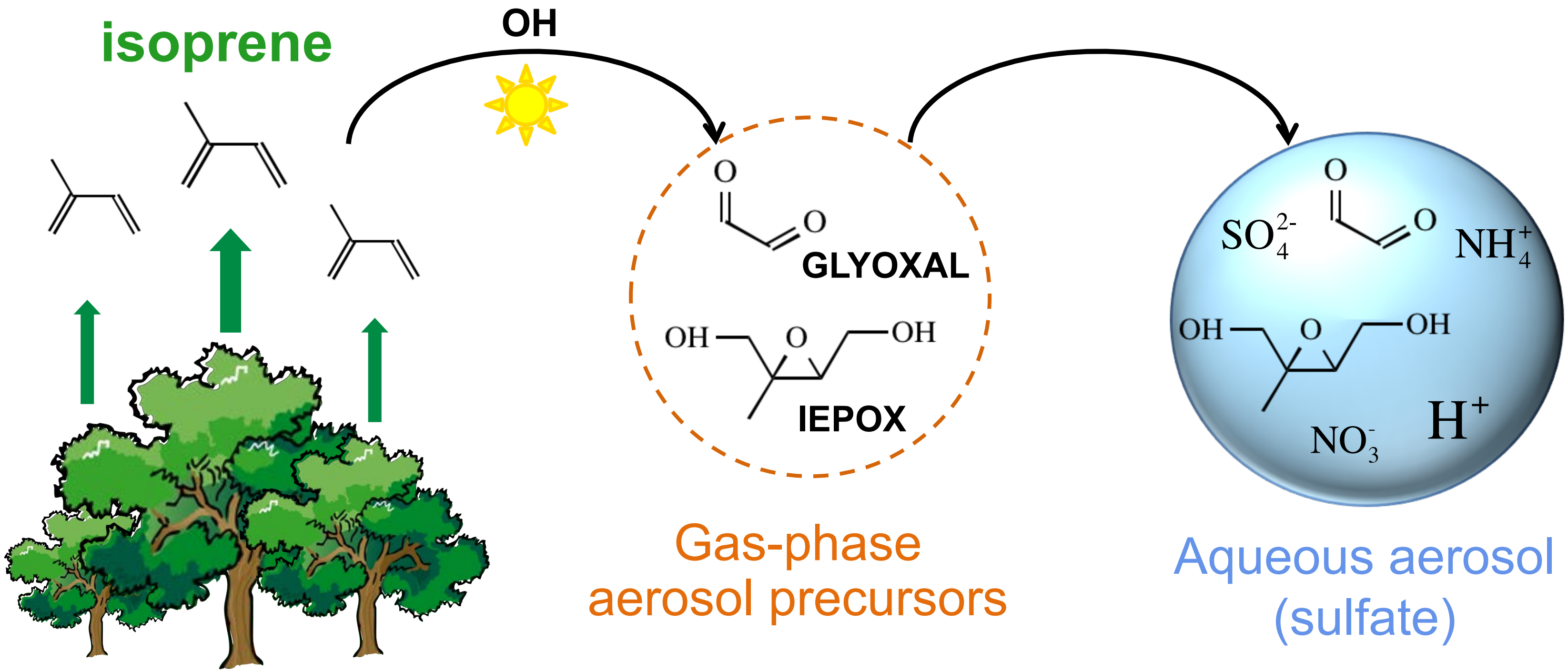
Dual air quality benefit of SO_2 emission controls by decreasing sulfate and secondary organic aerosol

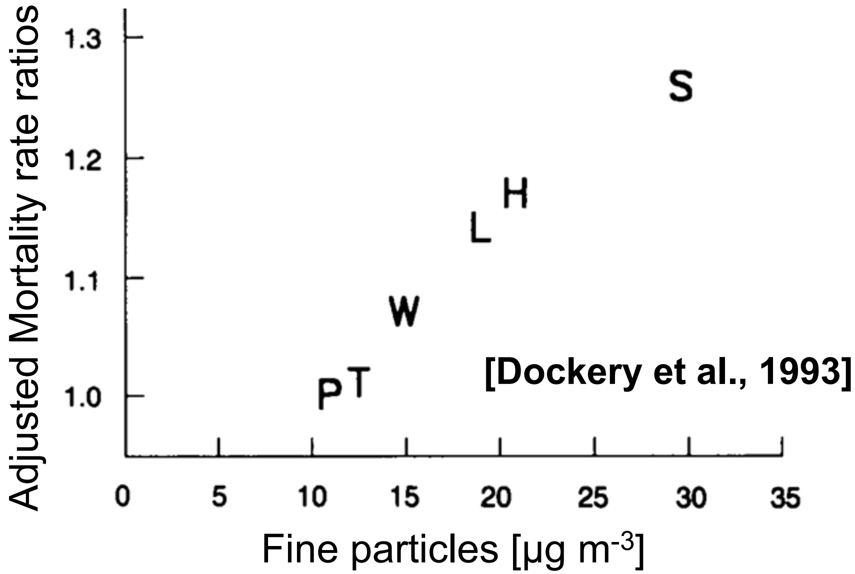


<u>Coauthors:</u> D. J. Jacob, J. L. Jimenez, P. Campuzano-Jost, D. A. Day, W. Hu, J. Krechmer, L. Zhu, P. S. Kim, C. C. Miller, J. A. Fisher, K. Travis, K. Yu, T. F. Hanisco, G. M. Wolfe, H. L. Arkinson, J. R. Turner, L. J. Mickley, H. O. T. Pye, K. D. Froyd, J. Liao, V. F. McNeill

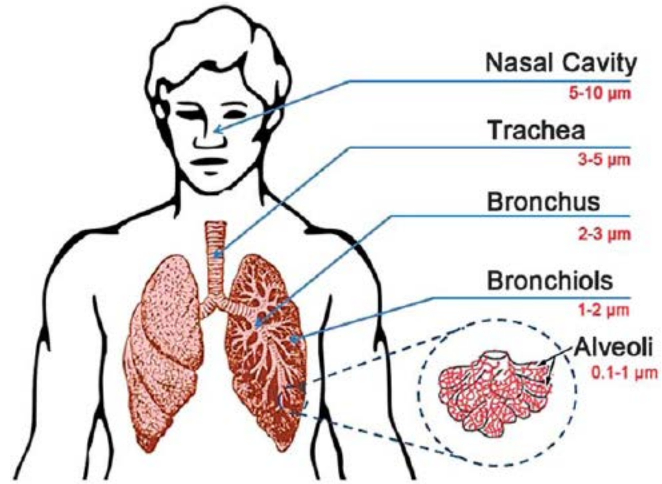
Eloïse A Marais
(e.a.marais@bham.ac.uk)

Aerosols Impact Health

Fine particles are associated with **increased mortality**

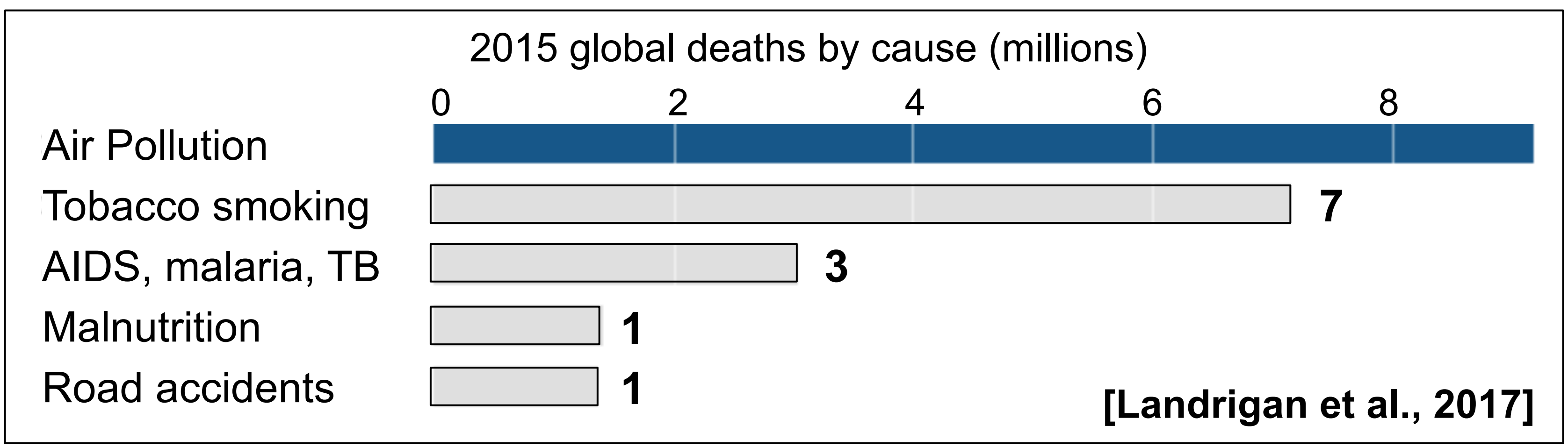


Fine particles travel deep into the lungs



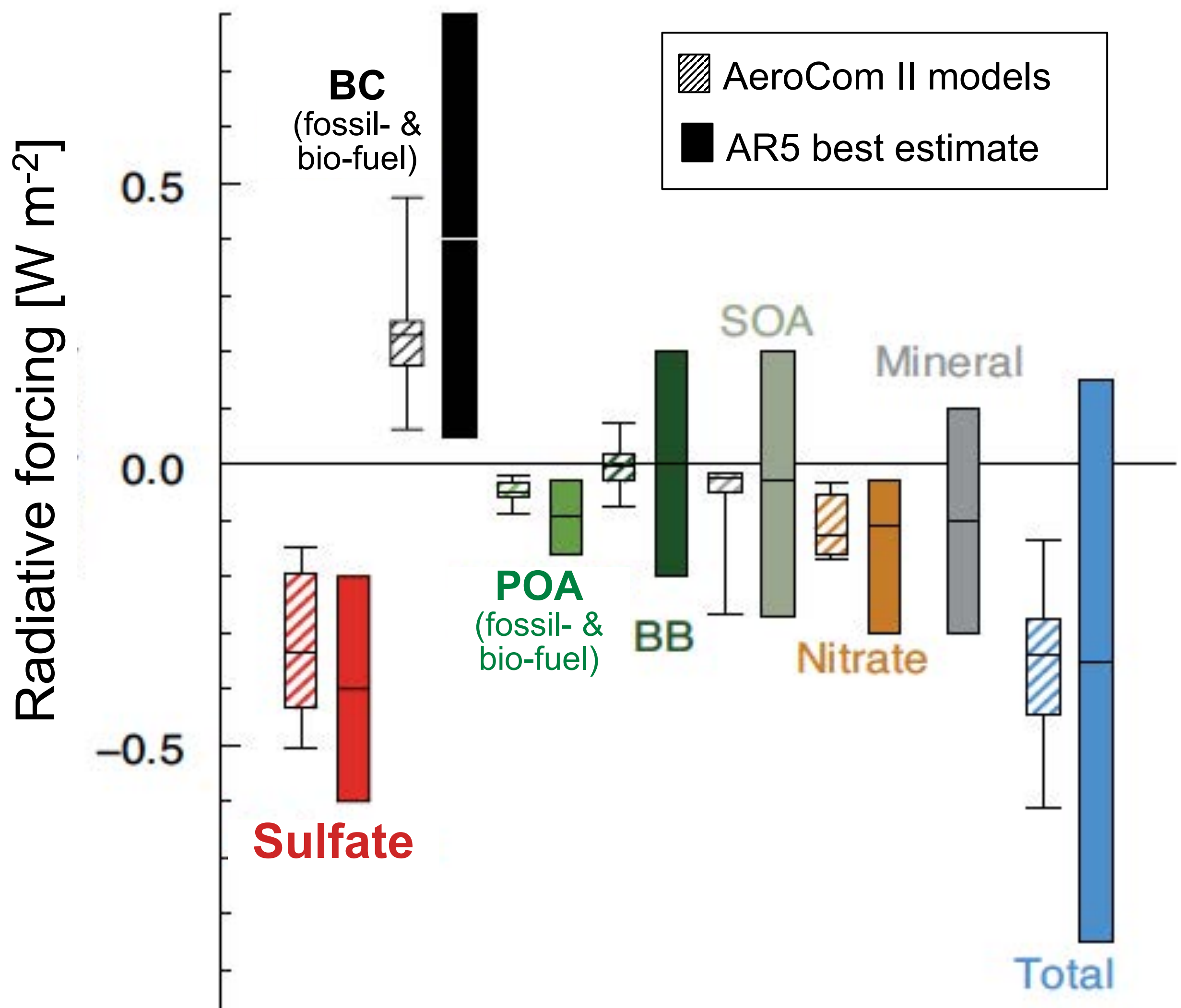
[Kumar et al., 2014]

Air pollution (mostly $PM_{2.5}$) is now the greatest health risk



Aerosols Impact Climate

Climate impact is uncertain



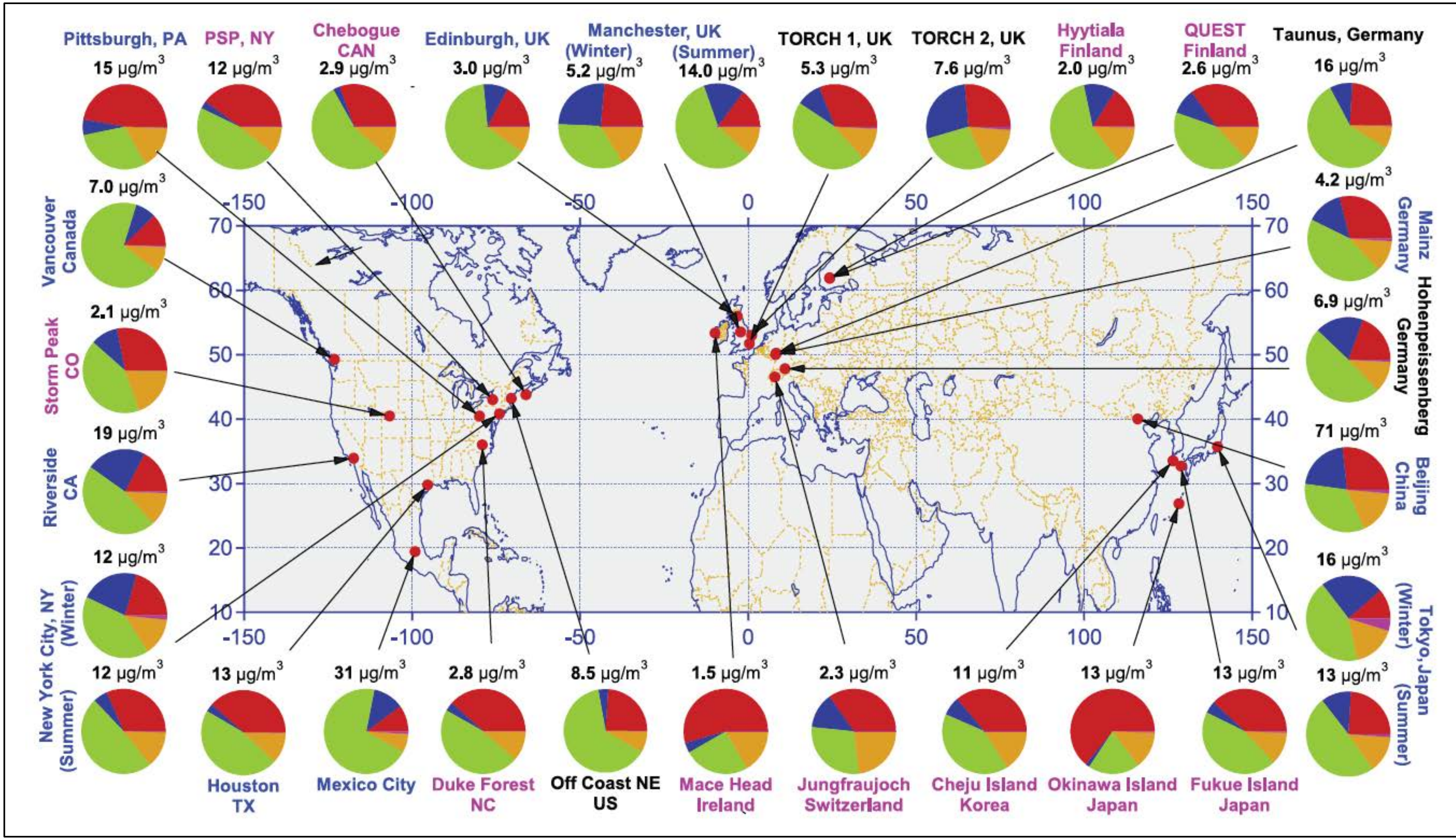
[IPCC AR5, 2013]

Aerosols Impact Visibility

[The Guardian, 23 Feb 2016]

