition

Acid-catalyzed ring cleavage to produce non-volatile species



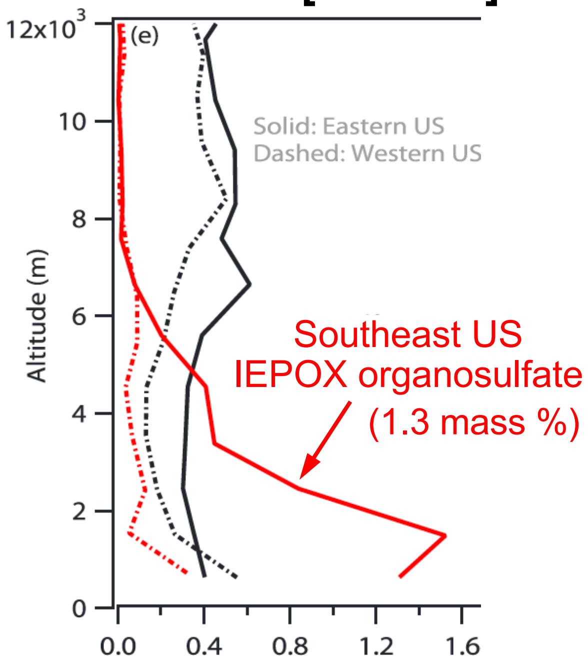
In our mechanism acid-catalyzed **sulfate addition is <u>10%</u>** and acid-catalyzed **H_2O addition is <u>90%</u>** of the fate of IEPOX

Aircraft observations constrain organosulfate formation

Additional support for limited role of sulfate channel from SEAC^{4}RS PALMS **IEPOX-organosulfate observations:**

IEPOX-organosulfate

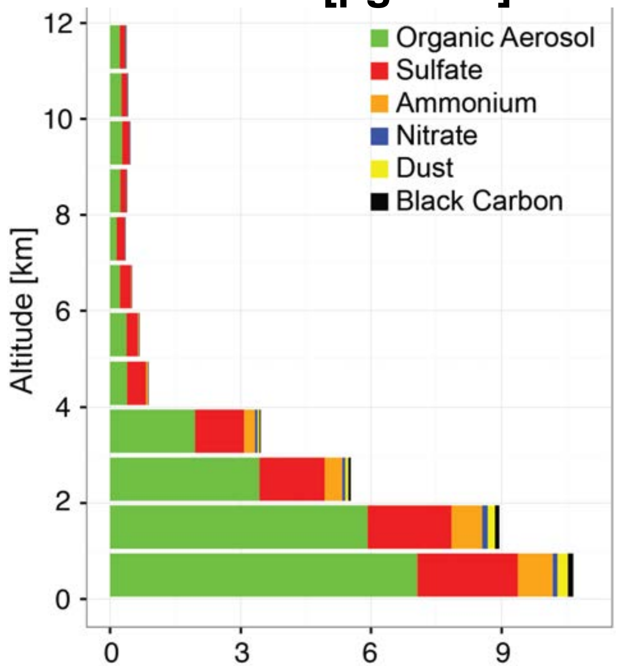
PALMS [mass %]



[Liao et al., 2015]

Total aerosol mass

AMS [μg sm^{-3}]



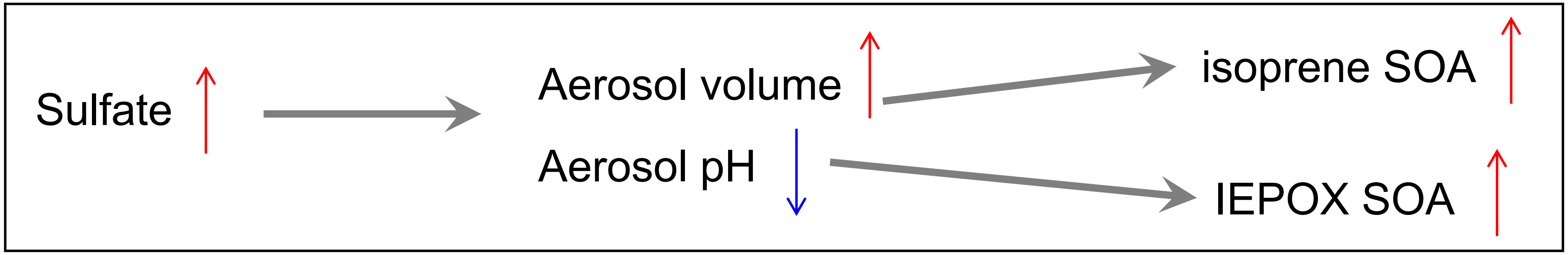
[Kim et al., 2015]

