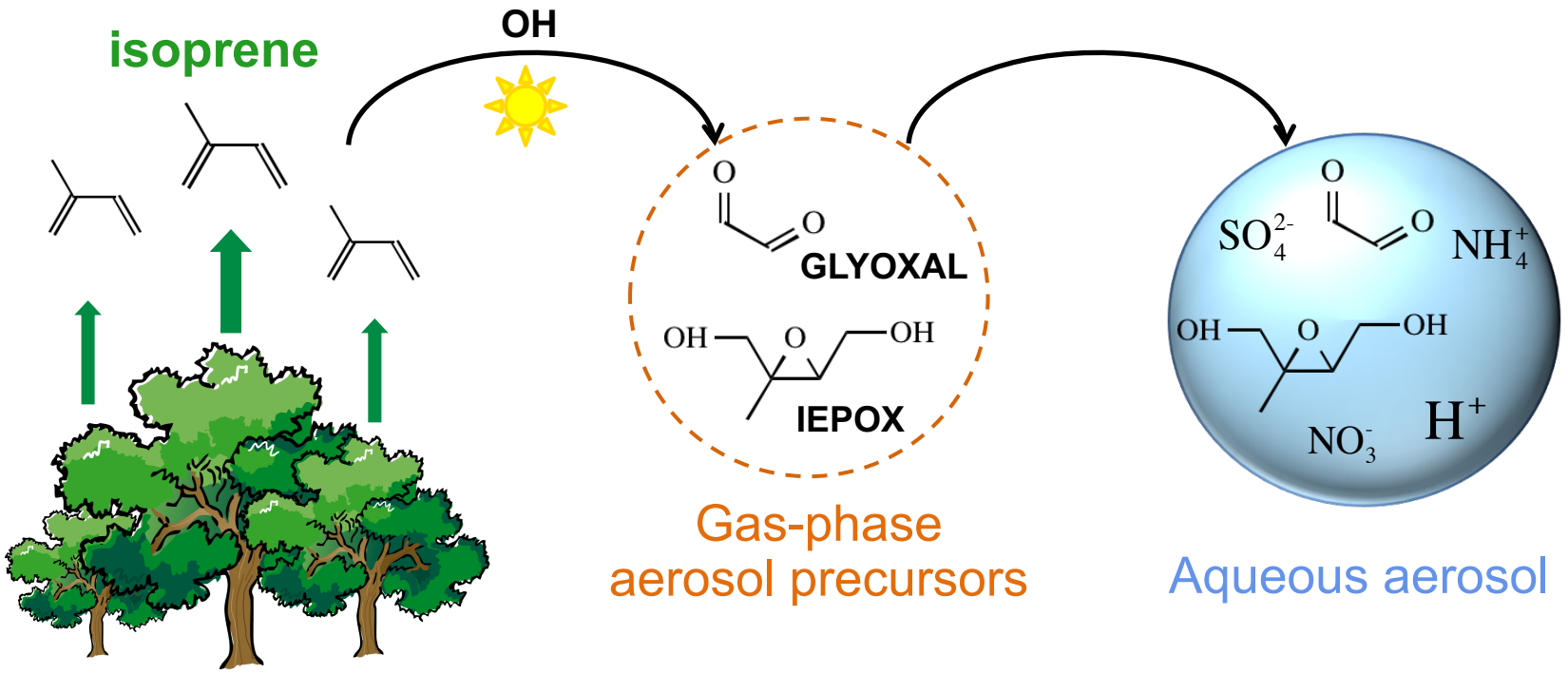
Aqueous-phase mechanism for secondary organic aerosol formation from isoprene:

Application to the Southeast US and co-benefit of SO_2 emission controls



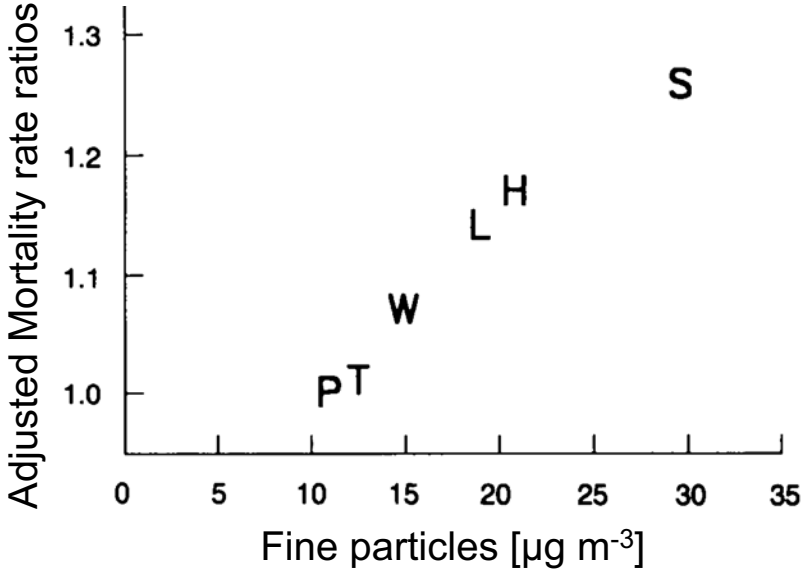
Coauthors: D. J. Jacob, J. L. Jimenez, P. Campuzano-Jost, D. A. Day, W. Hu, J. Krechmer, L. Zhu, P. S. Kim, C. C. Miller, J. A. Fisher, K. Travis, K. Yu, T. F. Hanisco, G. M. Wolfe, H. L. Arkinson, H. O. T. Pye, K. D. Froyd, J. Liao, V. F. McNeill

Eloïse A Marais (emarais@seas.harvard.edu)

Georgia Tech Seminar, 10/28/2015

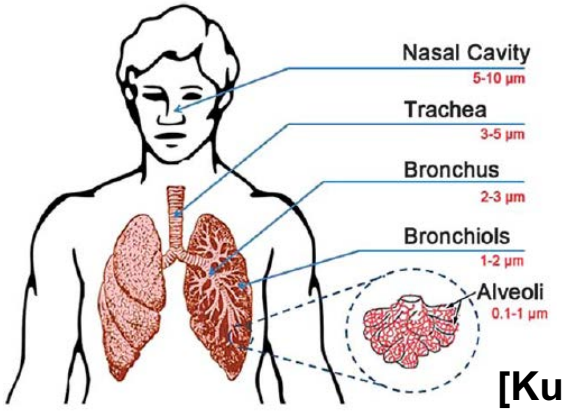
Aerosols Impact Climate, Human Health, and Visibility