Organic Aerosol is Ubiquitous in the Atmosphere

Northern hemisphere aerosol composition

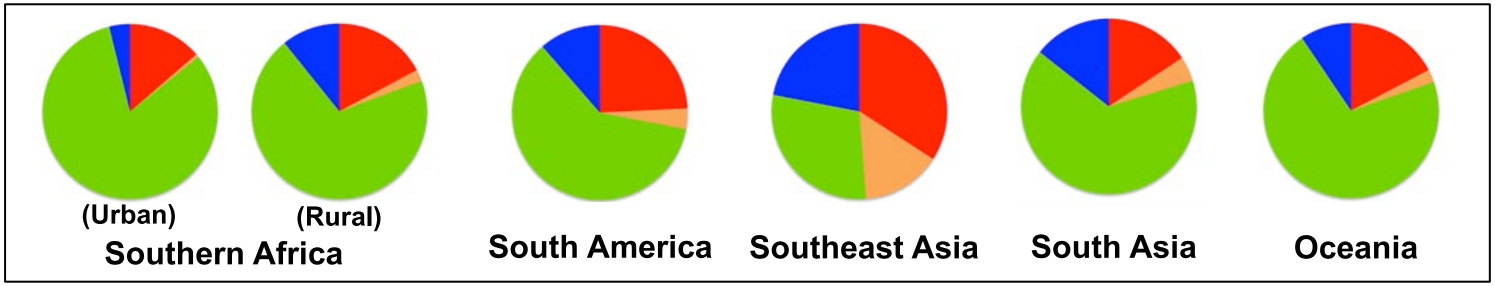


Sulfate Nitrate Ammonium Organics (OA)

[Zhang et al., 2007]

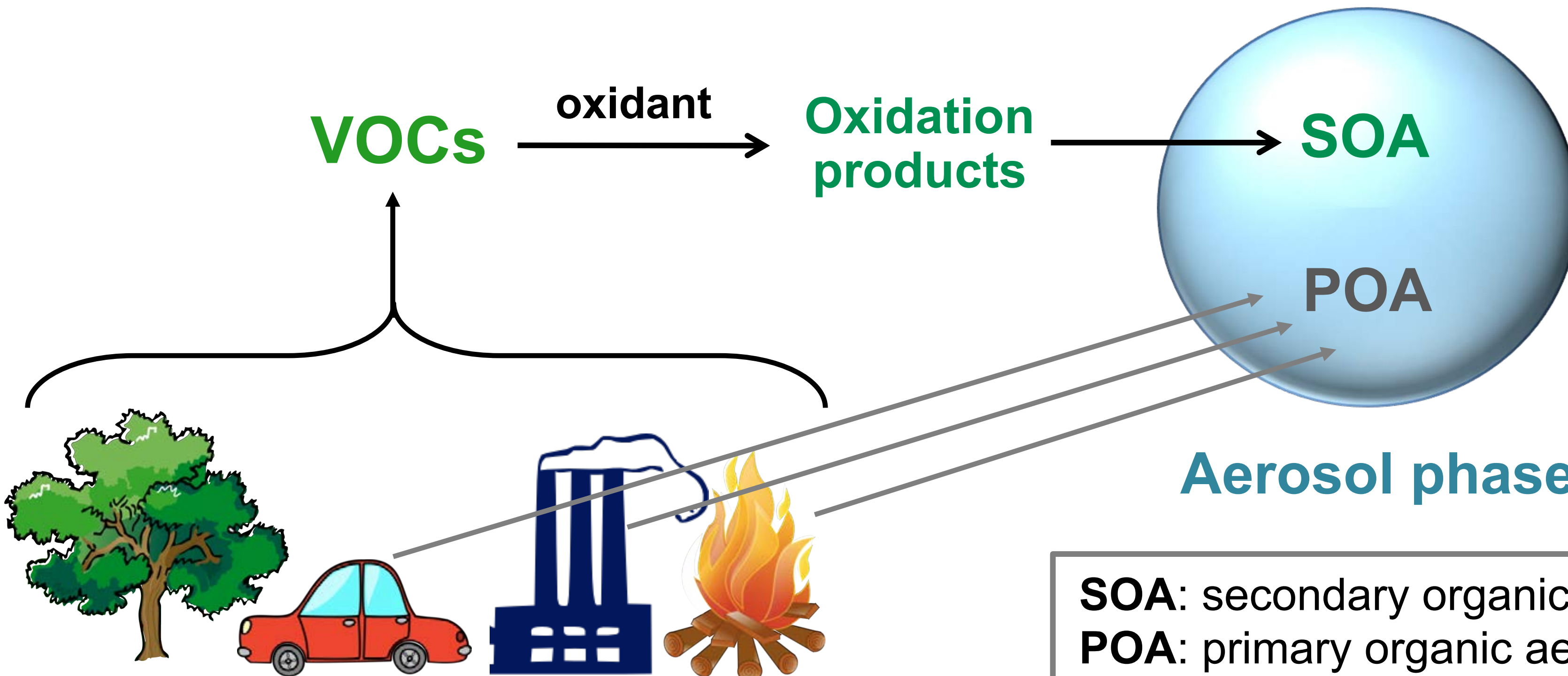
Organic Aerosol is Ubiquitous in the Atmosphere

Tropics and southern hemisphere aerosol composition



[IPCC, 2013]

Sulfate Nitrate Ammonium Organics (OA)

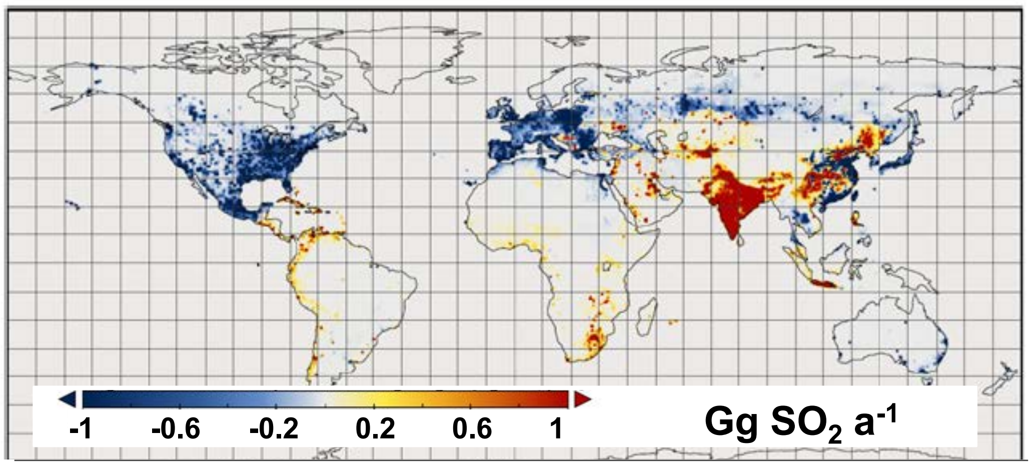


SOA: secondary organic aerosol
POA: primary organic aerosol

Organic Aerosol Fraction is Changing

Changes in sulfate alter the contribution of OA to $PM_{2.5}$

2010 minus 2005 SO_2 emissions

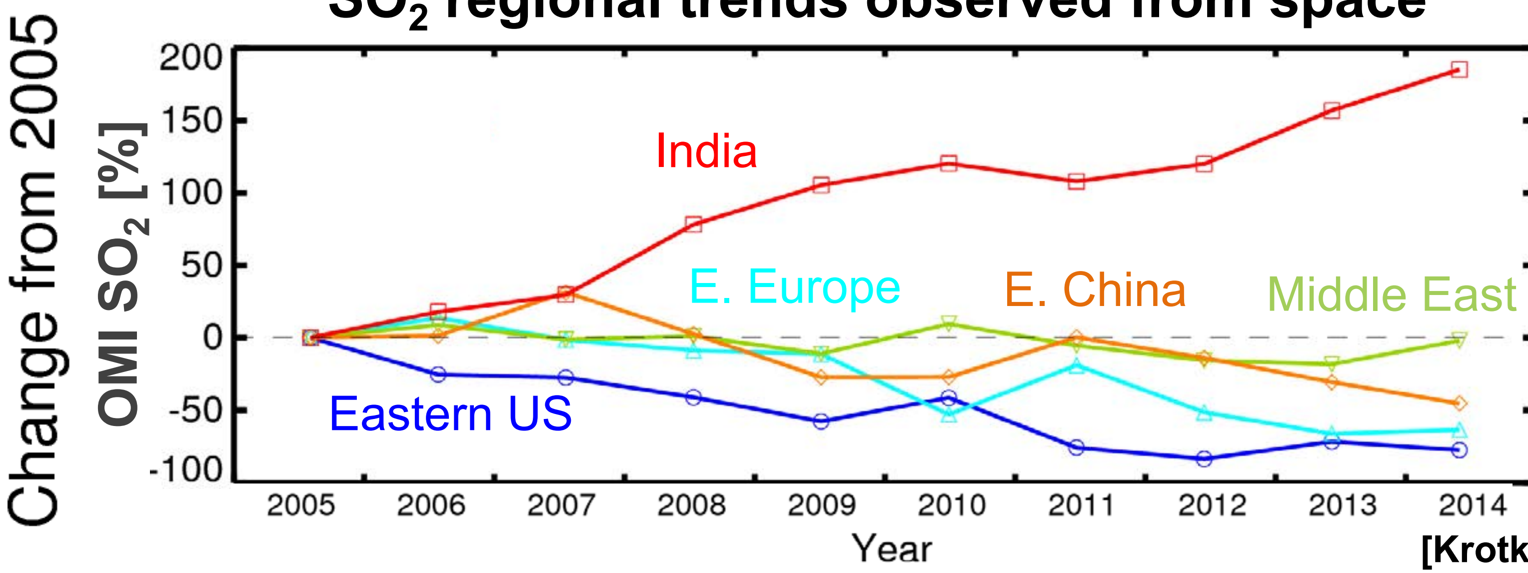


Global bottom-up emission inventory trends (left)

Corroborated by surface and satellite observations (below)

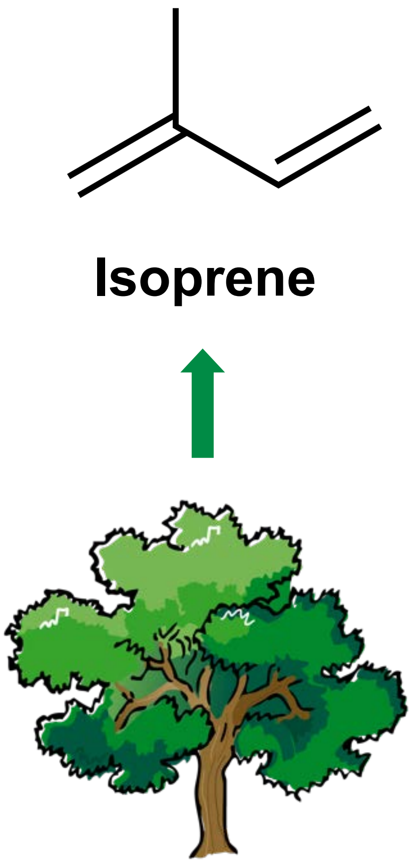
[Klimont et al., 2013]

SO_2 regional trends observed from space

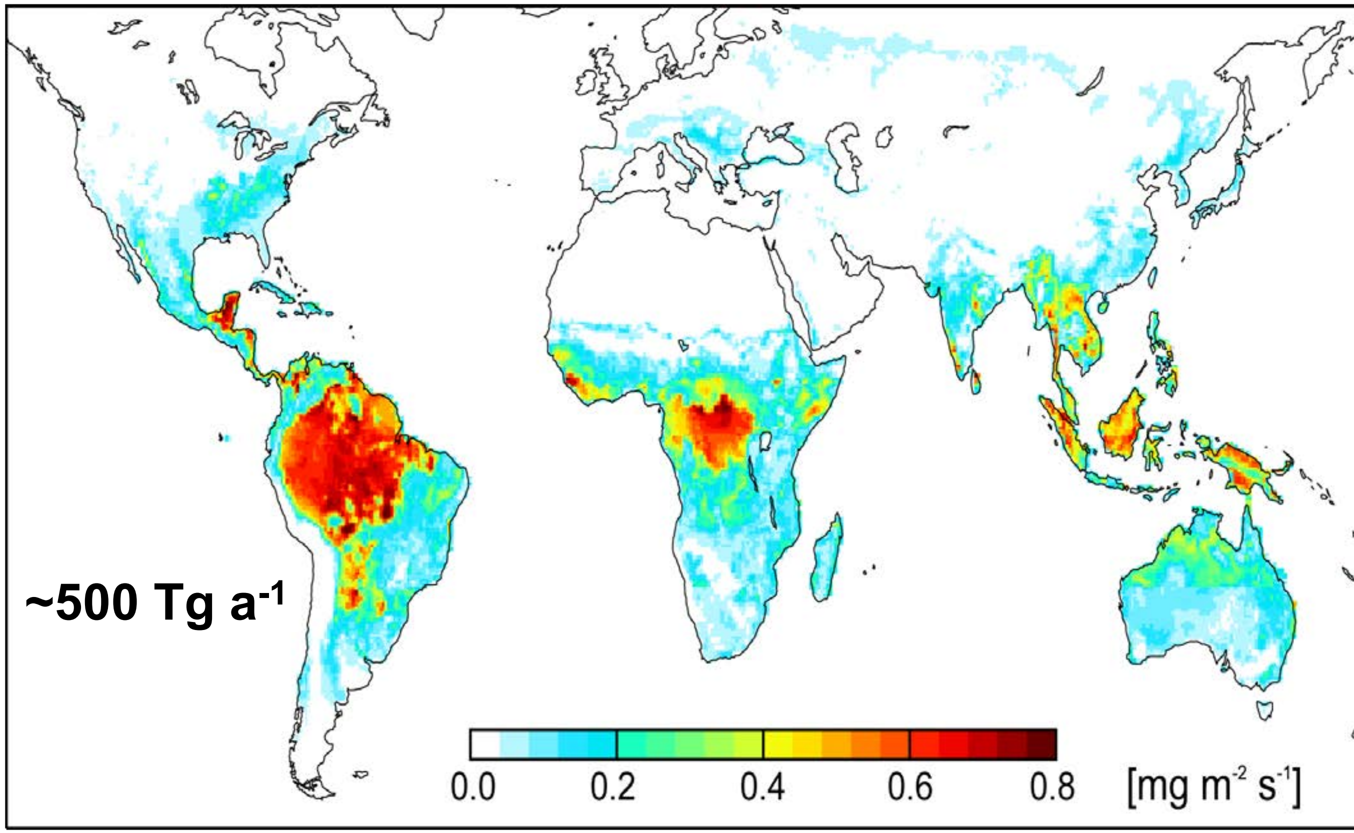


[Krotkov et al., 2015]

Isoprene as a precursor of secondary organic aerosol



Most isoprene is emitted by tropical trees



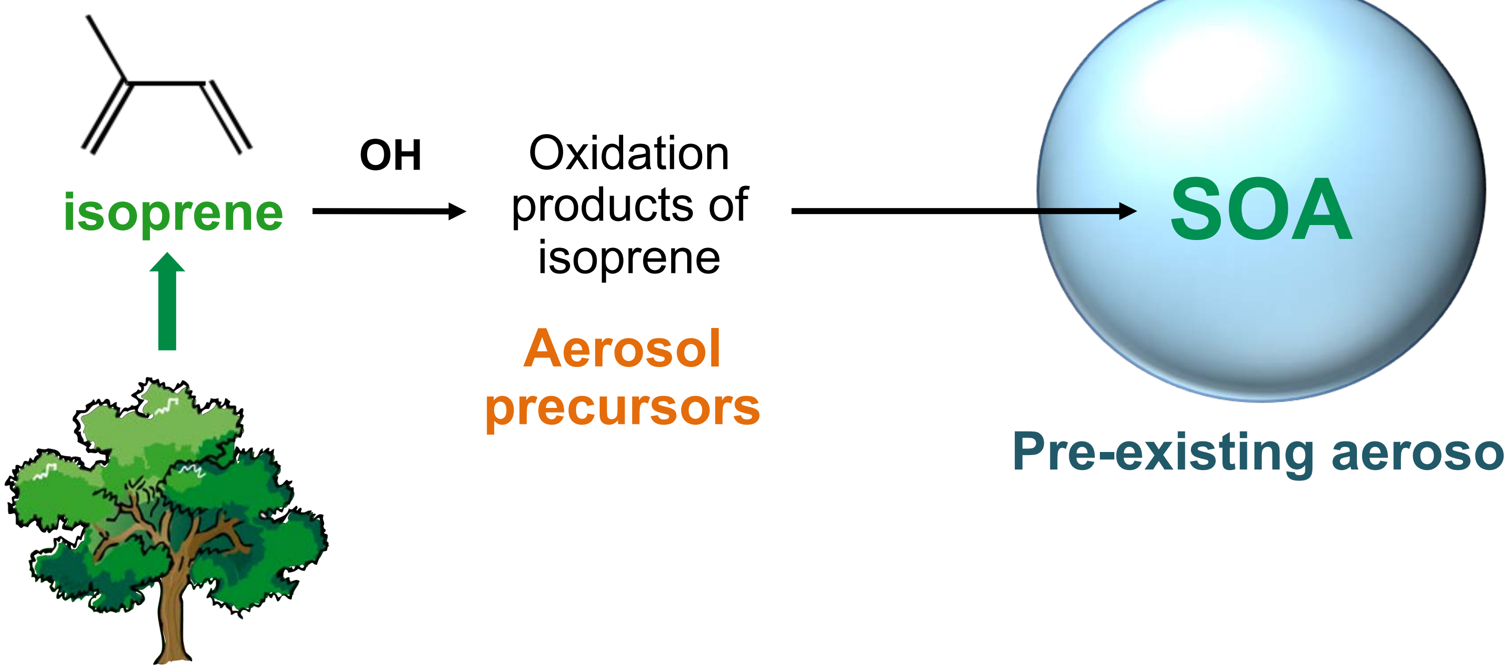
[Guenther et al., 2012]