Boundary-layer IEPOX-organosulfate: **0.14 μg sm^{-3}** (10% of IEPOX SOA)

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

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

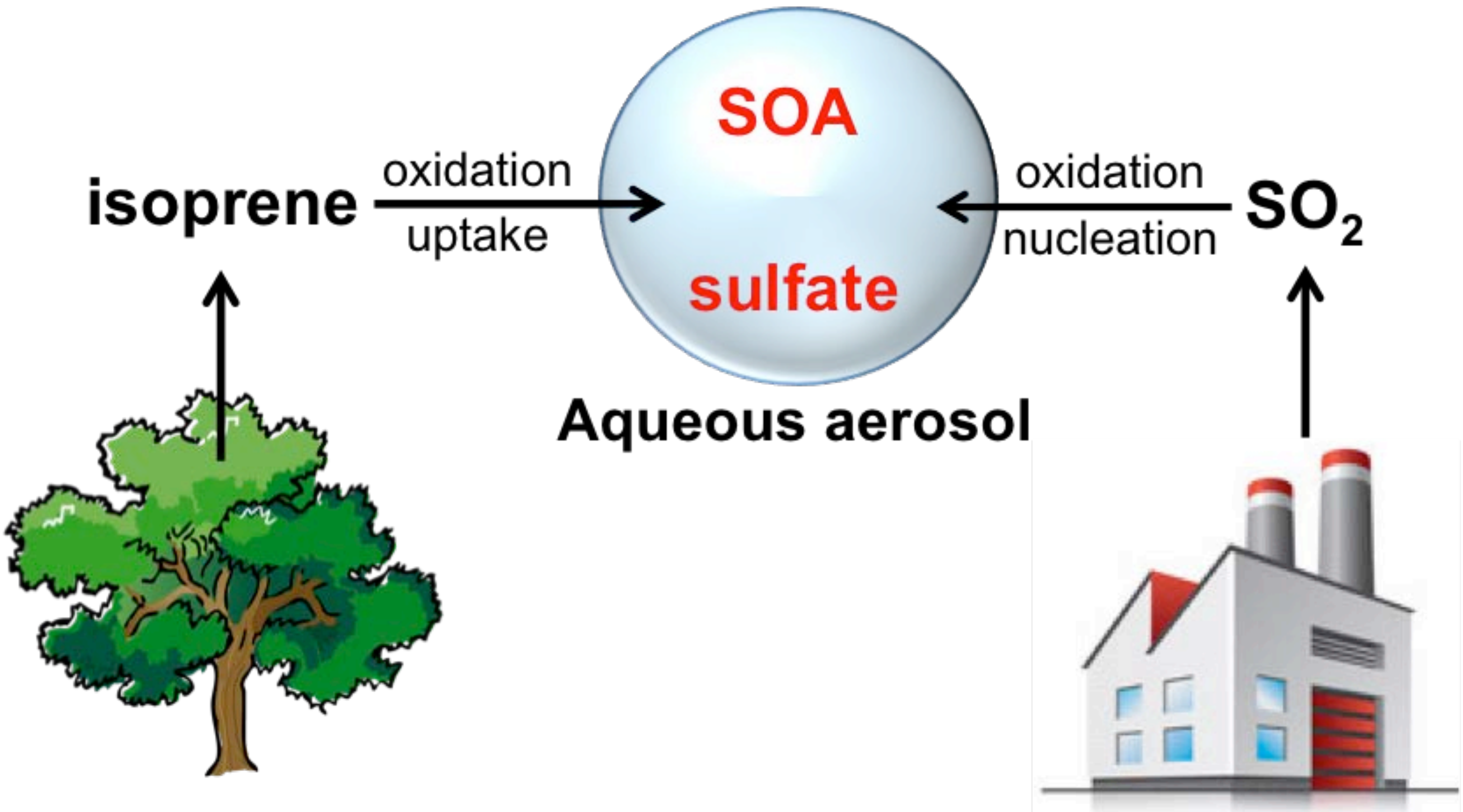
Sulfate impacts aerosol acidity and volume