Fine particles are associated with **increased mortality**



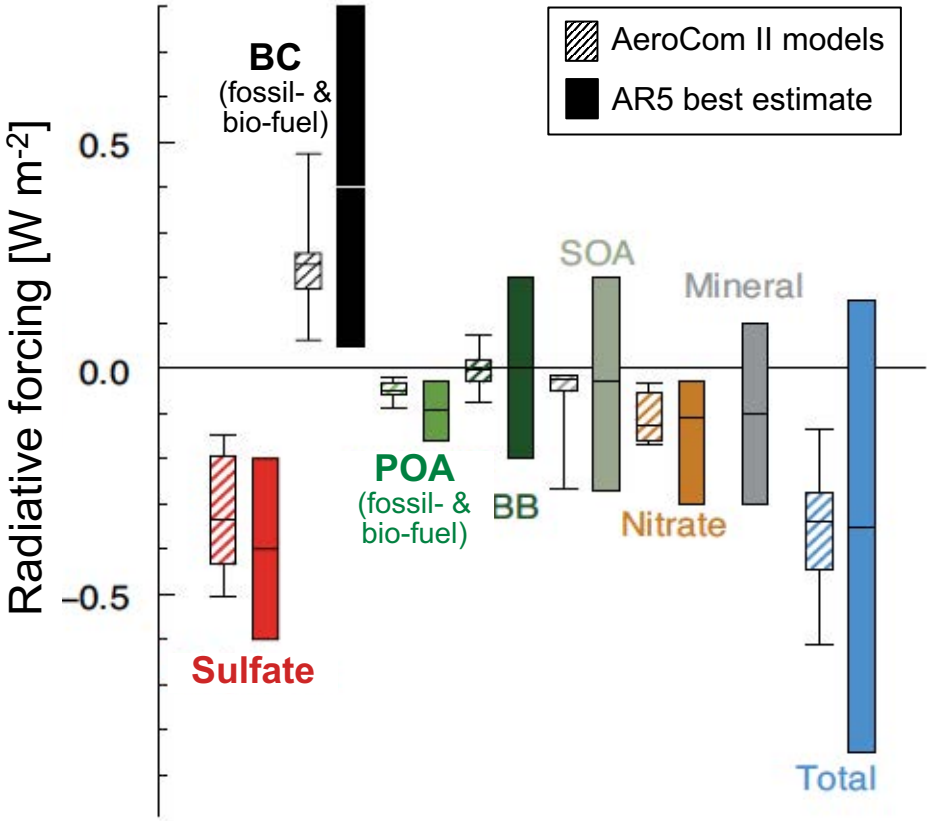
[Dockery et al., 1993]

Fine particles travel deep into the lungs



[Kumar et al., 2014]

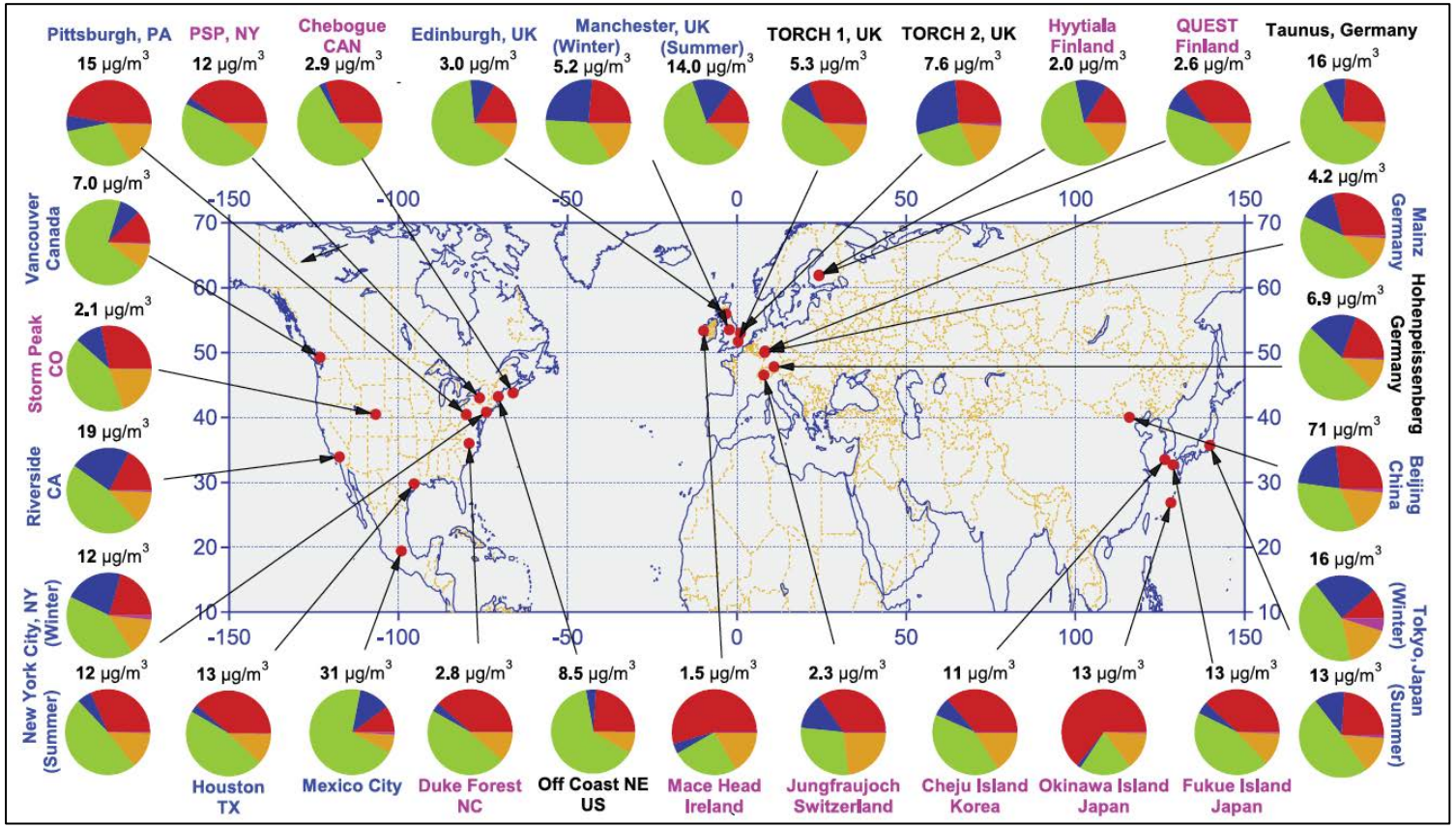
Climate impact of **aerosols** is uncertain

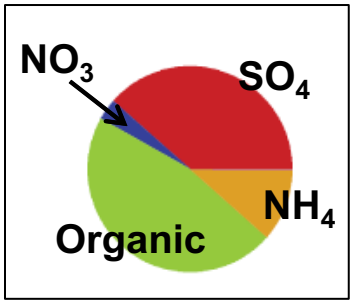


[IPCC AR5, 2013]

Organic Aerosol is Ubiquitous in the Atmosphere

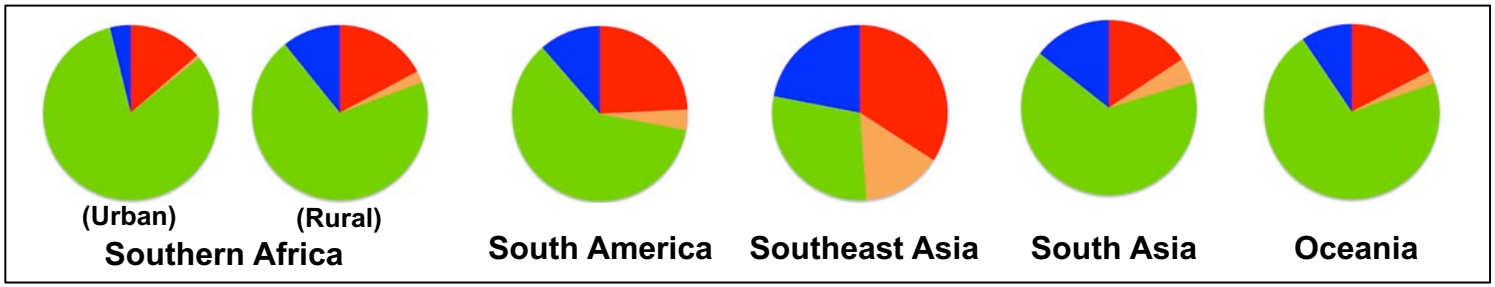
Northern hemisphere aerosol components





[Zhang et al., 2007]