Factors that affect emissions:

plant type, temperature, light, soil moisture, CO_2, plant physiology

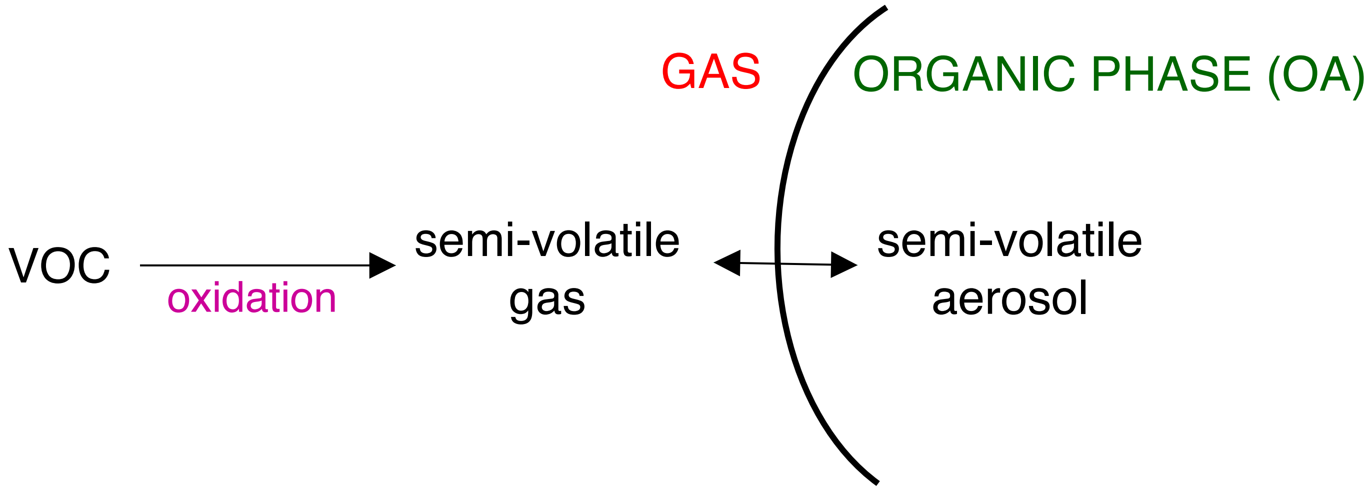
Isoprene as a precursor of secondary organic aerosol

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

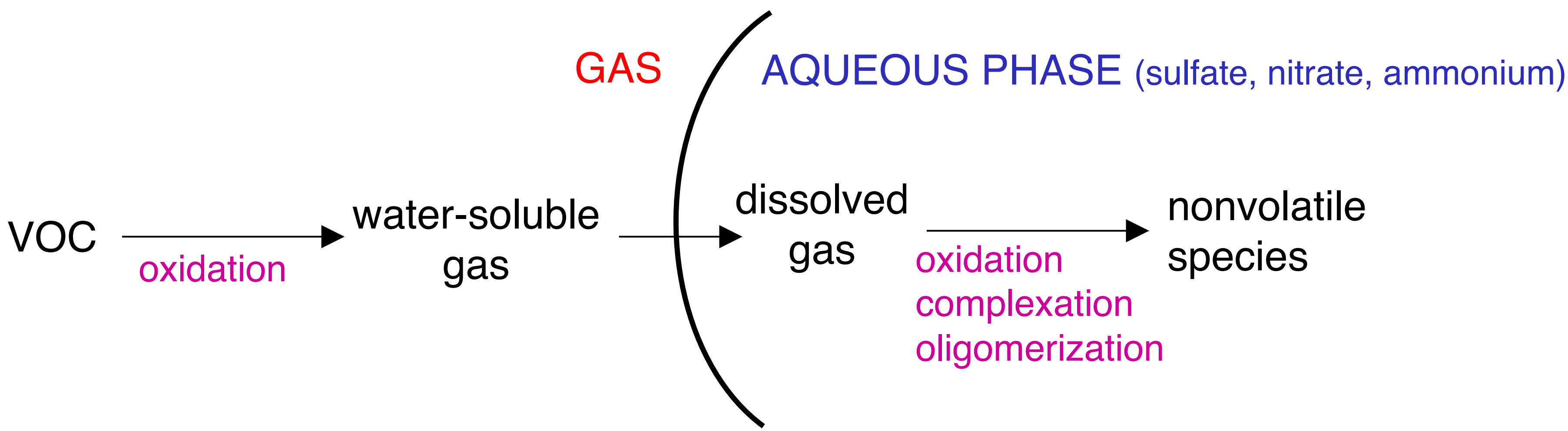


Two approaches to represent secondary organic aerosol

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



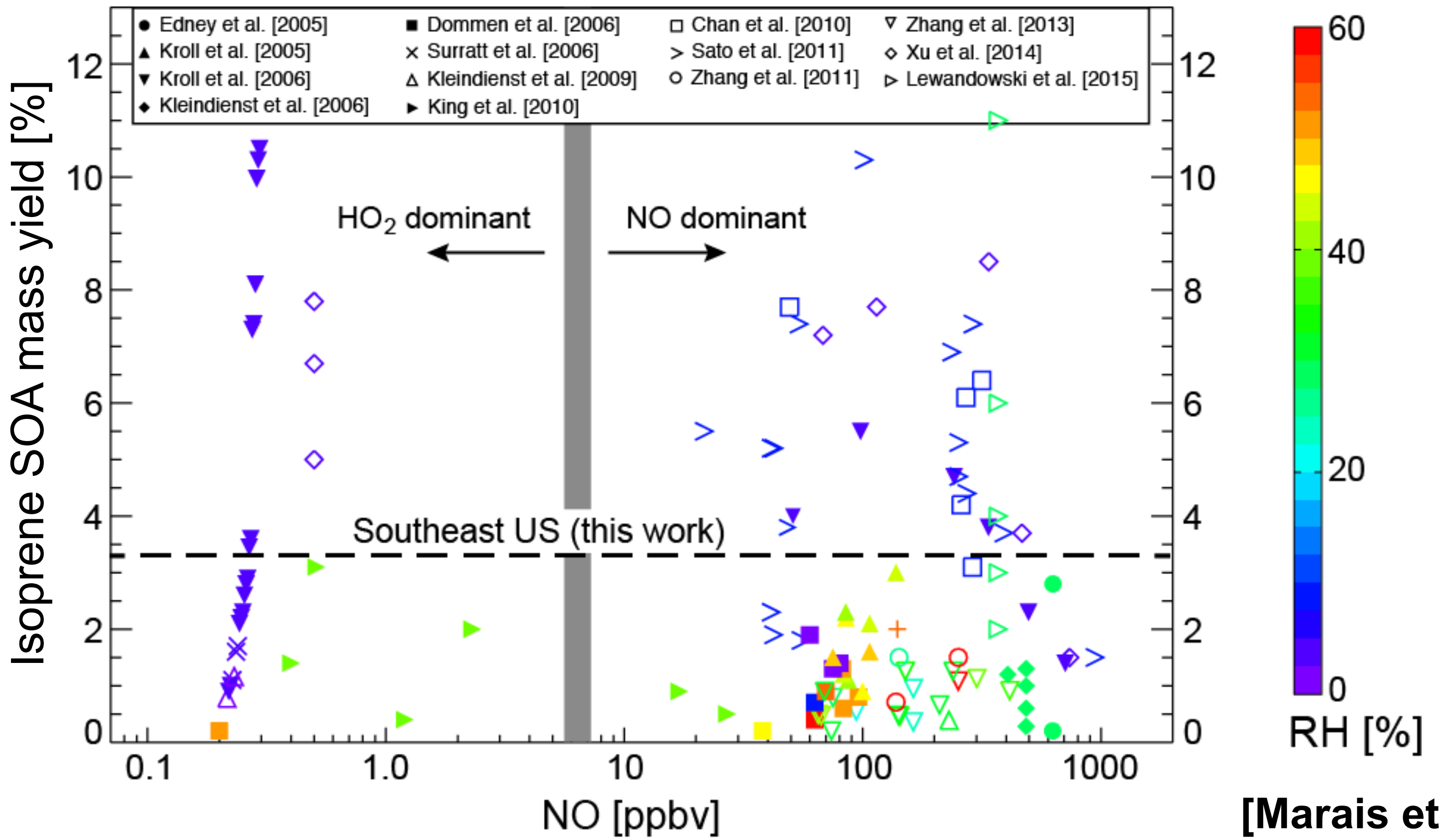
B. **Alternate model** for irreversible uptake by aqueous aerosol



Model Parameterizations of Isoprene Organic Aerosol

Traditional model based on chamber studies conducted at conditions far from ambient atmosphere

Compilation of chamber study isoprene + OH SOA mass yields

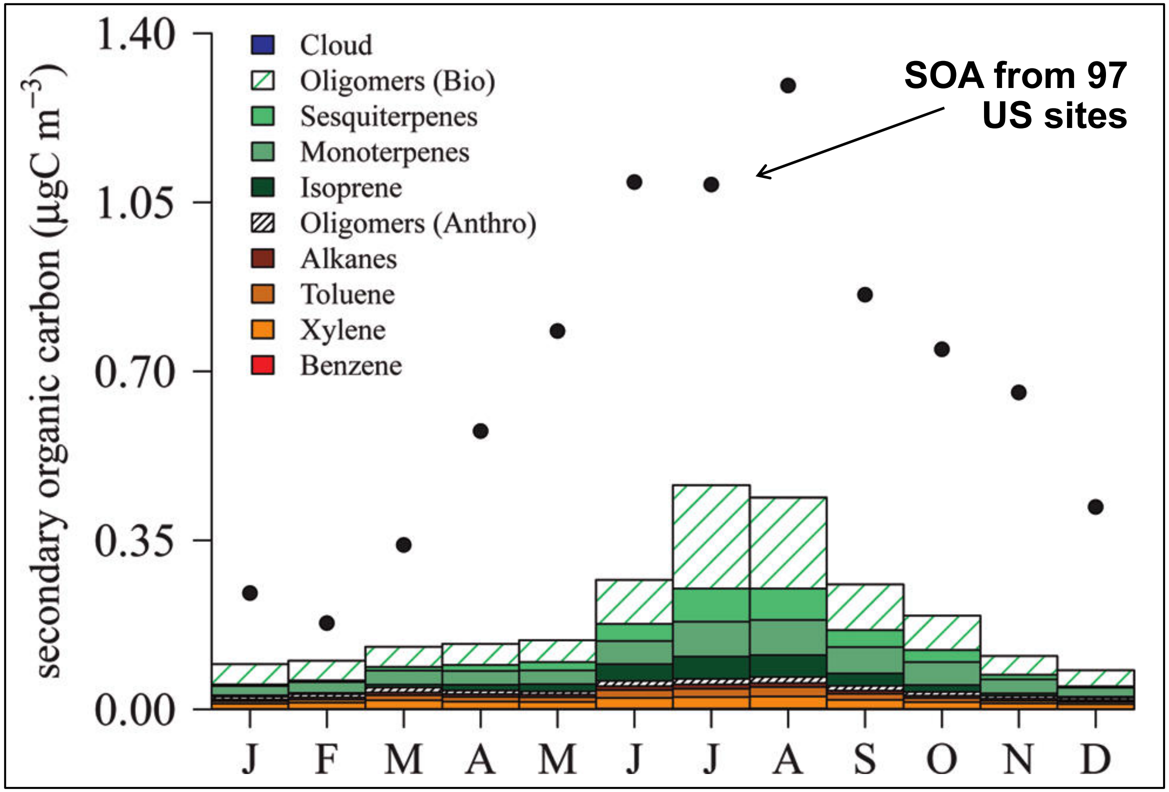


[Marais et al., 2016]

Southeast US Boundary-Layer Summer Conditions	RH = 72 ± 17 % NO = 0.053 ± 0.140 ppbv isoprene = 0.78 ± 0.85 ppbv

The classical model routinely misrepresents SOA

Measured vs modeled SOA across the US



[Carlton et al., 2010]

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

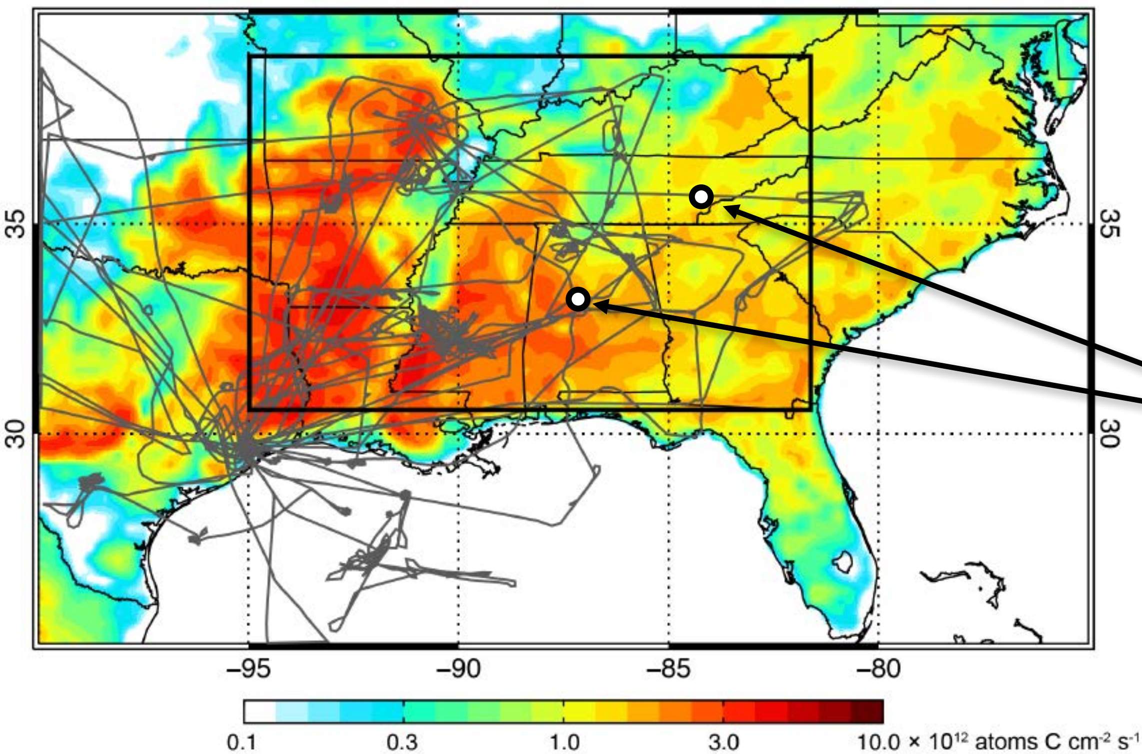
Limits ability to determine impact of isoprene SOA on **climate** and **human health**

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

The Southeast United States

Multiple summer 2013 campaigns to understand biogenic-anthropogenic interactions

MEGAN isoprene emissions, SEAC^{4}RS flight tracks, and SOAS monitoring sites



Aircraft campaign
(Aug-Sep 2013)