Why volume? Sulfate determines aqueous aerosol abundance

Why acidity? Relative increase in ammonia neutralizes aerosols

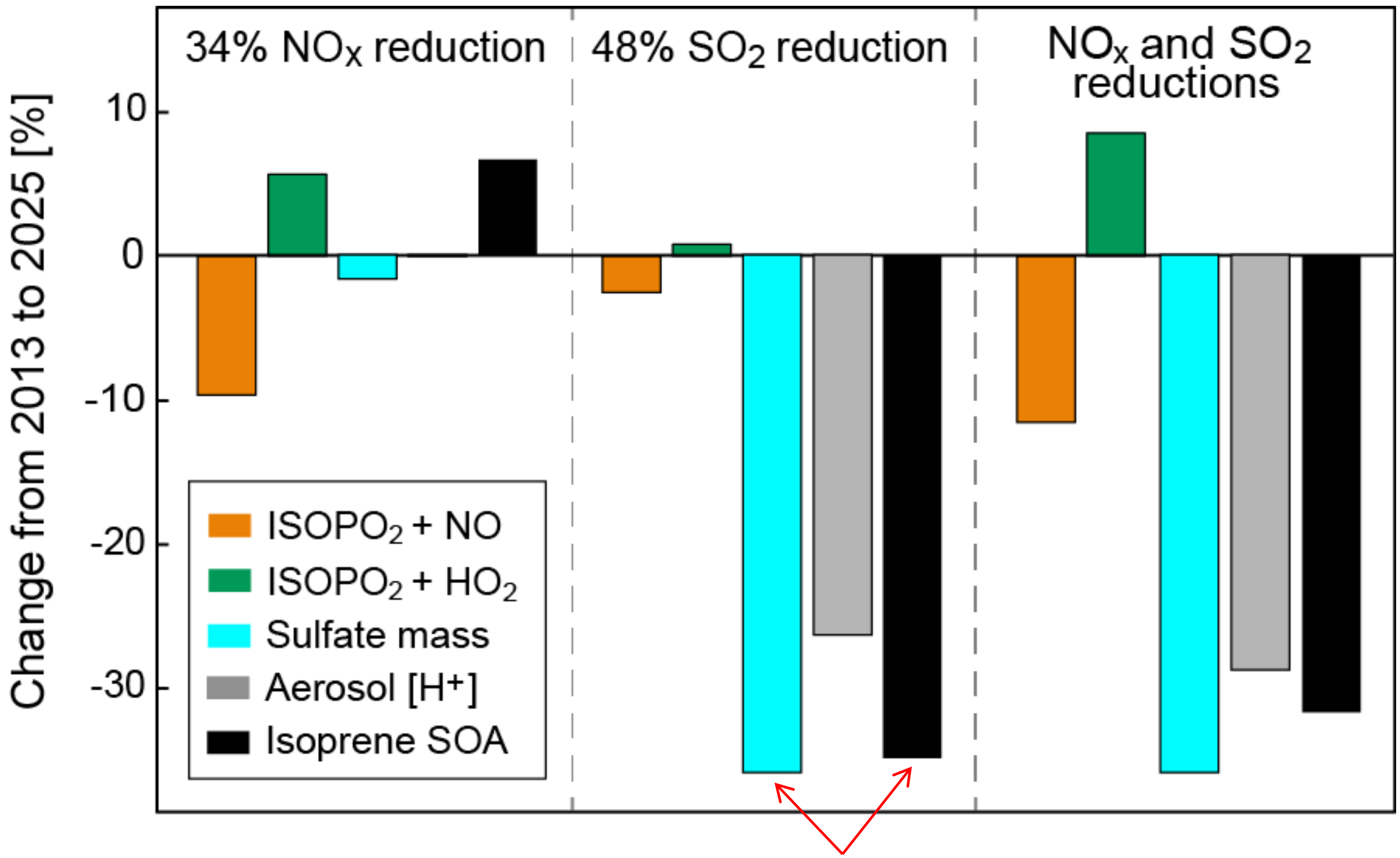
Anthropogenic Enhancement in Natural Aerosols