Tropics and southern hemisphere aerosol components

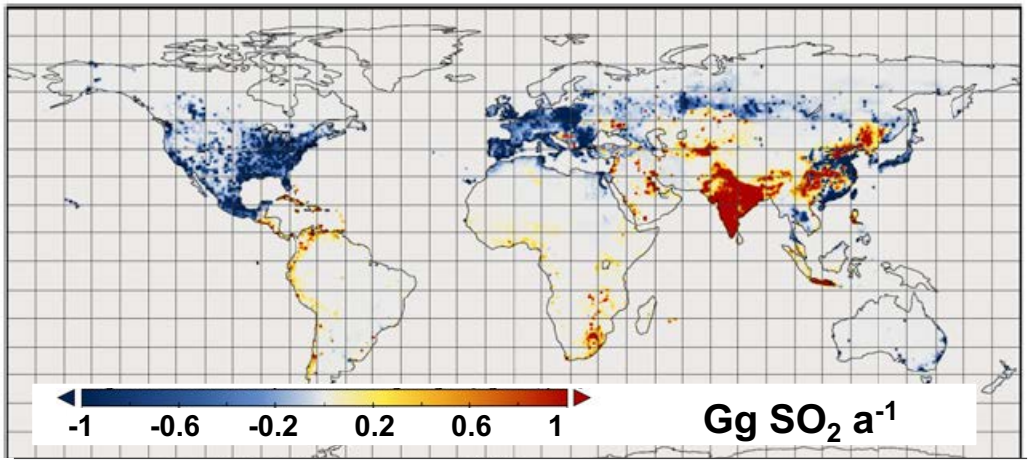


[IPCC, 2013]

Organic Aerosol Fraction is Increasing

In many parts of the world the organic aerosol contribution is increasing as SO_2 emissions (and sulfate) decline

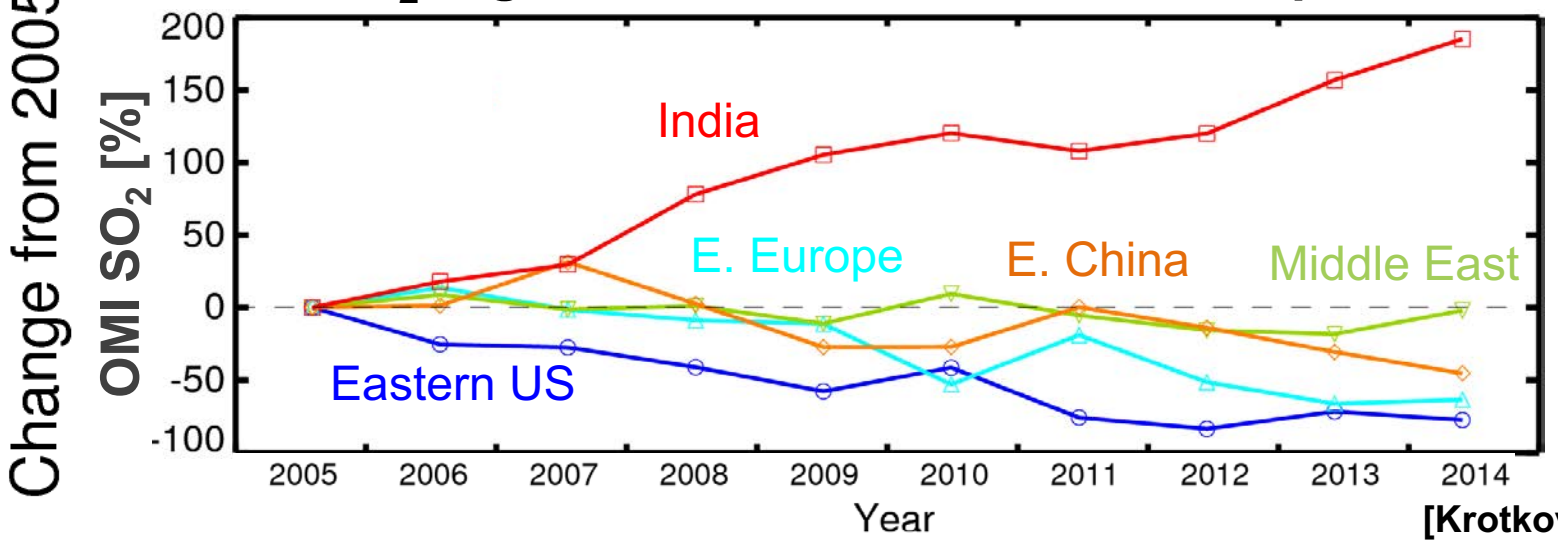
2010 minus 2005 SO_2 emissions



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

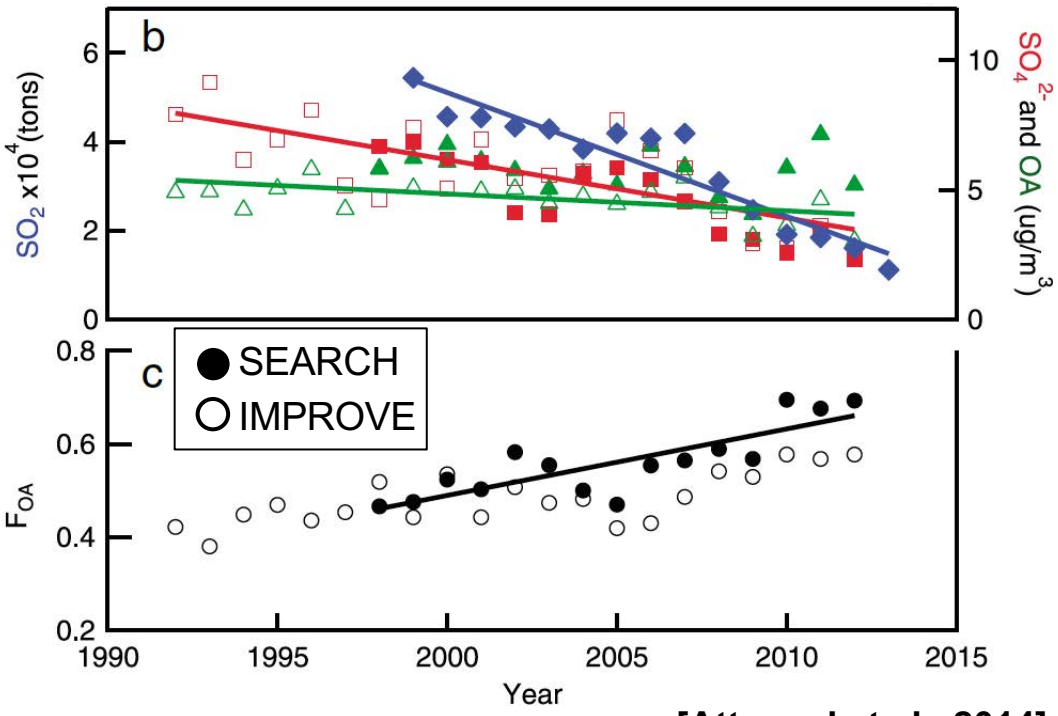


[Krotkov et al., 2015]