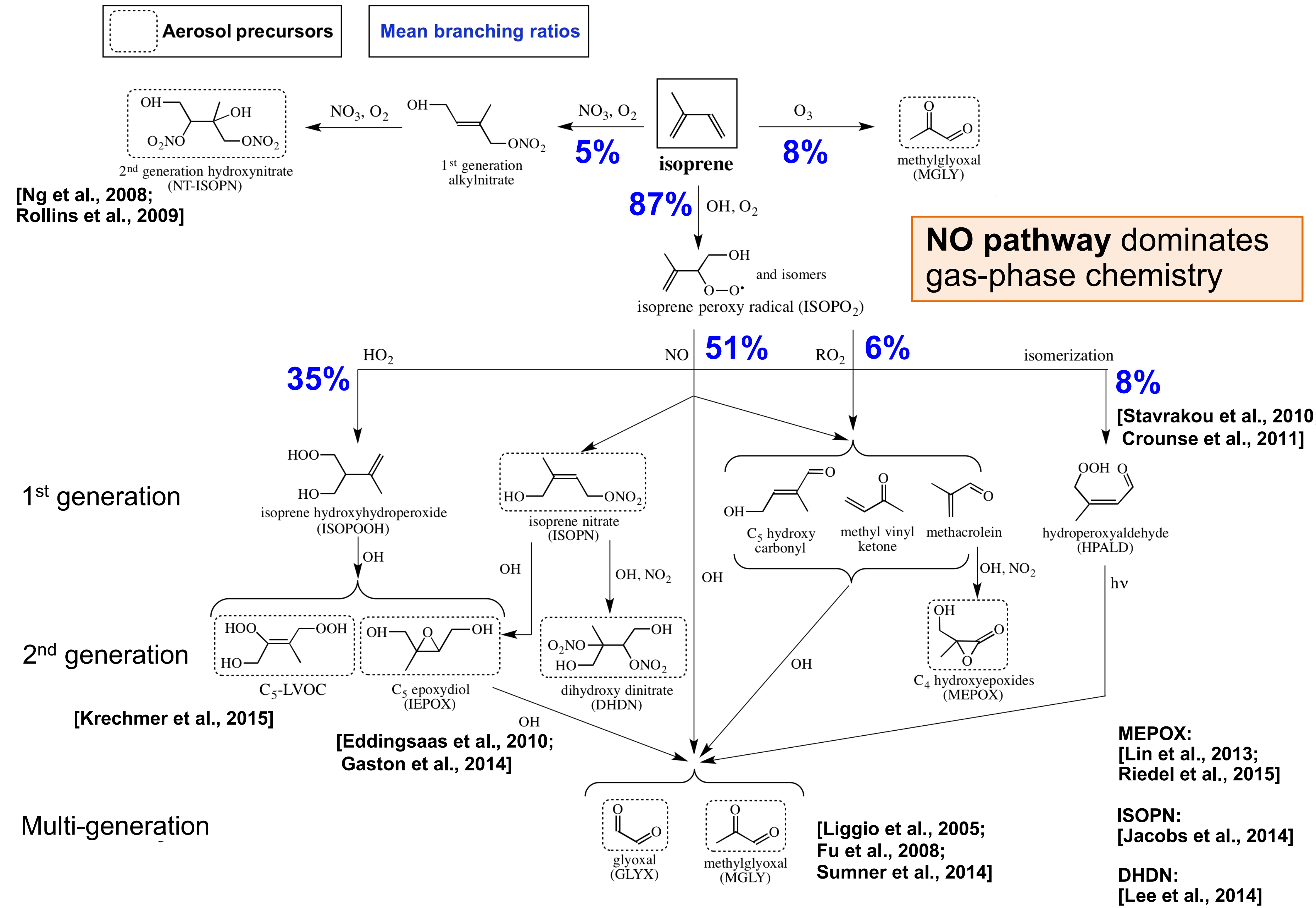
SOAS
Southern Oxidant & Aerosol Study

Surface campaign
(Jun-Jul 2013)

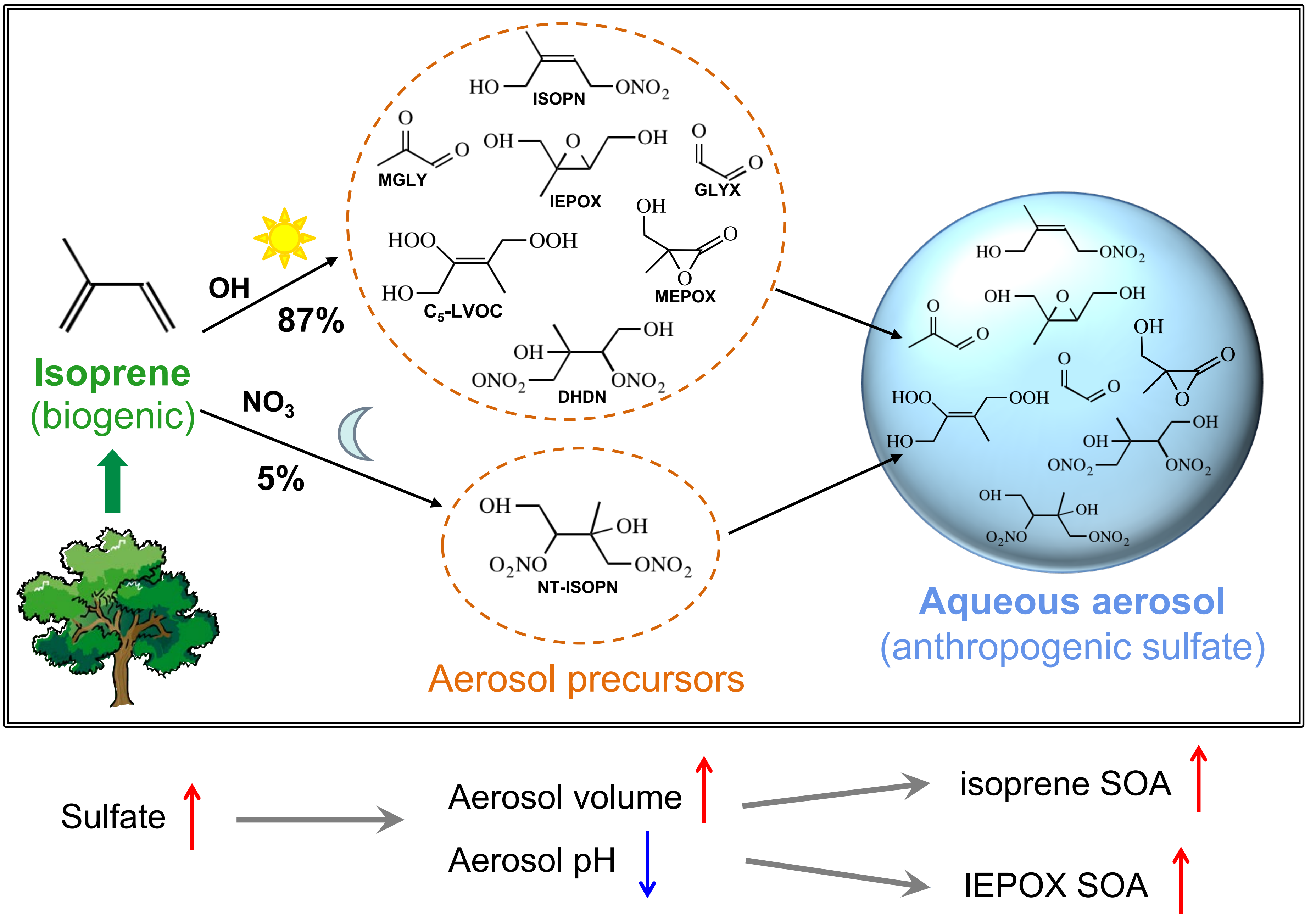
[Kim, P. et al., 2015]

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

Gas-phase Isoprene SOA precursors in GEOS-Chem



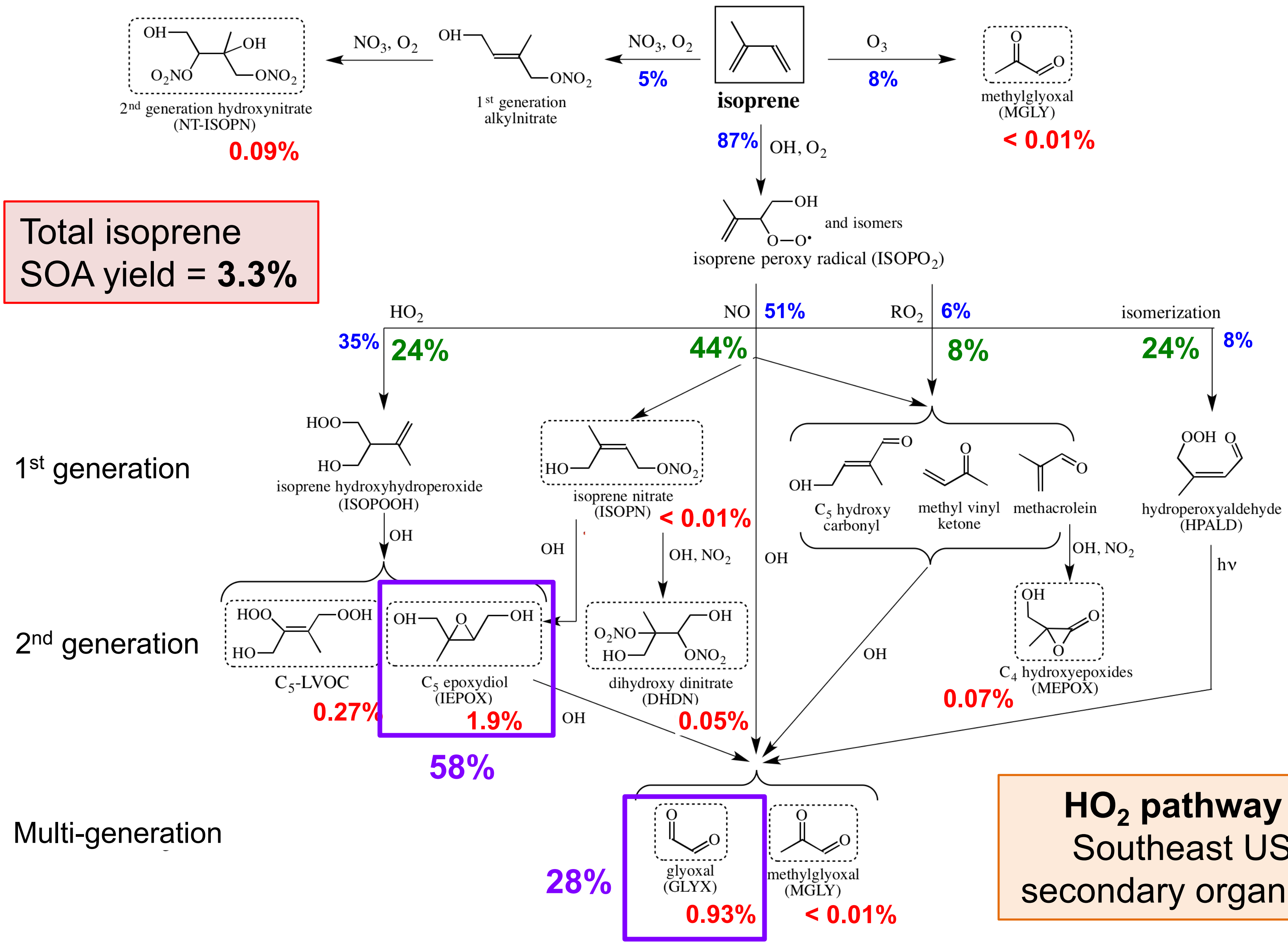
Aqueous-Phase Mechanism Framework



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%**



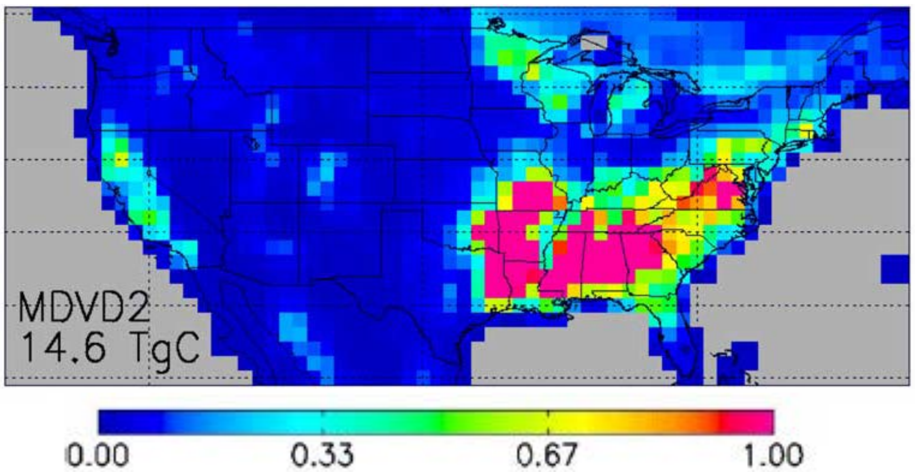
HO_2 pathway is **73%** of Southeast US isoprene secondary organic aerosol

OA-HCHO Relationship

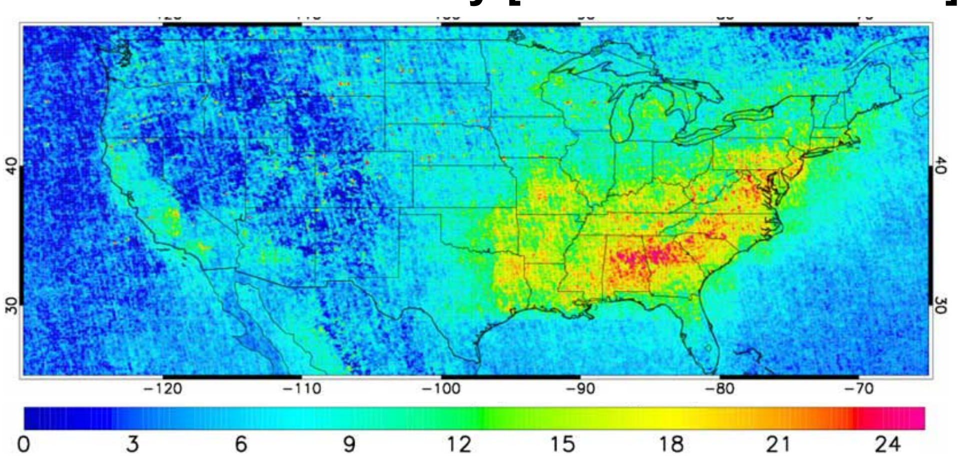
Relationship should be **sensitive to isoprene SOA yields**

Isoprene is the largest source of HCHO

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



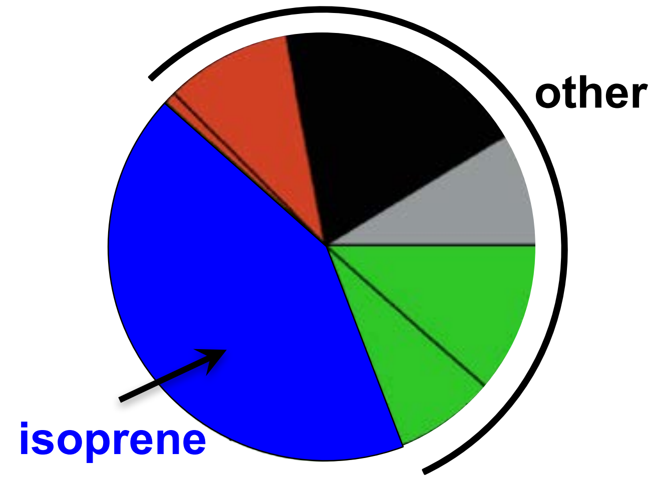
HCHO Column Density [10^{16} molecules cm^{-2}]



[Millet et al., 2008]

Isoprene SOA is 40% of OA

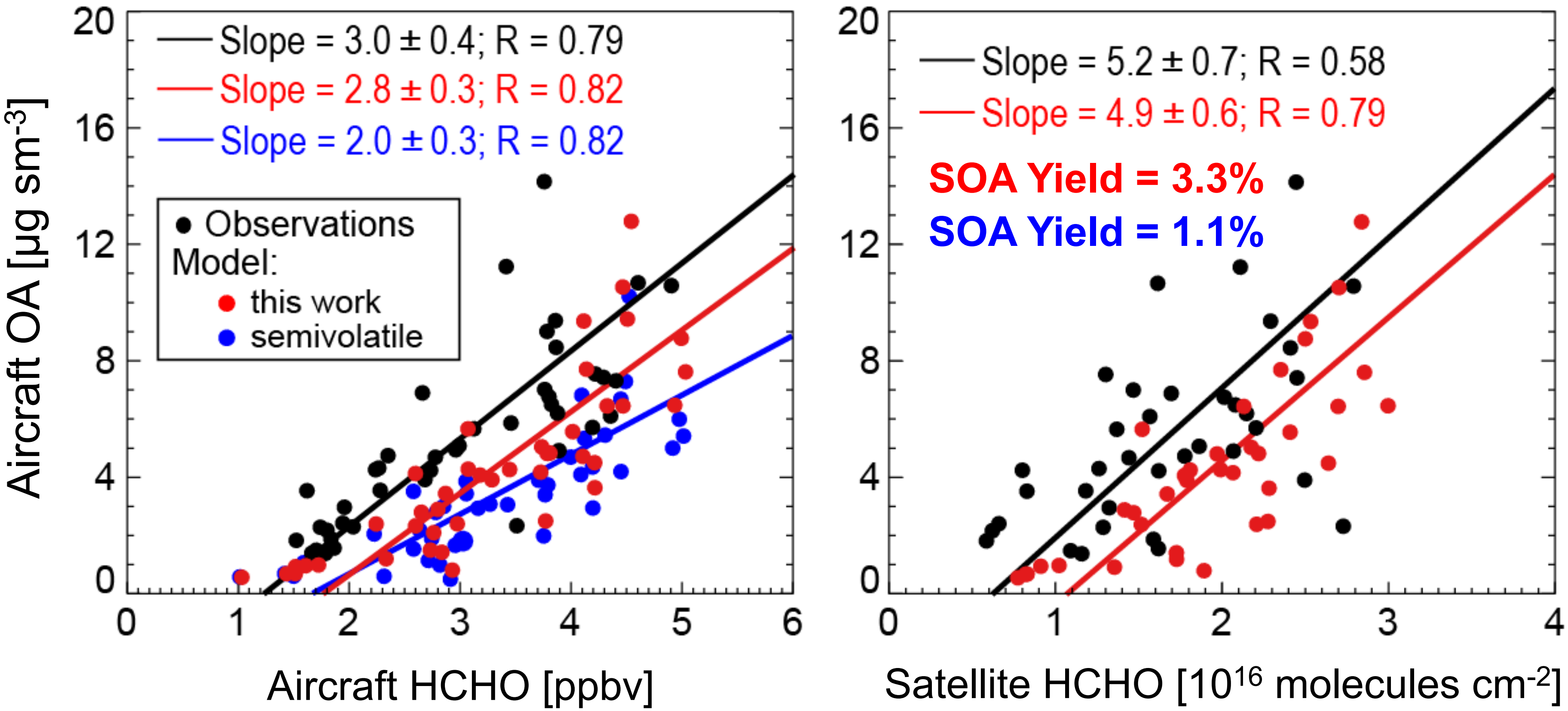
Southeast US OA



Adapted from Kim et al. [2015]