Effect of Anthropogenic Emission Reductions

US EPA projects emissions decline by **48% for SO_2** and **34% for NO_x** from 2013 to 2025

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

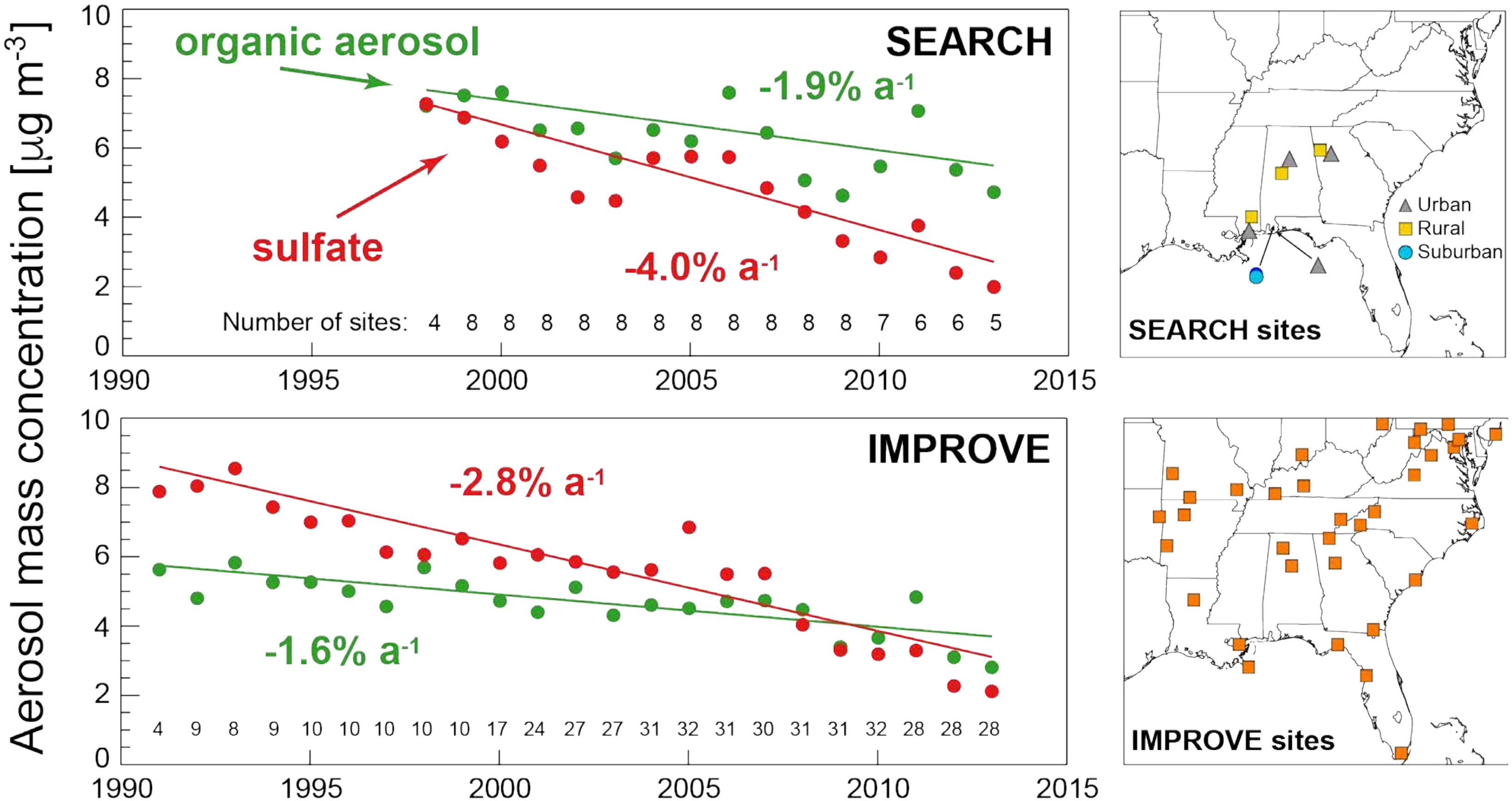


Near-equivalent response in **sulfate** and **isoprene SOA**

Factor of 2 co-benefit for $PM_{2.5}$ from SO_2 emission controls

Observed decline in sulfate and OA in the Southeast US