Organic Aerosol Fraction is Increasing – Southeast US

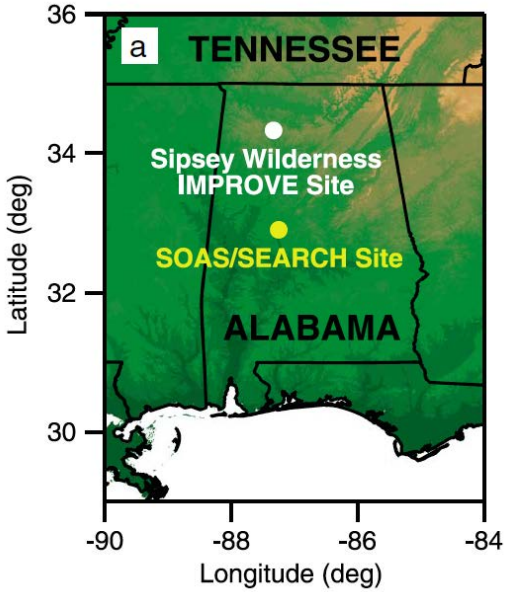
The increasing contribution of organic aerosol is apparent at a rural monitoring site in the Southeast US

SO_2 emissions, and sulfate aerosol and organic aerosol mass



[Attwood et al., 2014]

Rural Southeast US monitoring site



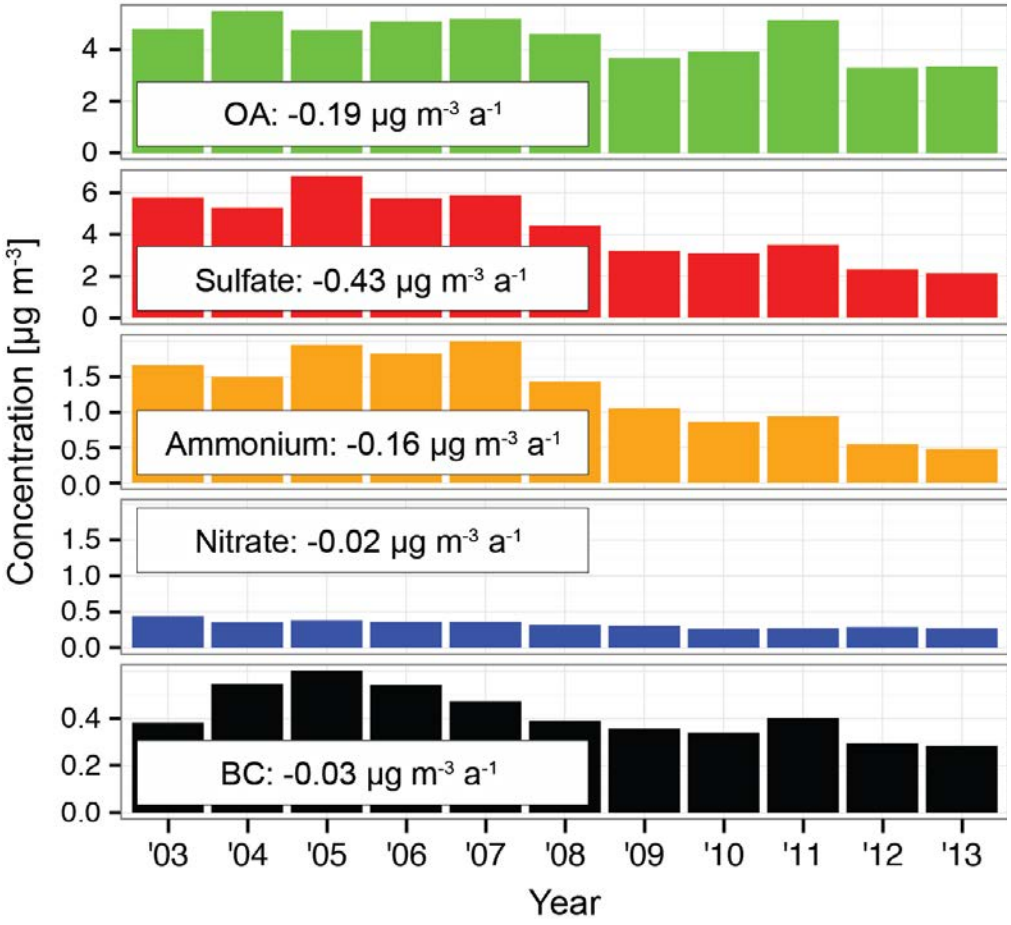
Site impacted by urban, industrial, **biogenic**, and agricultural emissions.

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

Organic Aerosol Component Is Increasing – Southeast US

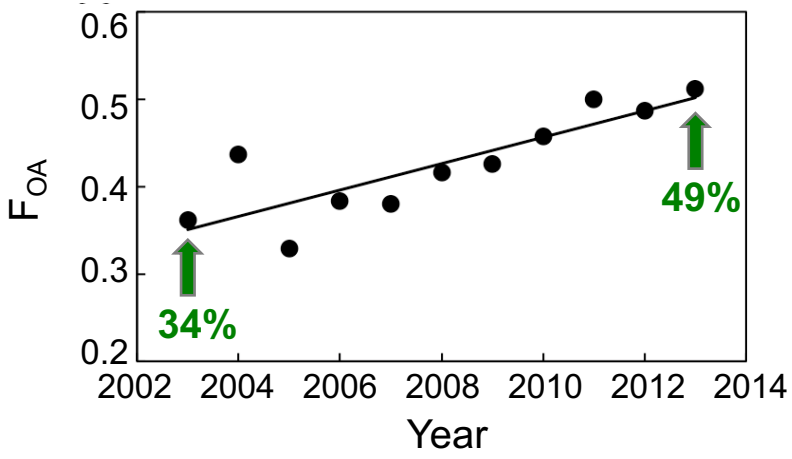
…And throughout the Southeast US

Trend in $PM_{2.5}$ components (summer)



[Kim et al., 2015]

Trend in OA fraction (JJA)



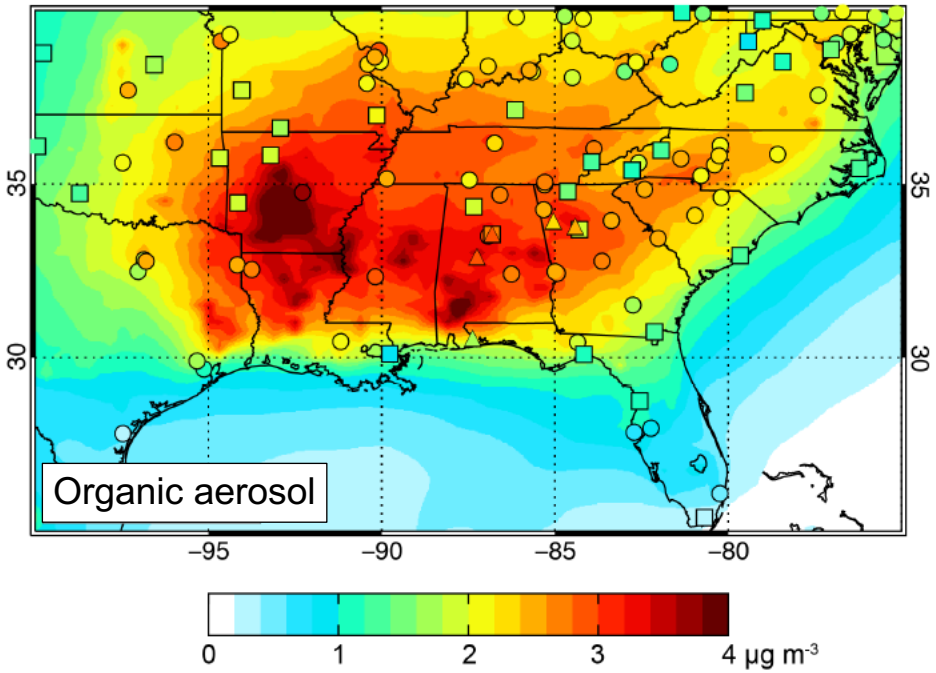
Data extracted from Kim et al. [2015]