OA-HCHO Relationship Constrains Isoprene SOA Yields

OA-HCHO Relationships during SEAC^{4}RS (Aug-Sep 2013)



Traditional scheme underestimates the slope

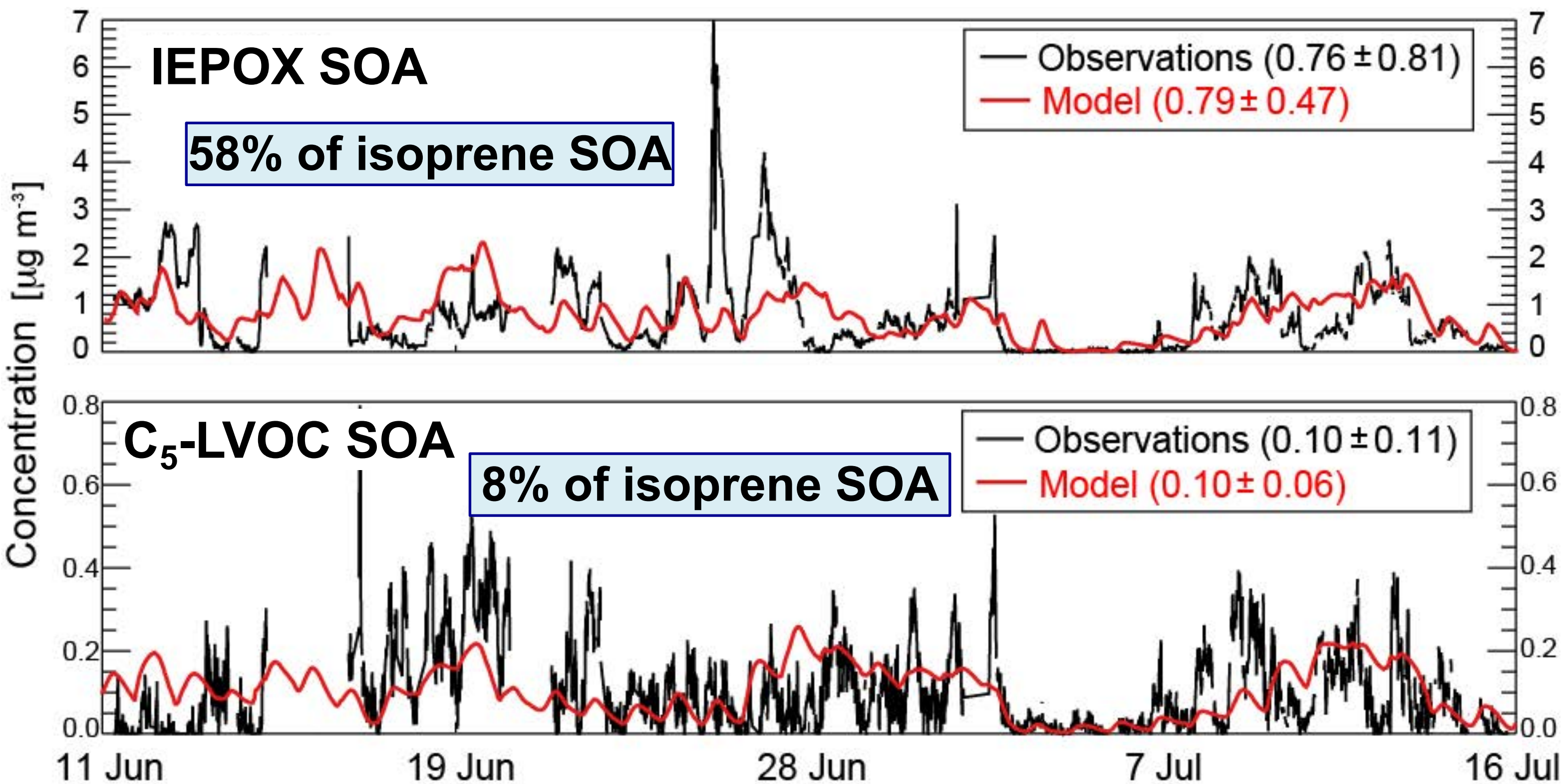
Irreversible uptake scheme reproduces observations: **3.3% isoprene SOA yield.**

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

Observational Constraints on Isoprene SOA Components

$$\text{ISOP} \xrightarrow[87\%]{\text{OH, } O_2} \text{ISOPO}_2 \xrightarrow[35\%]{HO_2} \text{ISOPOOH} \xrightarrow{\text{OH}} \begin{cases} \xrightarrow{75\%} \text{IEPOX} \\ \xrightarrow{0.5\%} C_5\text{-LVOC} \end{cases}$$

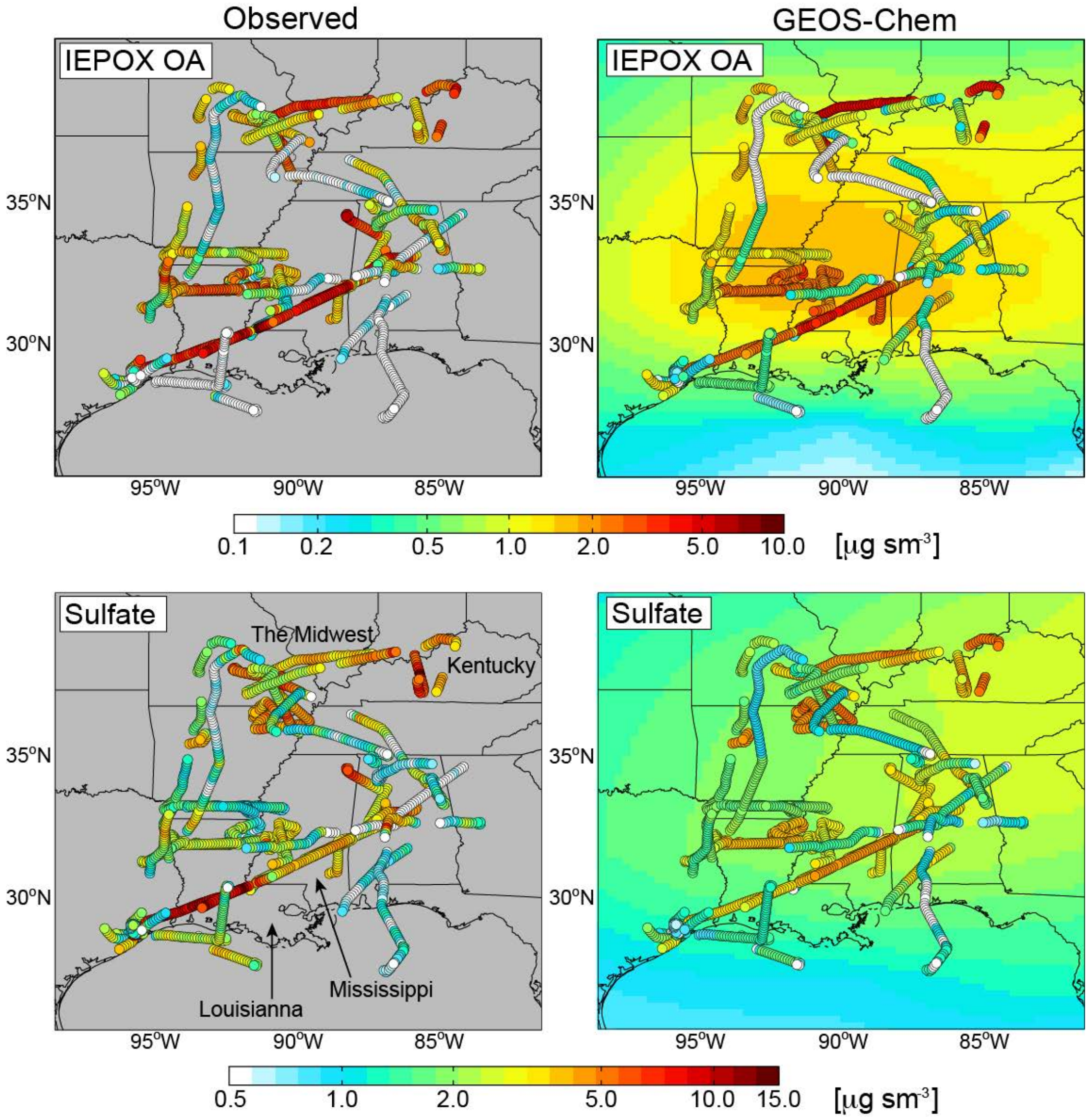
Secondary organic aerosol from IEPOX and C_5-LVOC at Centreville, AL (SOAS campaign; Jun-Jul 2013)



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

Spatial Distribution of IEPOX SOA

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



Points are data along the SEAC⁴RS flight tracks

Background is daytime mean during SEAC⁴RS

Mean IEPOX SOA:

Observations:

1.4 ± 1.4 μg sm^{-3}

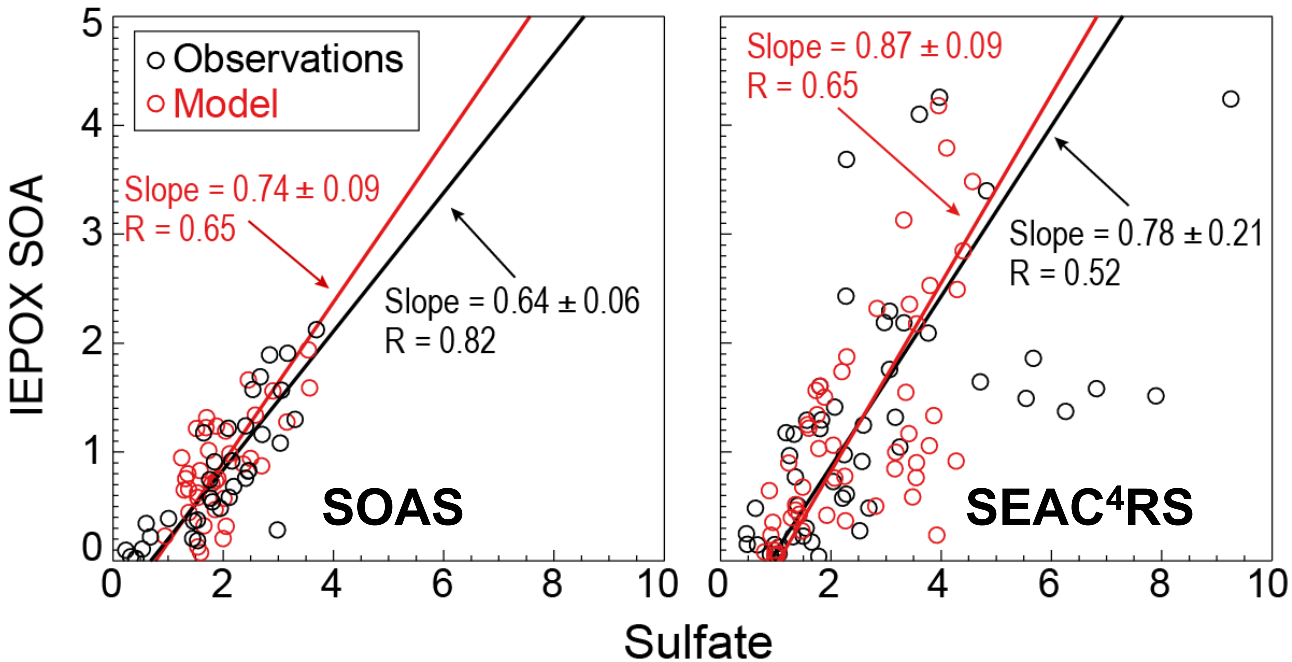
Model:

1.3 ± 1.2 μg sm^{-3}

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

What modulates IEPOX OA in the Southeast US?

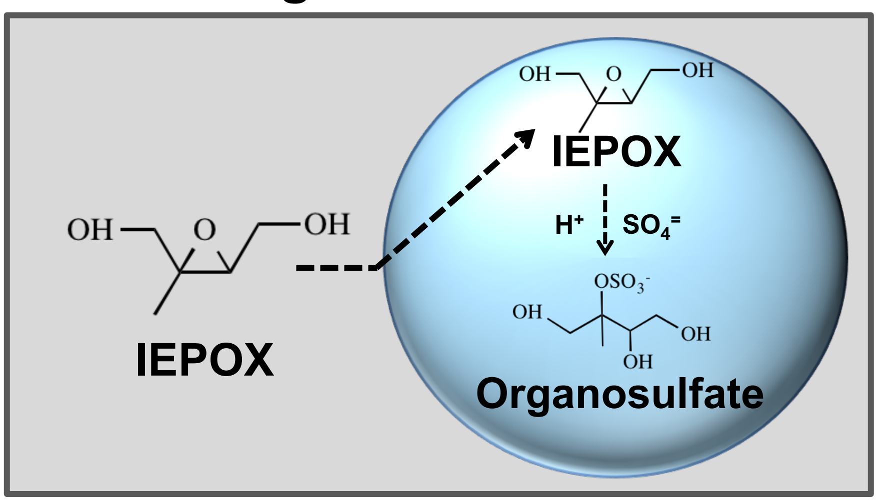
IEPOX SOA and Sulfate correlation during SOAS and SEAC^{4}RS



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

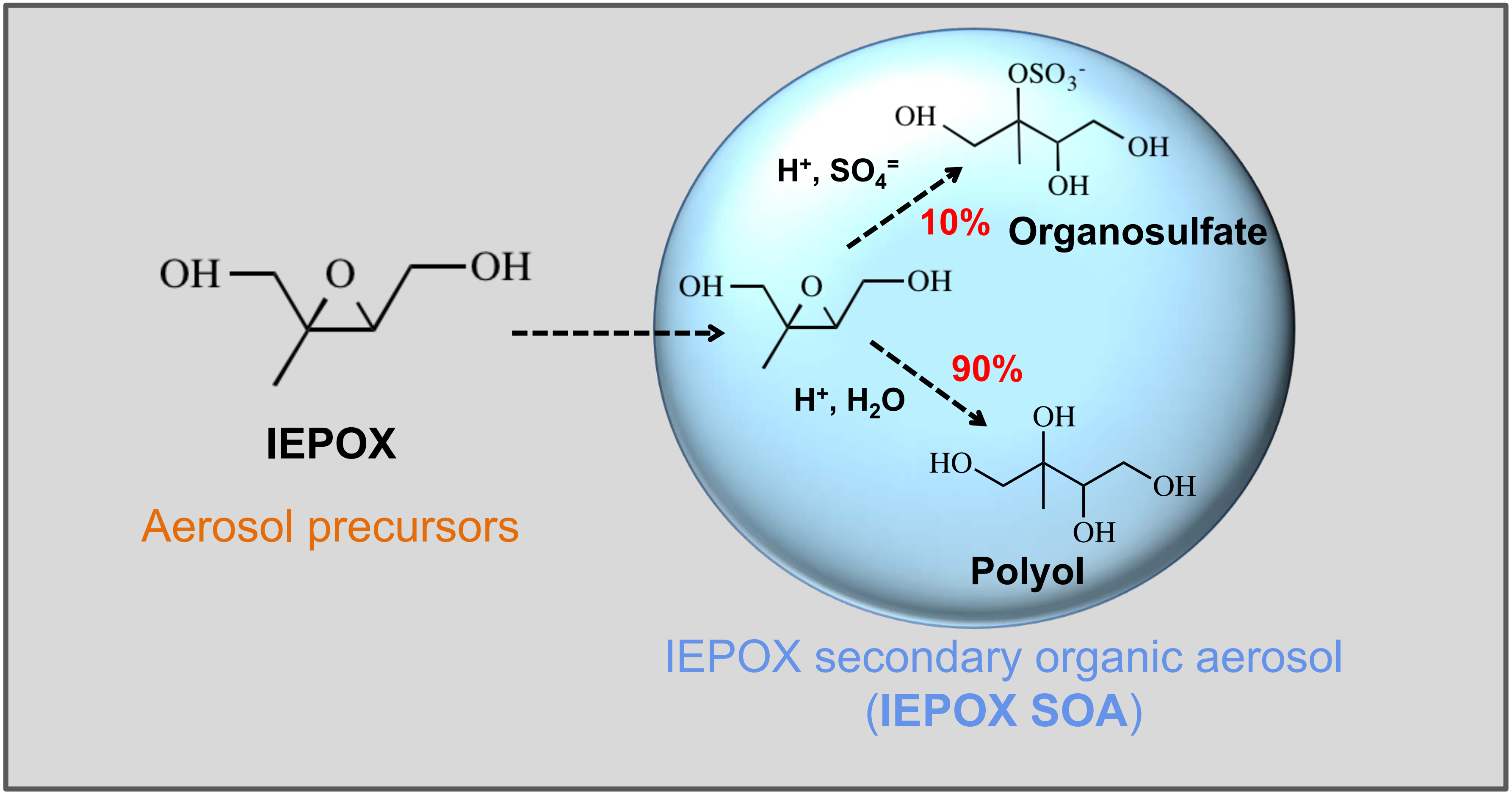
Correlation identified throughout the **Southeast US**:
Budisulistiorini et al. [2013, 2015];
Xu et al., [**2015a**, 2015b]; Hu et al. [2015]