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

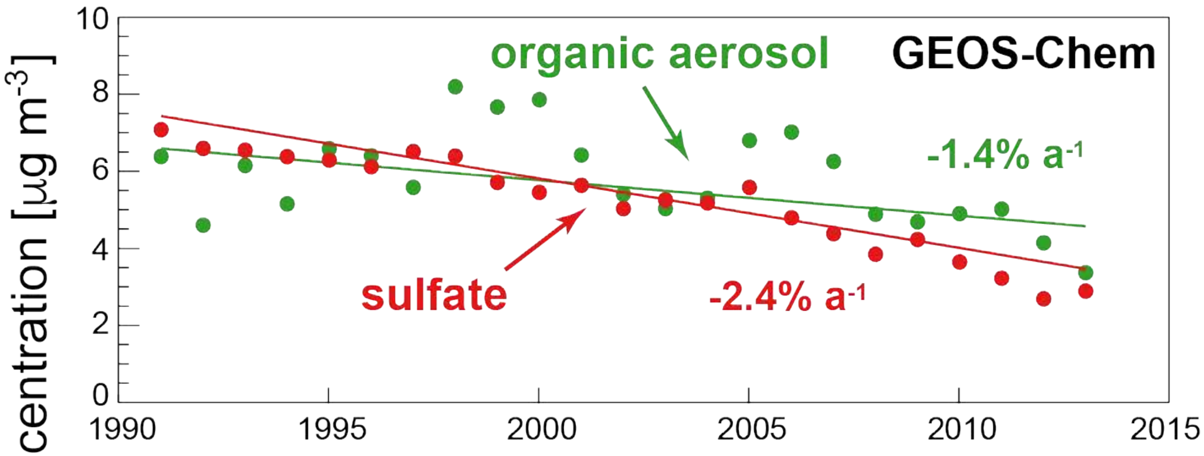


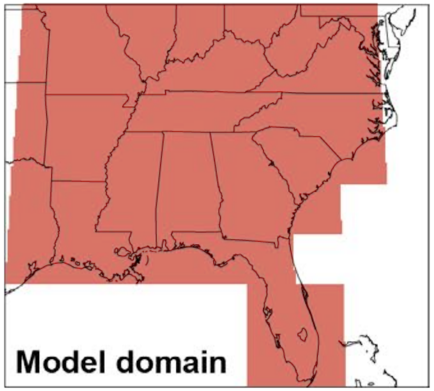
Steeper decline in sulfate at SEARCH than IMPROVE sites – greater urban influence.
Similar OA trends supports **biogenic SOA driving the trend**

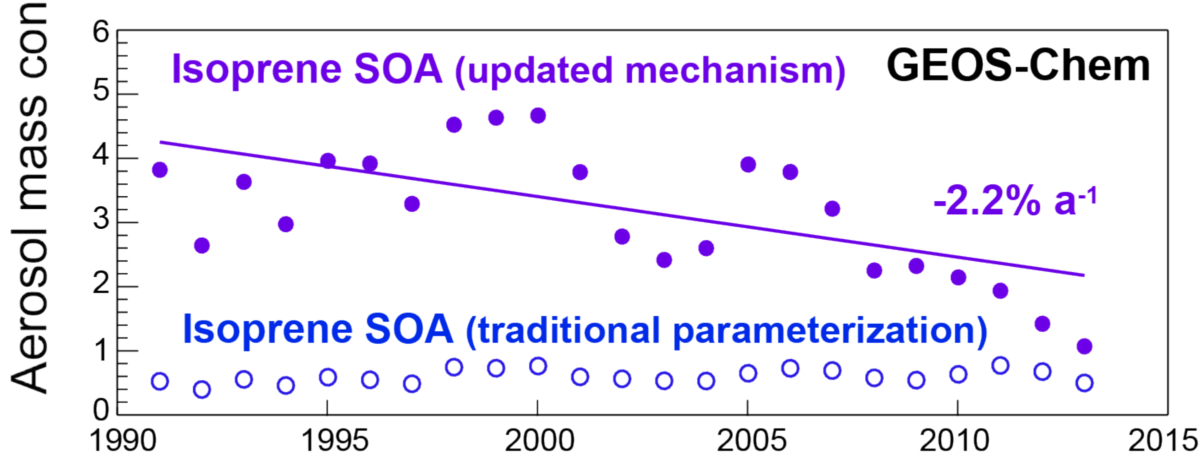
OA instead of sulfate is now the dominant $PM_{2.5}$ component in the Southeast US

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.