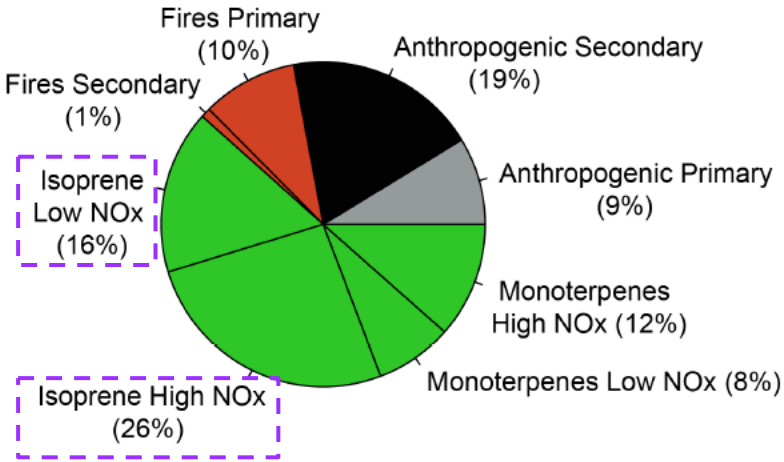
F_{OA} rate of increase across the Southeast US is **1.5% per year**.

F_{OA} (fraction of organic aerosol) increased from 34% in 2003 to 49% in 2013.

Secondary Organic Aerosol Formation from Isoprene

Surface organic aerosol mass in the southeast US in August-September 2013





Background: GEOS-Chem
- IMPROVE
- EPA CSN
- SEARCH

[Kim et al., 2015]

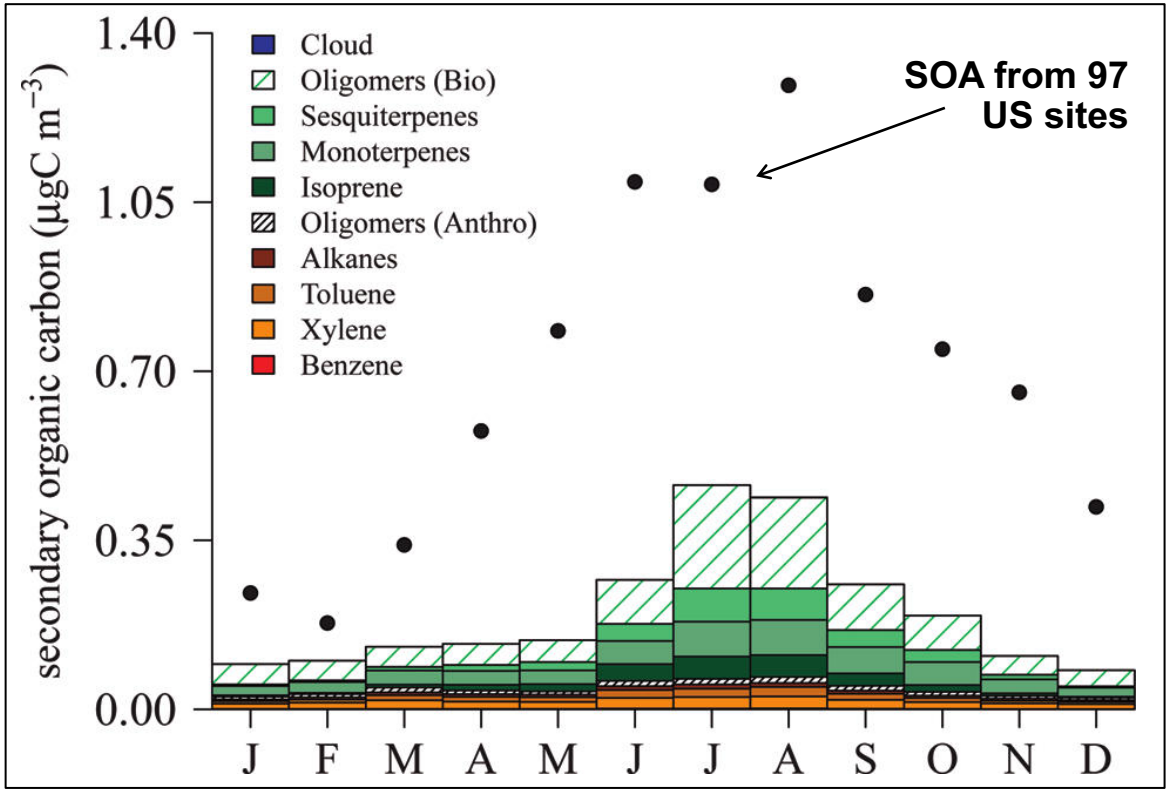
SOA mass yields higher from monoterpenes (**5%**) than isoprene (**3%**).

But... Isoprene emissions (**12.2 Tg C**) are 3 times higher than monoterpene emissions (**4.1 Tg C**).

Isoprene secondary organic aerosol dominates (**>40%**) organic aerosol mass in the Southeast US in summer.

Models Routinely Underestimate Southeast US SOA

Measured vs modeled SOA across the US



[Carlton et al., 2010]

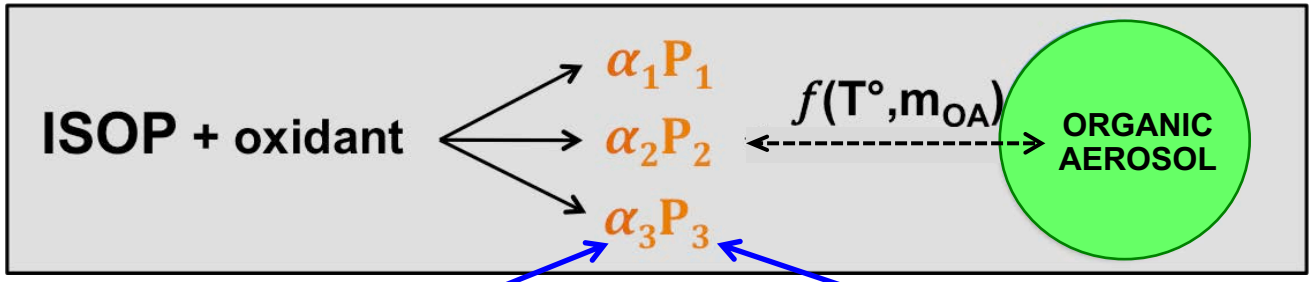
Indicates fundamental flaw in understanding secondary organic aerosol formation

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

Increasing evidence for reactive uptake of isoprene oxidation products to **aqueous aerosol**, but models rely on equilibrium partitioning to **dry organic aerosol**