IEPOX-organosulfate formation



Sulfate correlation not due to nucleophilic addition

Acid-catalyzed ring cleavage to produce non-volatile species

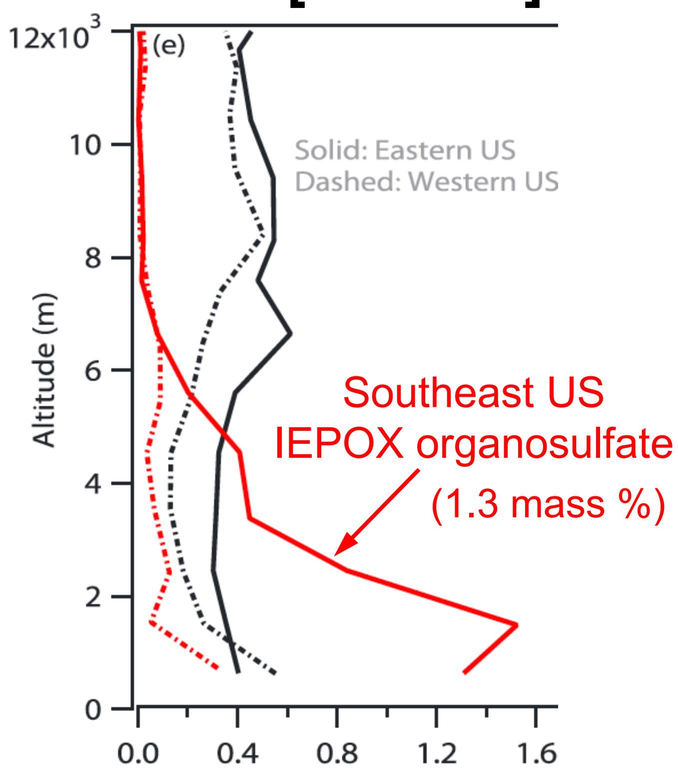


In our mechanism acid-catalyzed **sulfate addition is <u>10%</u>** and acid-catalyzed **H_2O addition is <u>90%</u>** of the fate of IEPOX

Aircraft observations constrain organosulfate formation

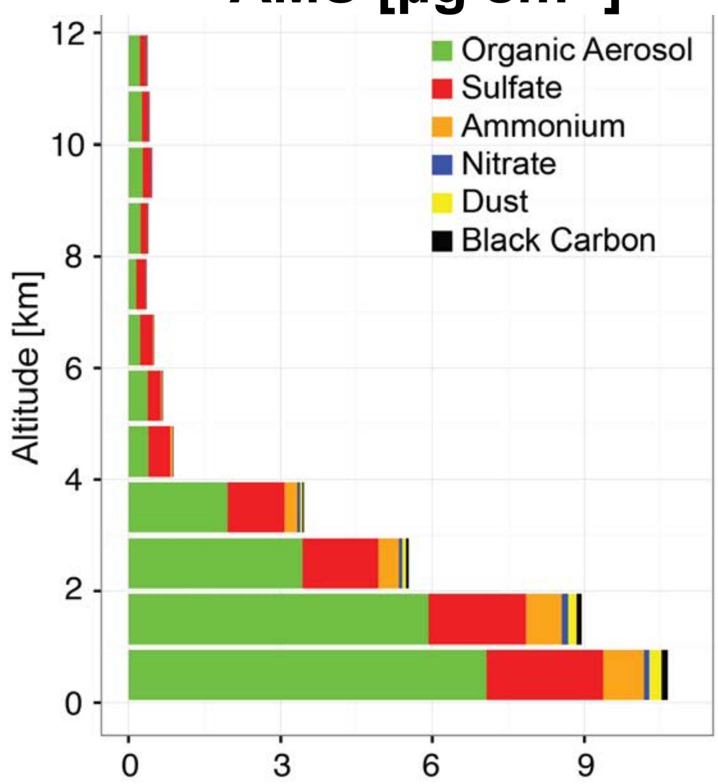
Additional support for limited role of sulfate channel from SEAC^{4}RS PALMS **IEPOX-organosulfate observations:**

PALMS [mass %]



[Liao et al., 2015]

AMS [μg sm^{-3}]



[Kim et al., 2015]

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

IEPOX-organosulfates long-lived, so remain intact throughout the aerosol lifetime

Sulfate impacts aerosol acidity and volume

Anthropogenic sulfate influences isoprene SOA formation

↓ **SO_2** → ↓ **Sulfate** → ↓ Aerosol abundance, ↑ Aerosol pH → ↓ **isoprene SOA**

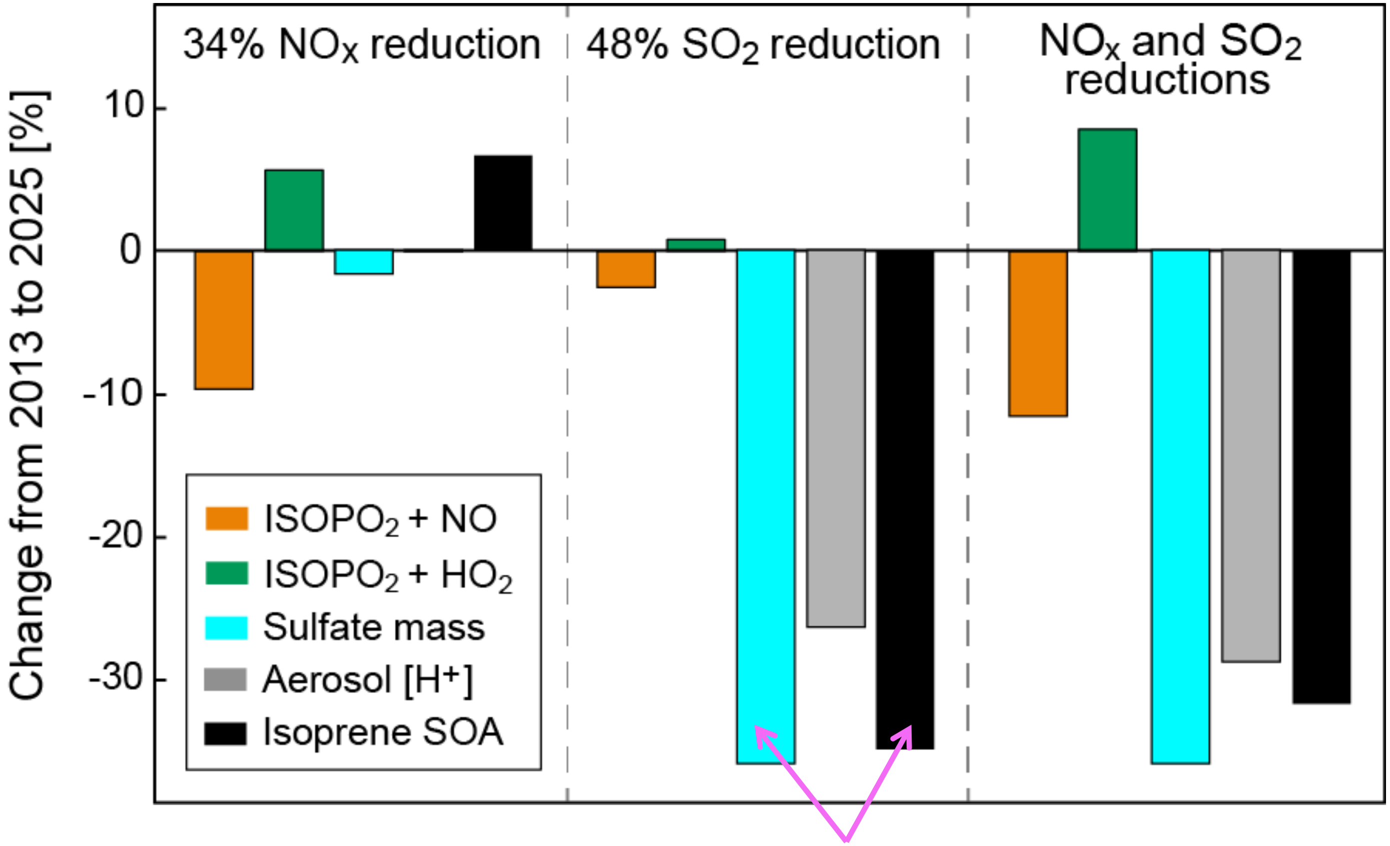
Aqueous aerosol **abundance** impacts **all isoprene SOA precursors**

Aerosol **acidity** impacts **IEPOX**

Effect of Anthropogenic Emission Reductions

Test the effect of future SO_2 and NO_x emission controls on isoprene SOA

Changes in sulfate, aerosol pH, and isoprene SOA



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

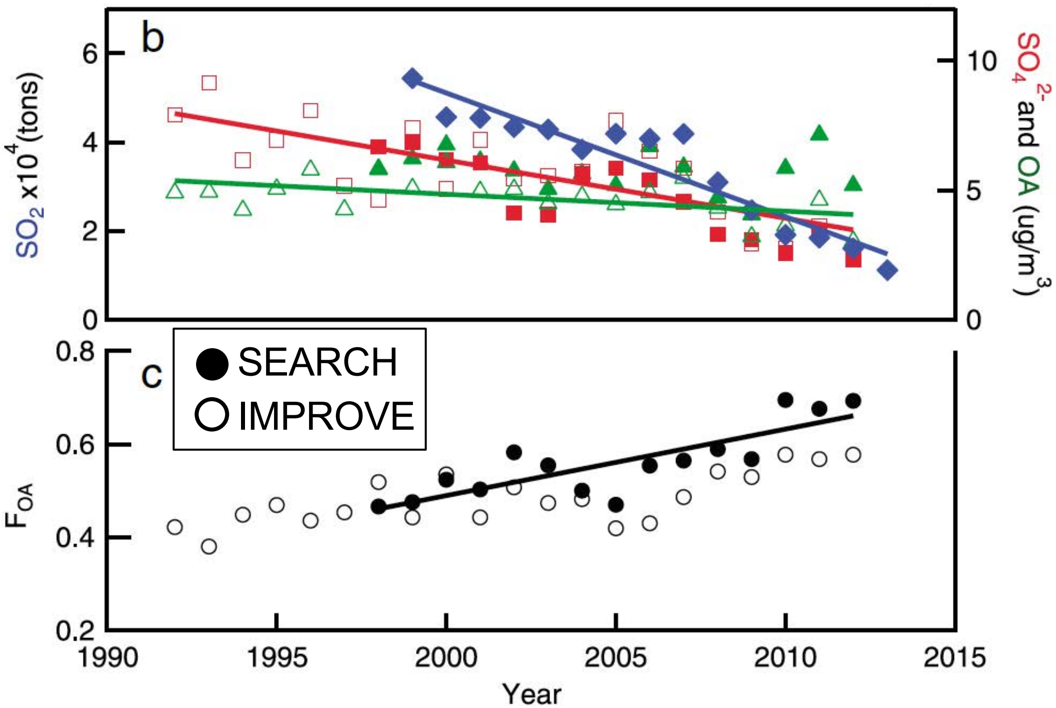
Policy implication: Dual benefit from targeting SO_2 sources

[Marais et al., ACP, 2016]

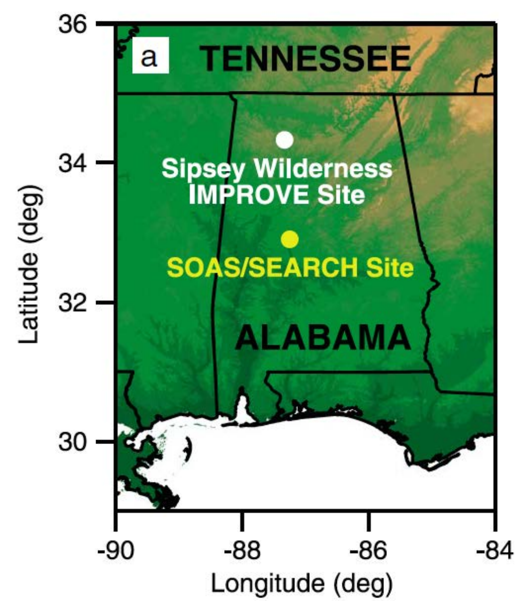
Organic Aerosol Fraction is Increasing – Southeast US

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

SO_2 emissions, and sulfate aerosol and organic aerosol mass



Rural Southeast US monitoring site



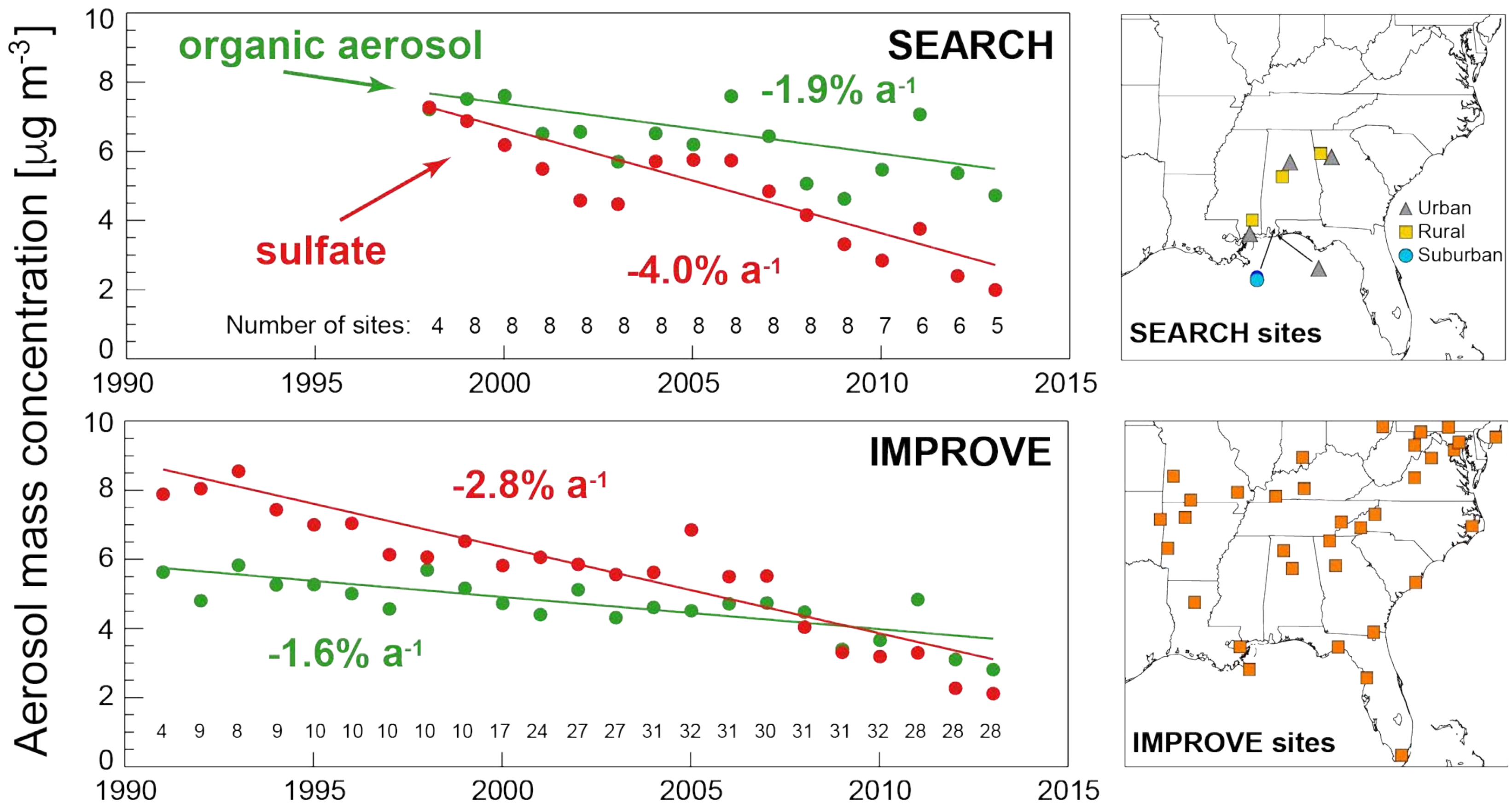
[Attwood et al., 2014]