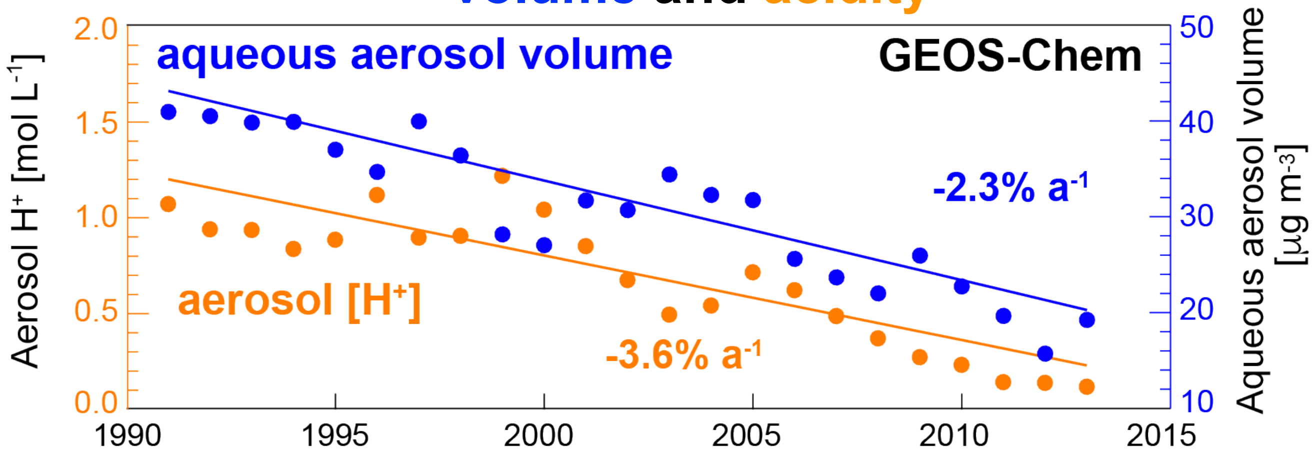
Model includes annual trends in anthropogenic emissions of SO_2, NO_x, and VOCs.

Isoprene emissions exhibit large interannual variability driven by temperature.

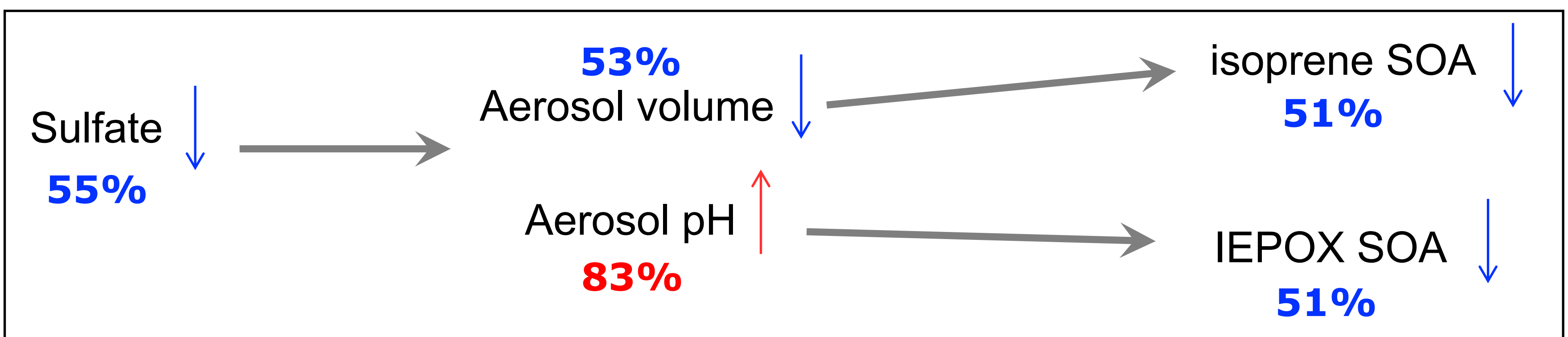
Majority of decline in modelled OA is due to isoprene SOA