Model Parameterizations of Isoprene Organic Aerosol

Traditional semivolatile partitioning scheme

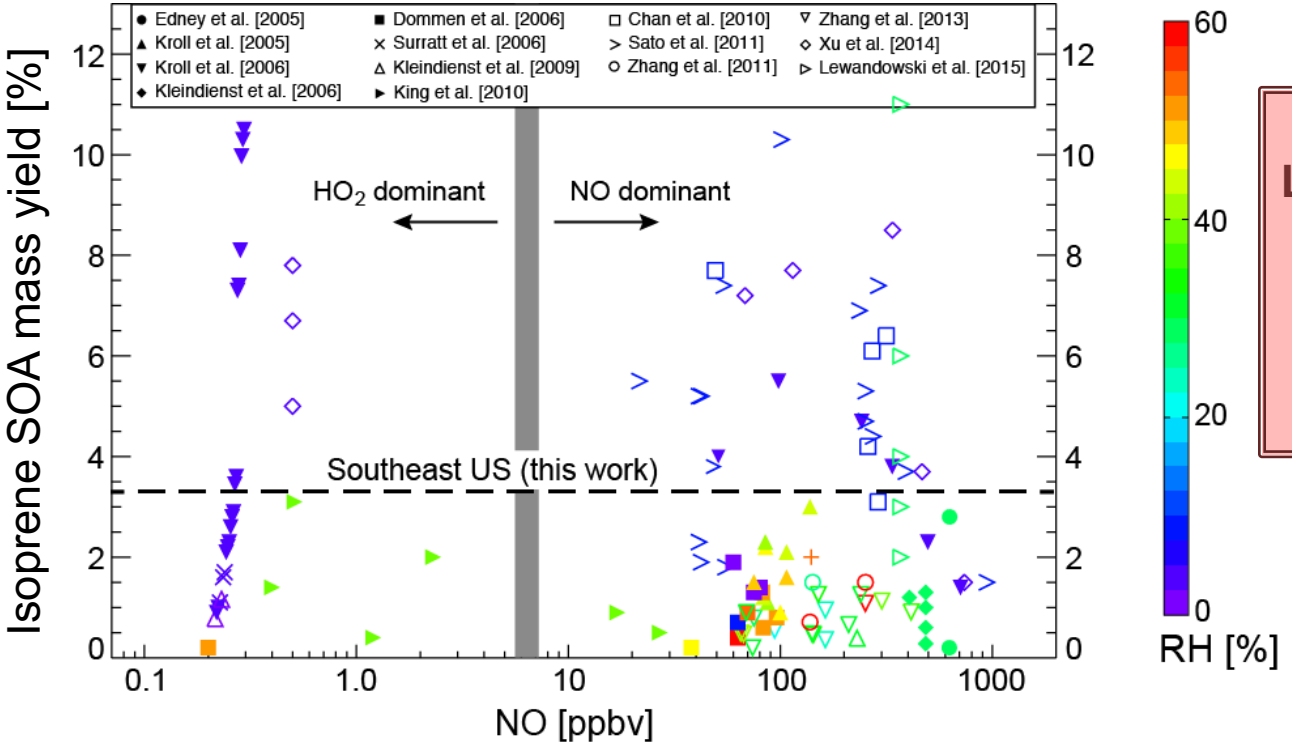


[Pye et al., 2010]

Fixed yield from chamber studies

Aerosol precursor

Compilation of chamber study isoprene + OH SOA yields



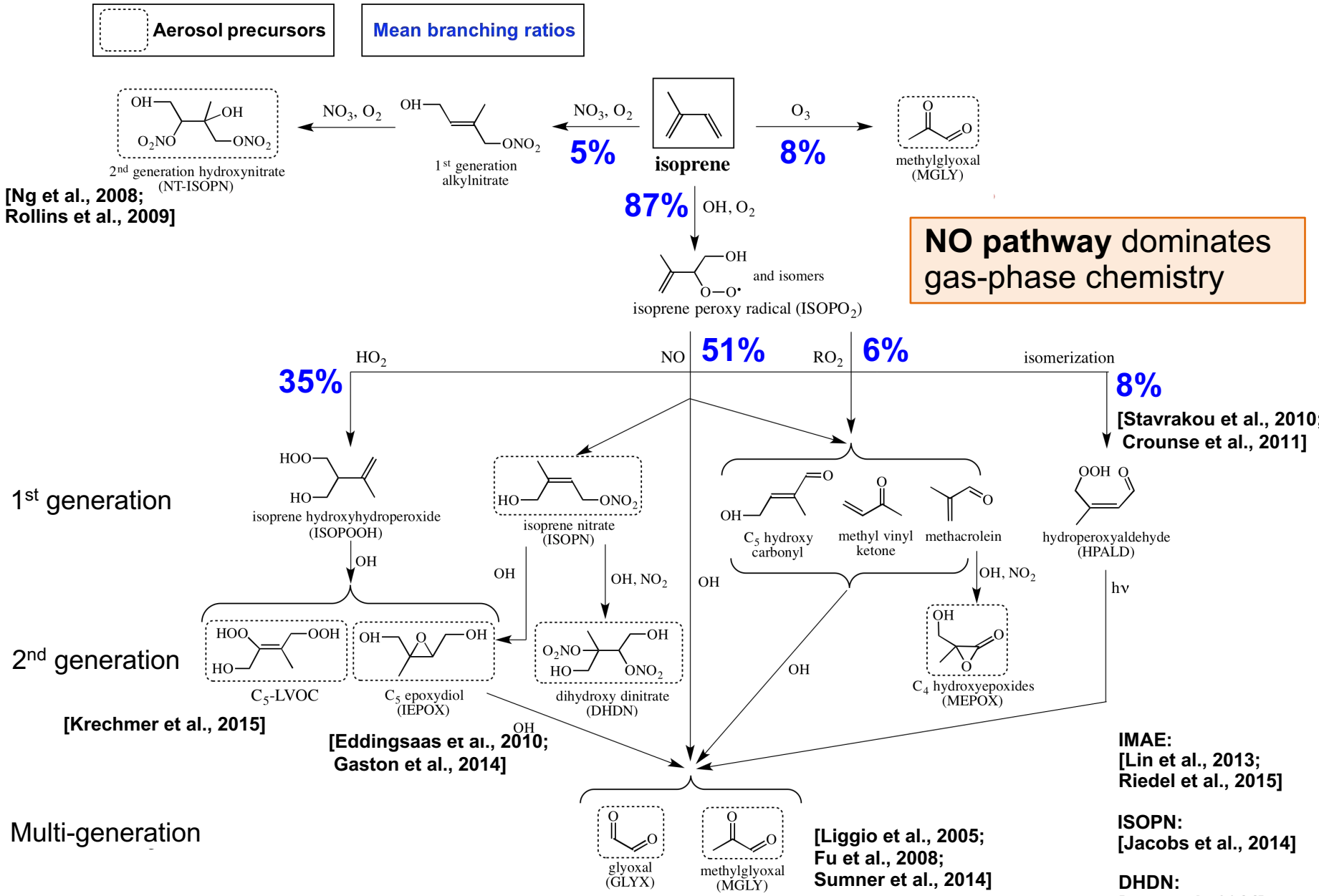
Southeast US Boundary-Layer Summer Conditions