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

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

Observed decline in sulfate and OA in the Southeast US

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

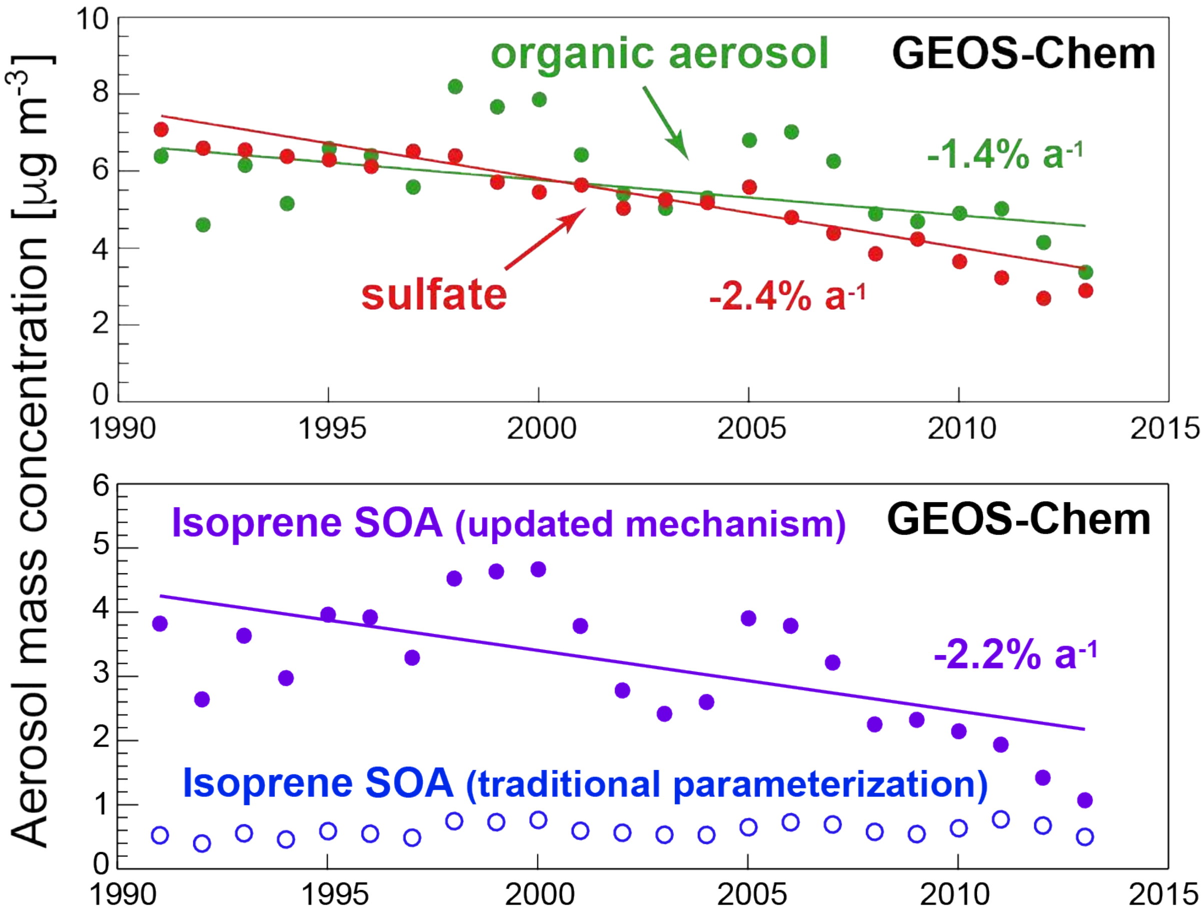


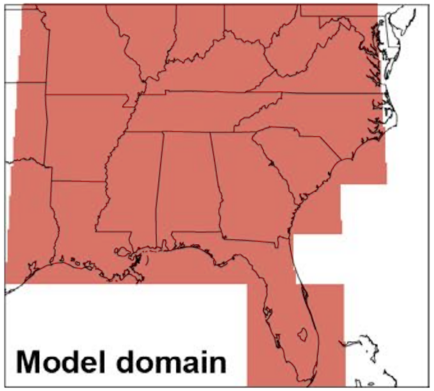
Steeper decline in sulfate at SEARCH than IMPROVE sites – greater urban influence. Similar OA trends supports **biogenic SOA driving the trend**

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)





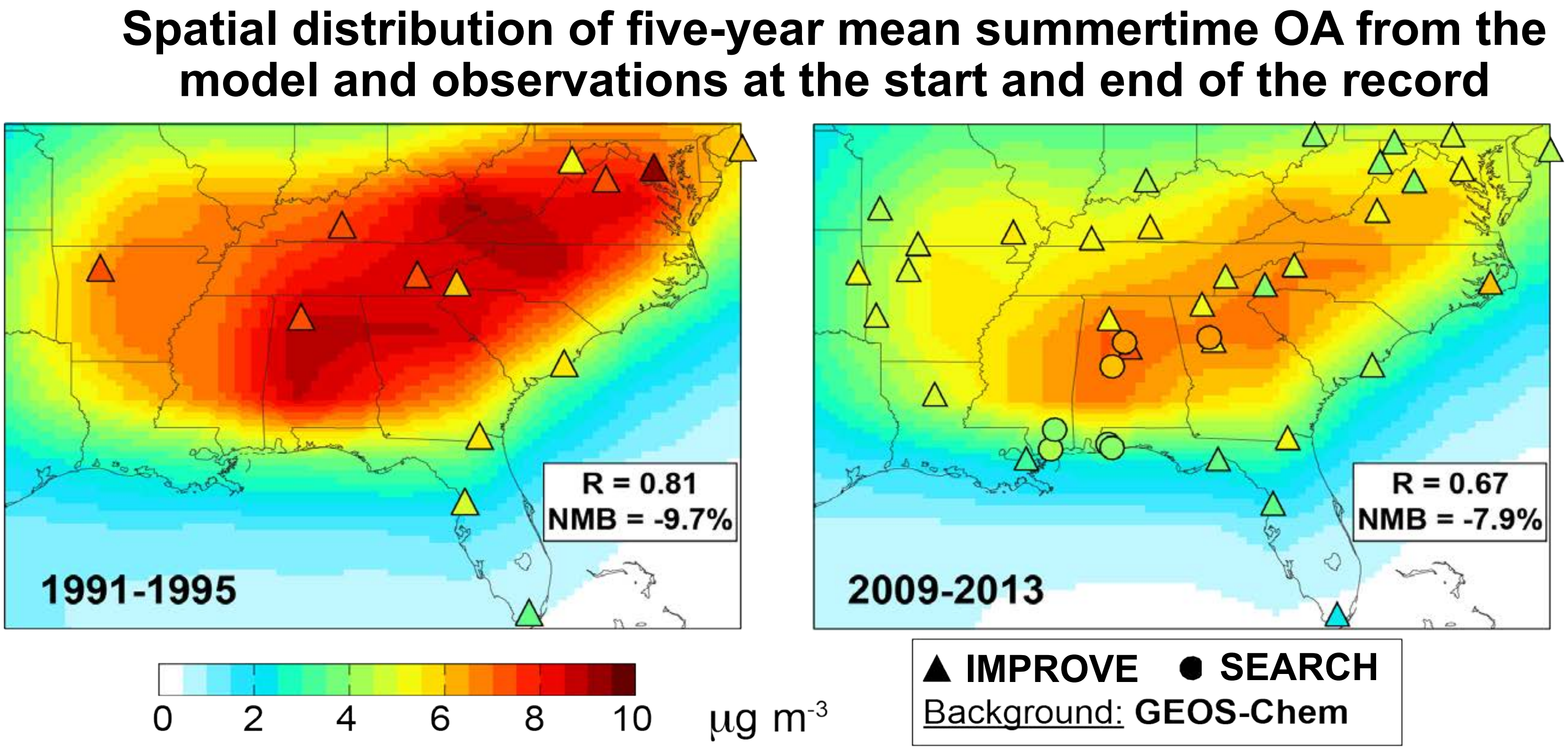
No significant trend in traditional scheme.

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

Large OA interannual variability due to isoprene emissions.

Majority of decline in modelled OA is due to isoprene SOA

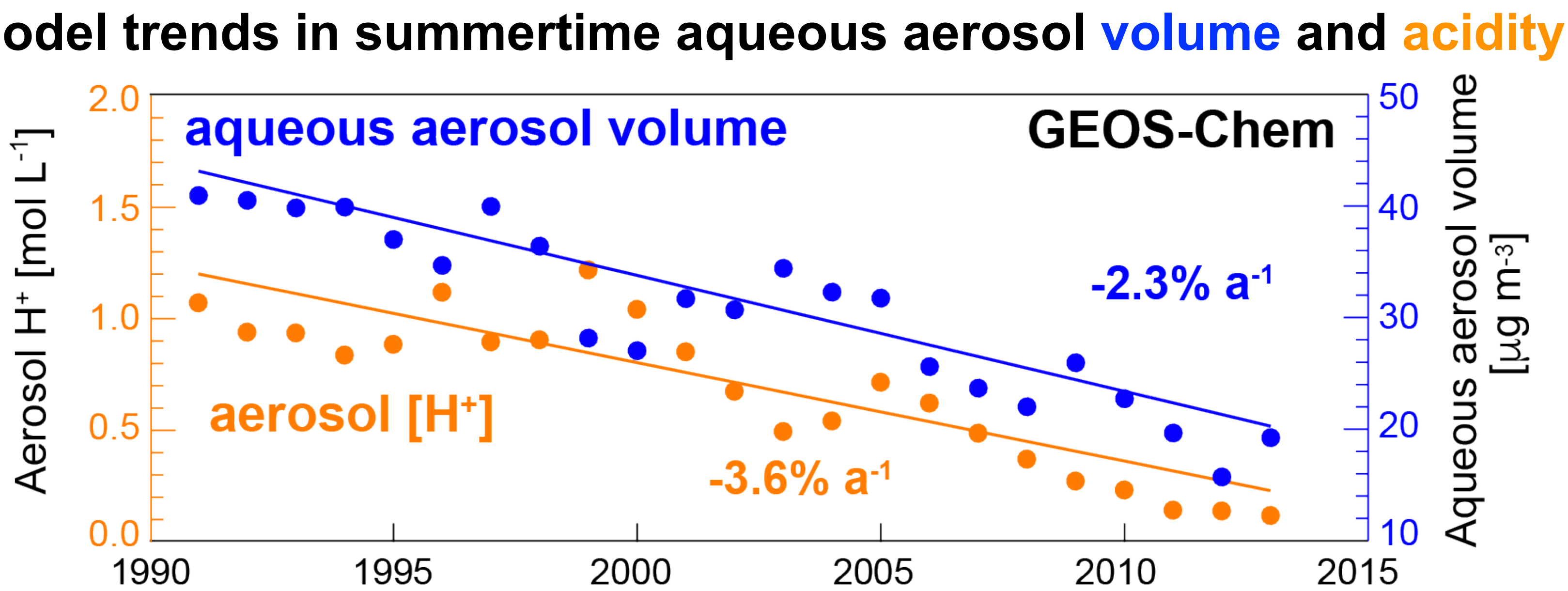
Spatial distribution of organic aerosol trends



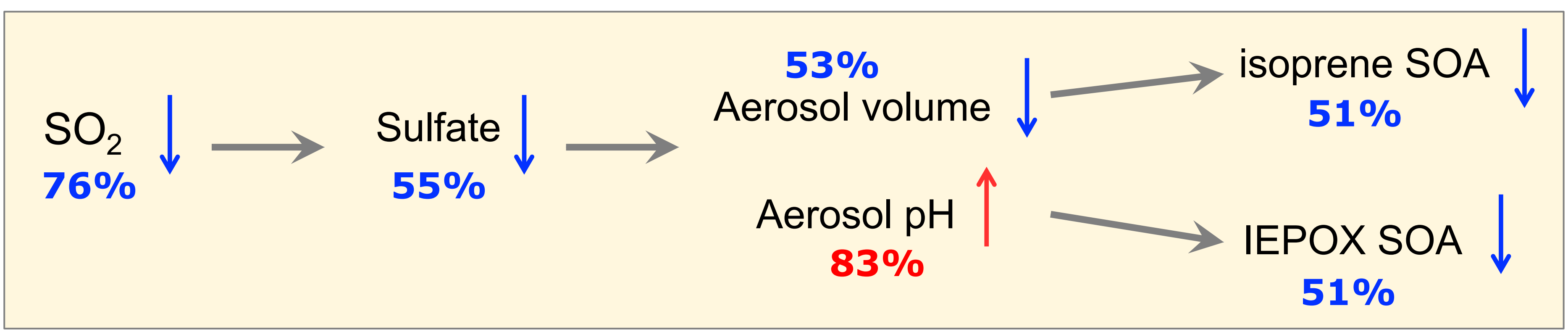
No significant change in OA spatial distribution in the observations or model supports biogenic SOA driving the OA trend.

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

Modelled isoprene SOA decreases due to decline in sulfate

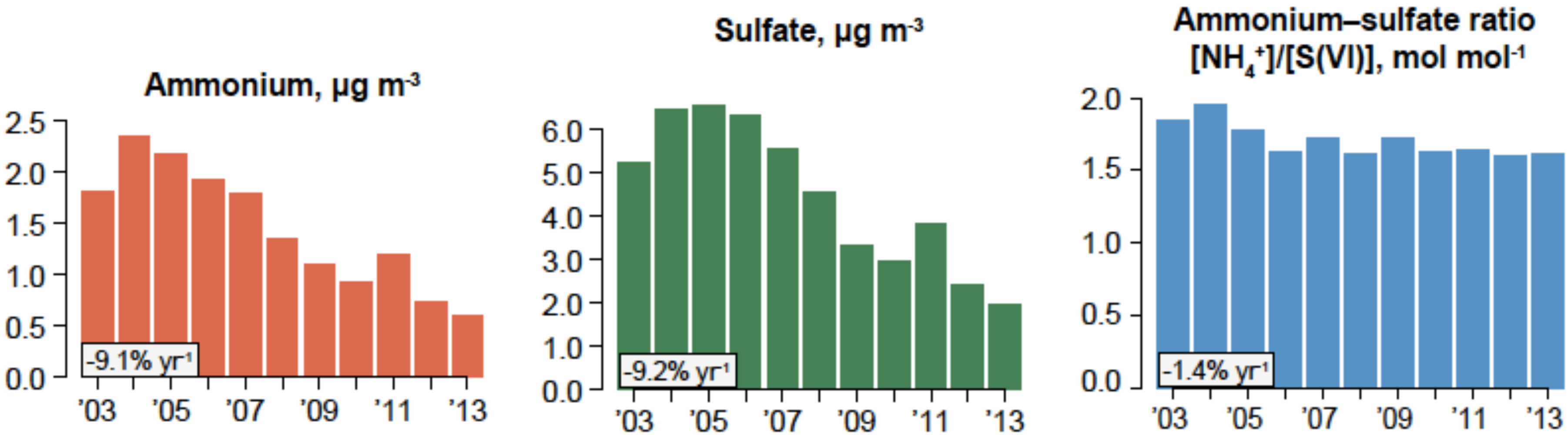


Decline in sulfate (dominant aqueous aerosol component) **decreases aqueous aerosol volume** and **increases aqueous aerosol pH**