Modelled isoprene SOA decreases due to decline in sulfate

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

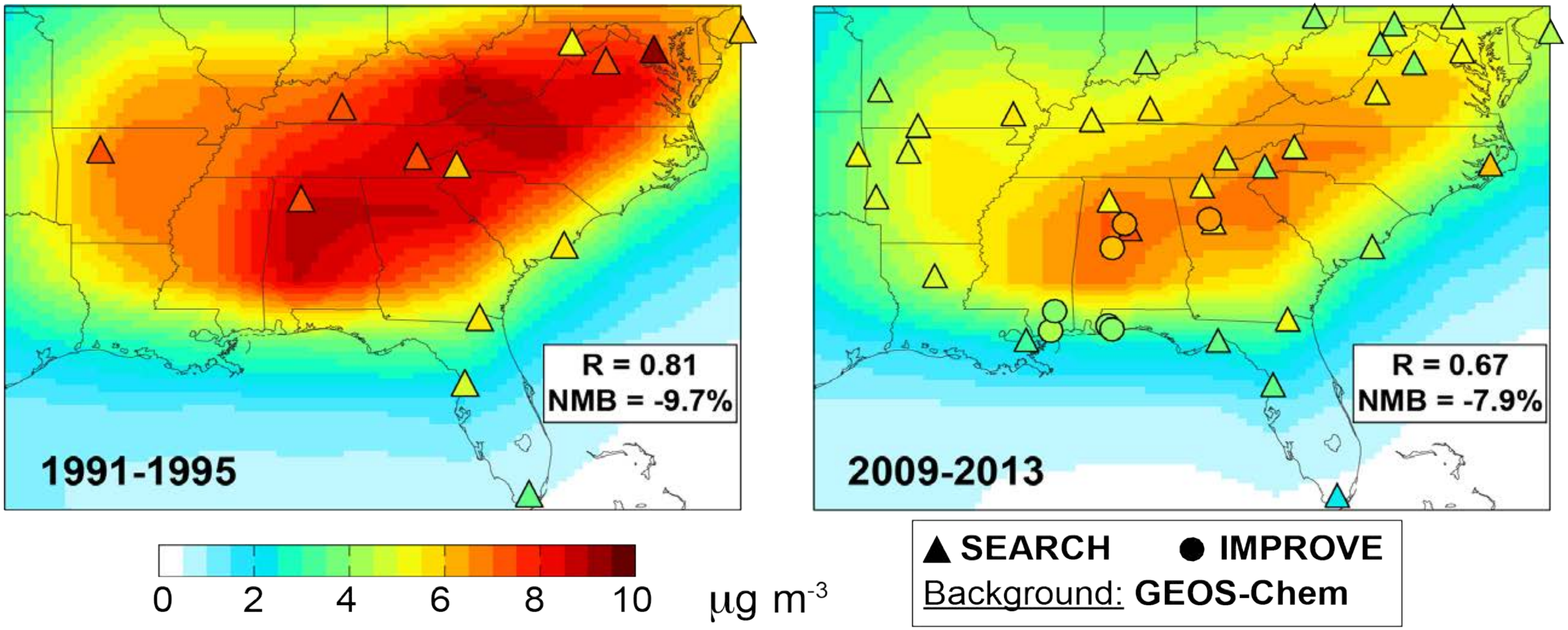


Decline in sulfate (dominant aqueous aerosol component) **decreases aqueous aerosol volume** and **increases aqueous aerosol pH**