RH = 72 ± 17 %

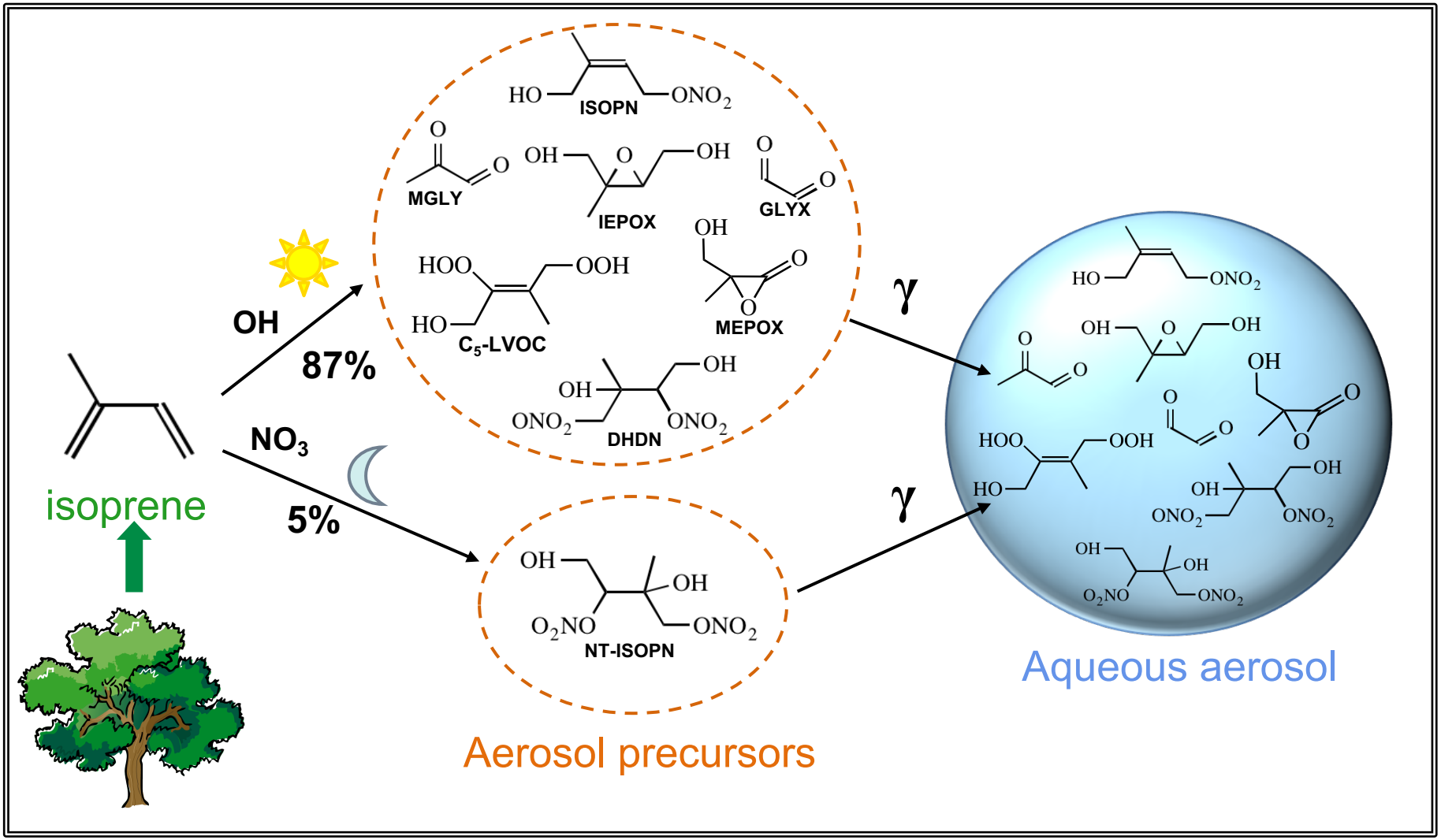
NO = 0.053 ± 0.140 ppbv

isoprene = 0.78 ± 0.85 ppbv

Gas-phase Isoprene SOA precursors in GEOS-Chem



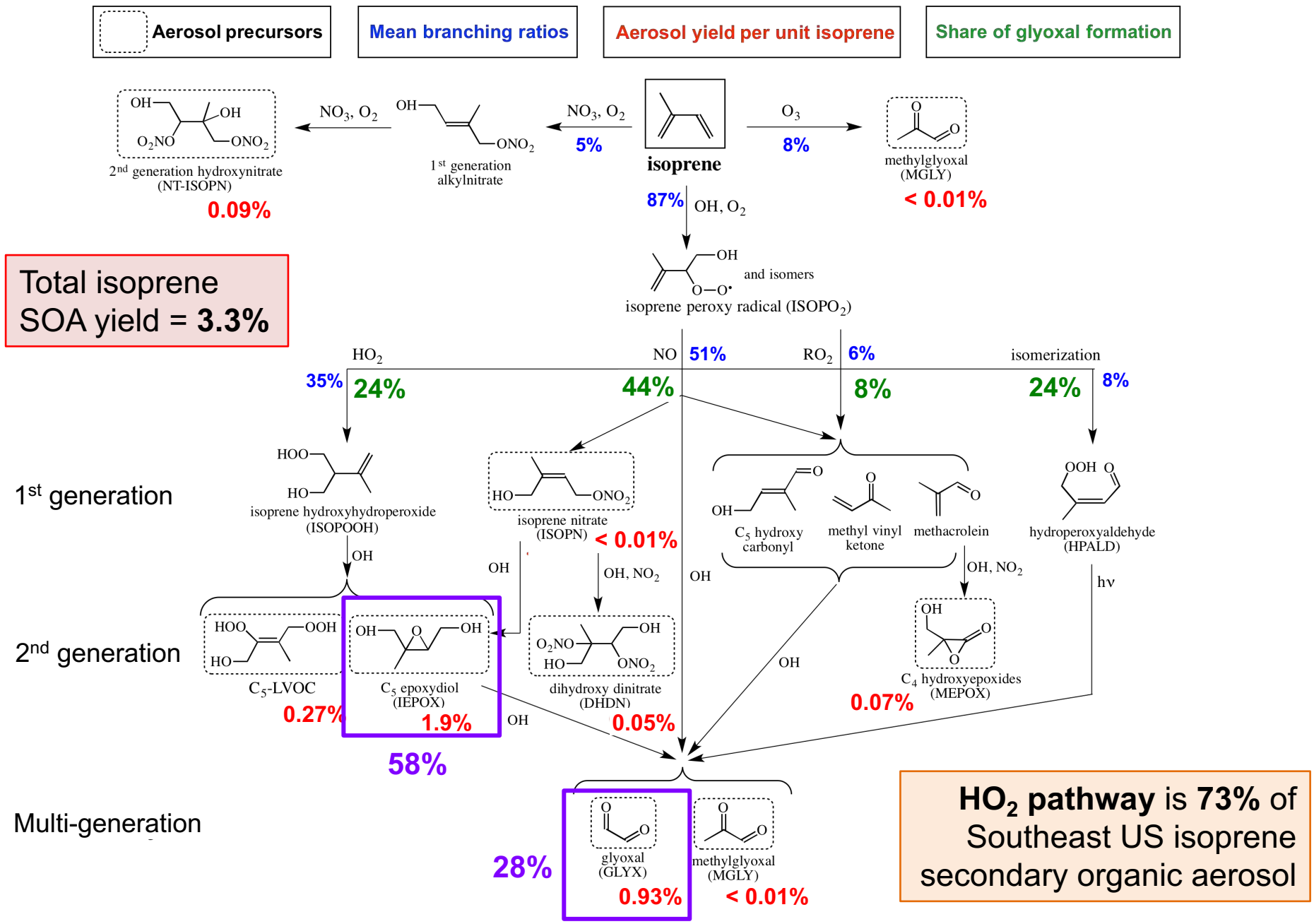
Aqueous-Phase Mechanism Framework



γ **fixed** (GLYX, MGLY, C_5-LVOC, NT-ISOPN), or ...