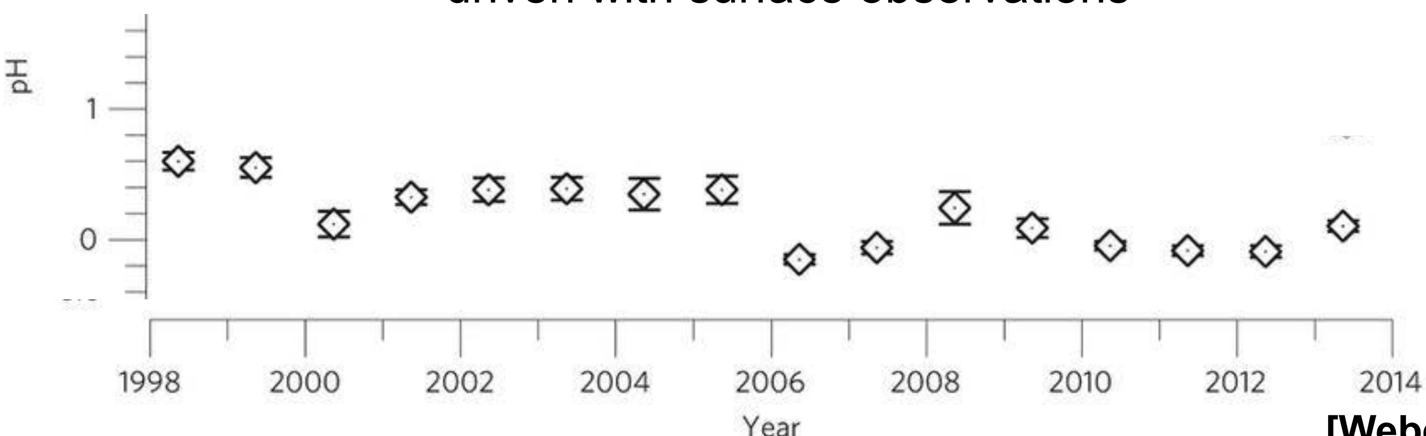
Aerosol Acidity Trend is Controversial

Observations (2003-2013) show decrease in ammonium and sulfate even though emissions of NH_3 have remained steady:



[Silvern et al., 2017]

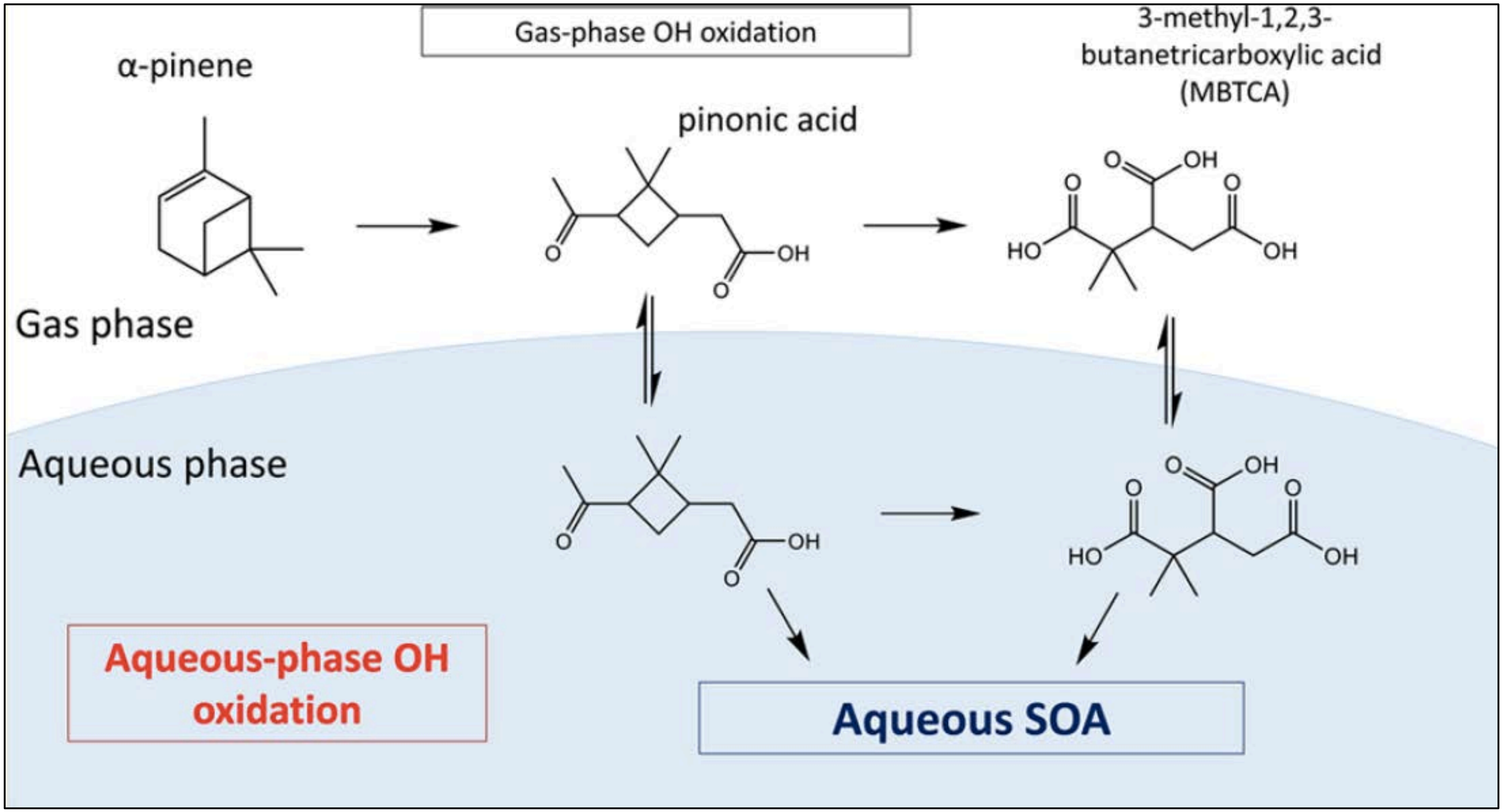
Aerosol acidity may instead be increasing, according to a thermodynamic model driven with surface observations



[Weber et al., 2016]

What about monoterpenes?

First chamber study showing aqueous-phase monoterpene SOA formation:



[Aljawhary et al., 2016]

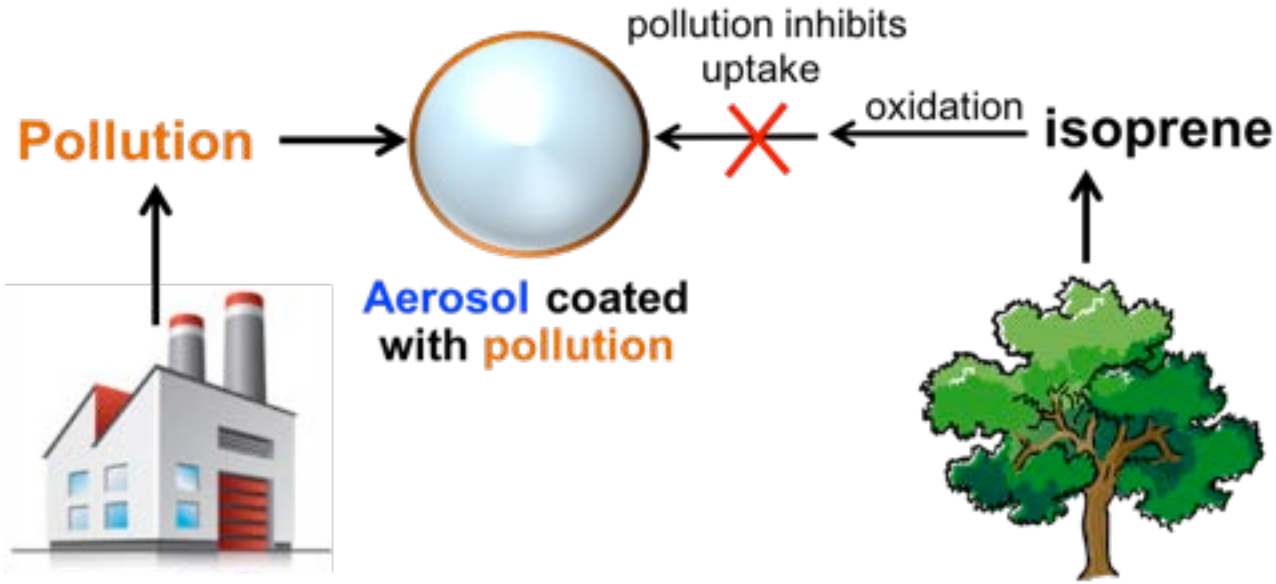
Implies **relationship** between aqueous aerosol abundance (**sulfate**) and **monoterpene SOA**.

Concluding Remarks

- Coupled explicit isoprene SOA formation mechanism to detailed gas-phase chemistry in the GEOS-Chem model
- Extensively evaluated isoprene SOA composition with surface and aricraft observations.
- Linear relationship between sulfate and isoprene SOA that in the model is due to dependence of isoprene SOA on aqueous aerosol abundance and acidity.
- This represents a dual air quality benefit of SO_2 emission controls by concurrently decreasing sulfate and isoprene SOA.
- We find support for long-term (1991-2013) decline in OA in the Southeast US in summer as due to decline in isoprene SOA driven by decline in sulfate.
- The implication is that countries in the isoprene-rich tropics will experience devastating air quality degradation if SO_2 emissions increase there.

Cascade of Research Questions

What is the global impact of complex biogenic-anthropogenic interactions constrained with process-based information from chamber experiments?



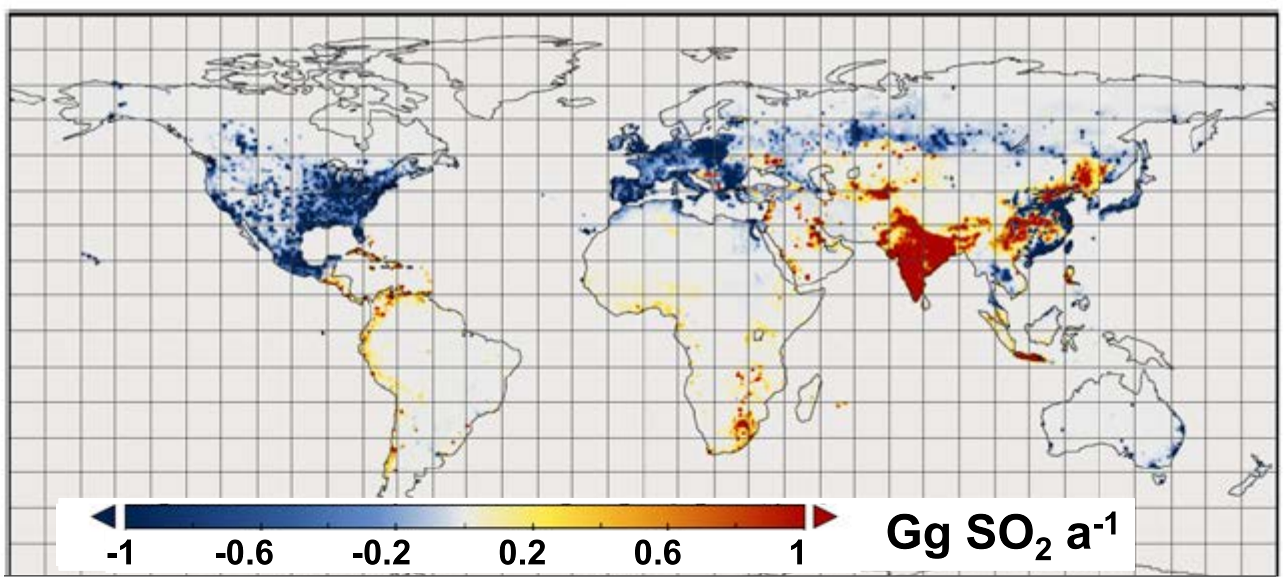
Collaborators: Jason Surratt (UNC Gillings School of Public Health, Chapel Hill)

Also submitted a NERC DTP studentship application.

Cascade of Research Questions

What is the impact of future development in the isoprene-rich tropics on local air quality?

2010 minus 2005 SO_2 emissions



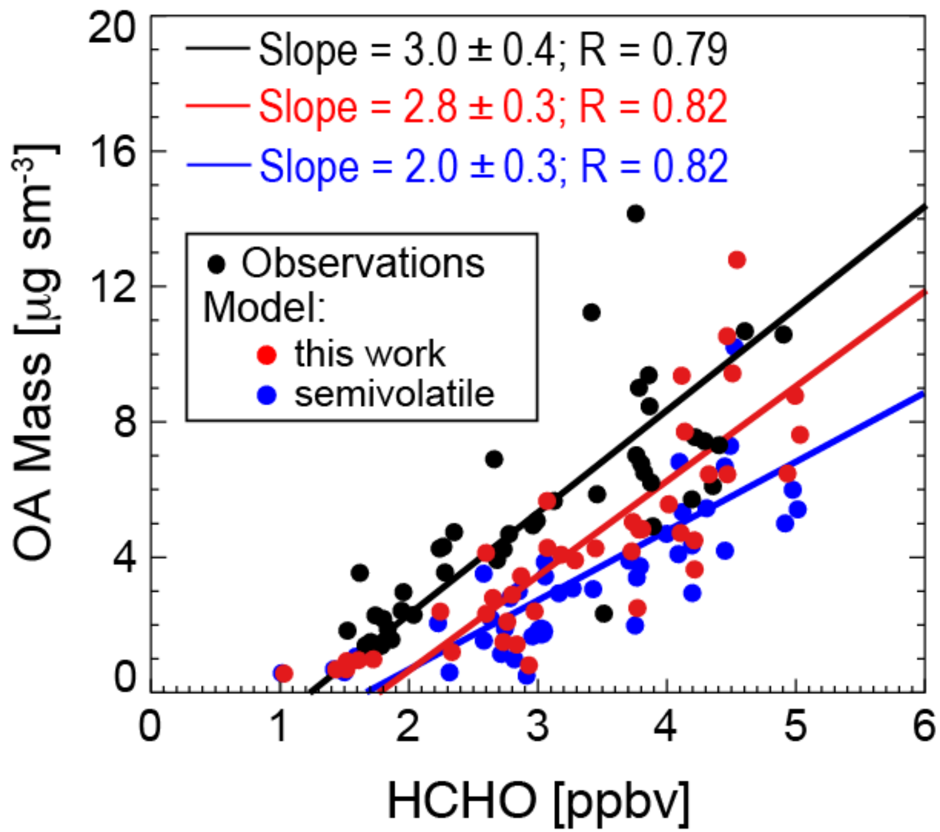
[Klimont et al., 2013]

Investigate how biogenic SOA responds to changes in SO_2 emissions

Collaborators: Paul Palmer (U. Edinburgh), Ben Langford, Eiko Nemitz (CEH)

Cascade of Research Questions

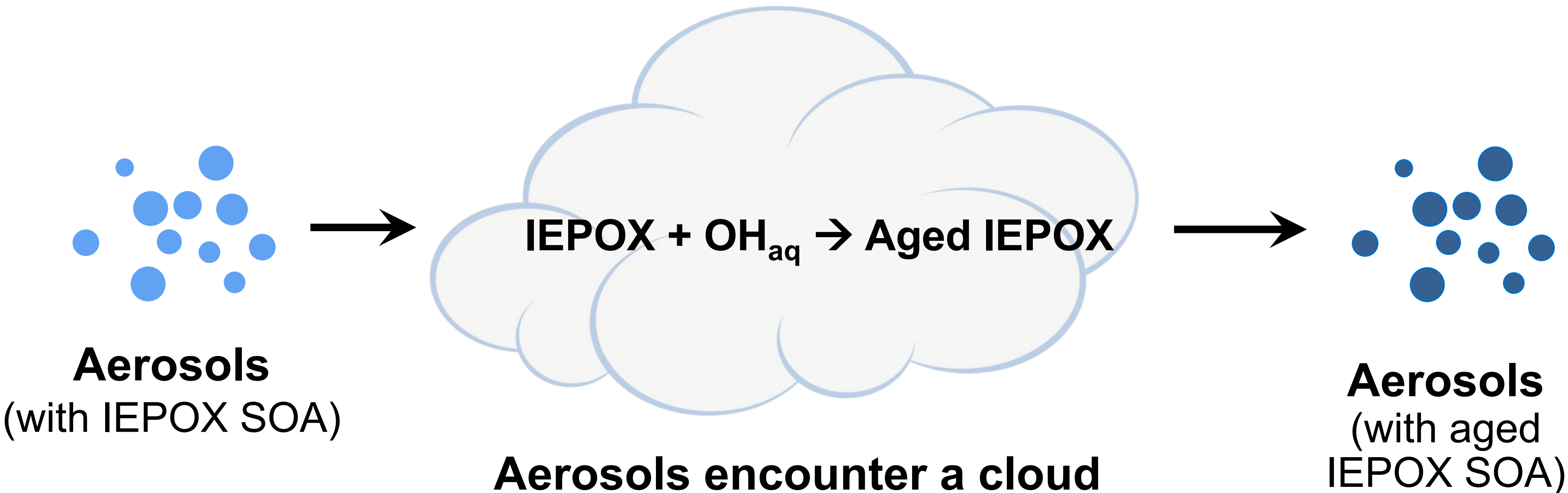
What is the contribution of OA sources to the relationship between OA and formaldehyde?



Led by: NASA (Jin Liao, Thomas Hanisco)

Cascade of Research Questions

Apply new laboratory and field measurements to the model to investigate interactions between clouds and biogenic SOA.



Led by: José Jimenez, Pedro Campuzano-Jost (UC Boulder).