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

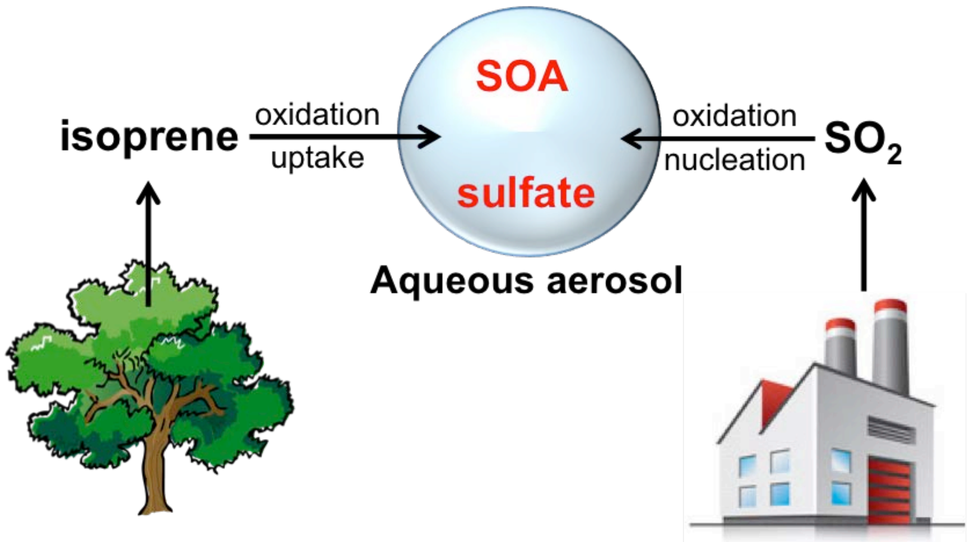


No significant change in OA spatial distribution in the observations or model supports biogenic SOA driving the OA trend.

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

Implications for the tropical regions that are undergoing rapid development.

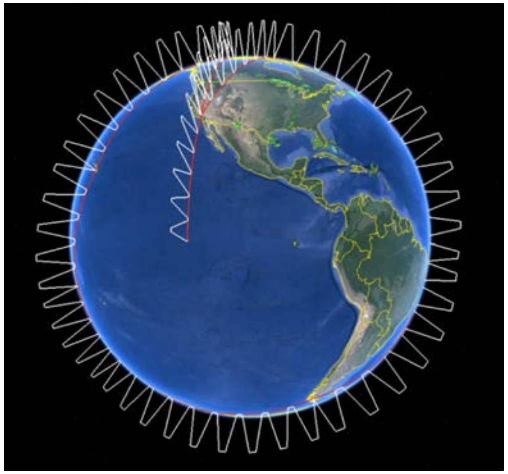
Concluding Remarks



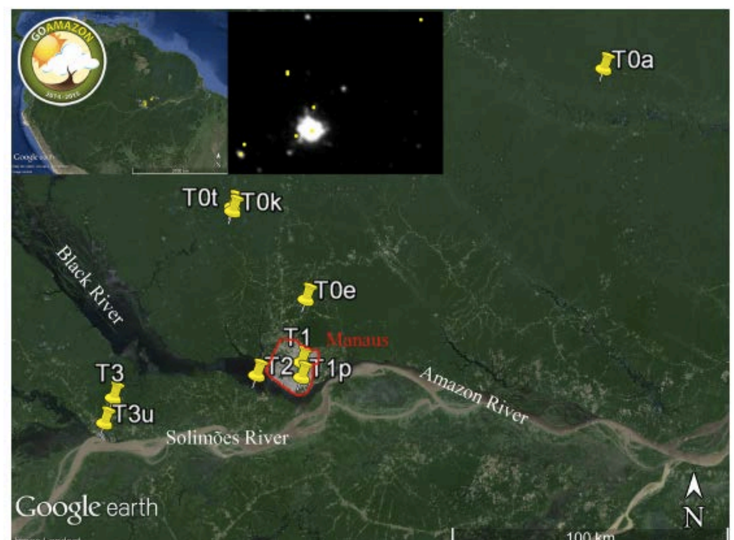
- Biogenic isoprene secondary organic aerosol (SOA) formation by reactive uptake to aqueous aerosol is modulated by sulfate that in turn drives changes in aqueous aerosol volume and acidity.
- Observations in the Southeast US show a large long-term (1991-2013) decline in summertime (Jun-Aug) OA, but 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 SO_2 emission controls to decrease sulfate have had a large air quality co-benefit in the Southeast US by also decreasing organic aerosol (OA).

Ongoing Research

Isoprene SOA processing and aging



Isoprene SOA and pollution in South America



[Martin et al., 2016]