γ depends on ***H**** & **aqueous-phase reactions** (IEPOX, MEPOX, ISOPN, DHDN)

GEOS-Chem Isoprene SOA Yields in the Southeast US

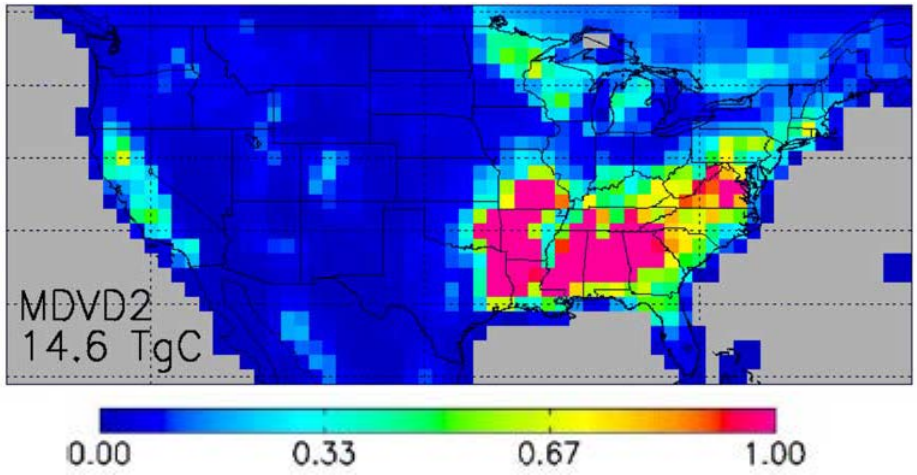


OA-HCHO Relationship Constrains Isoprene SOA Yields

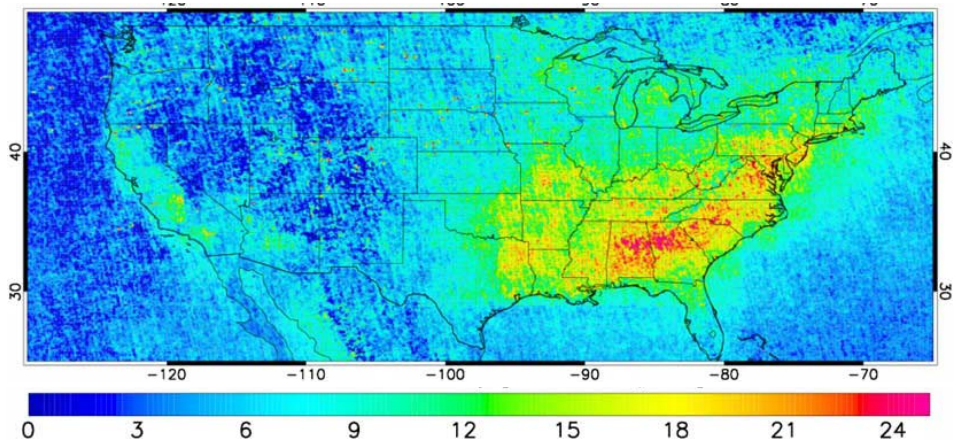
In the Southeast US...

Isoprene is the largest source of HCHO

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



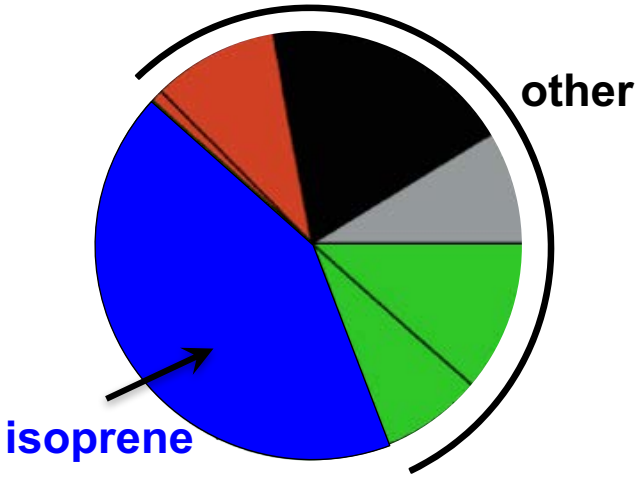
HCHO Column Density [10^{16} molecules cm^{-2}]



[Millet et al., 2008]

Isoprene SOA is 40% of OA

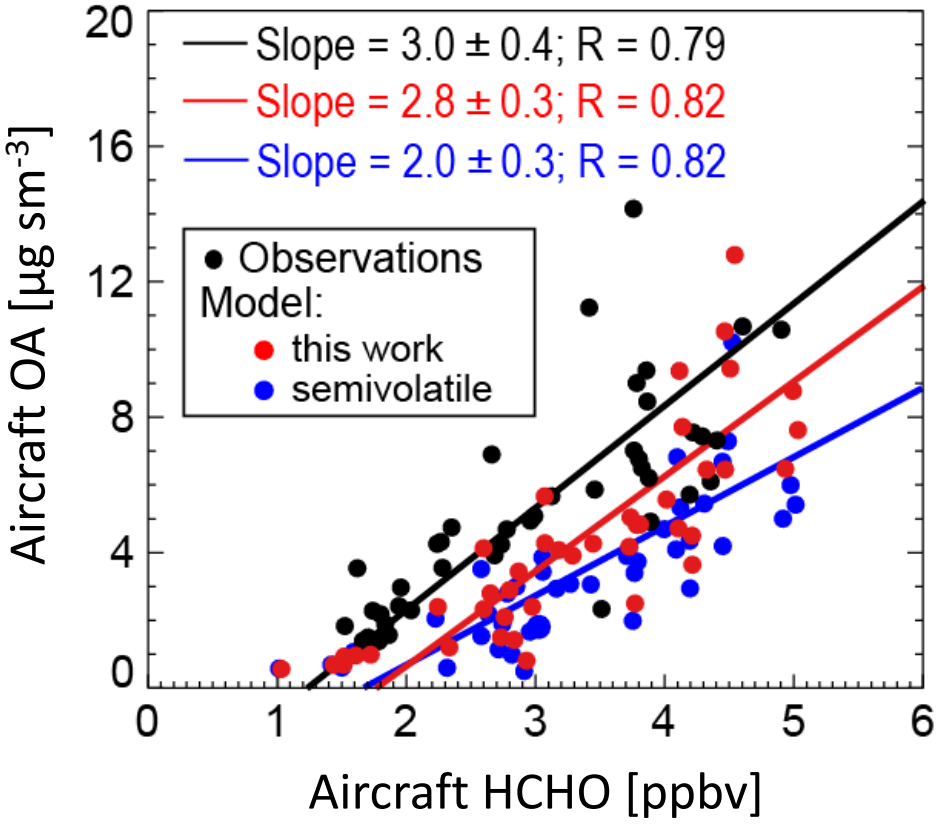
Southeast US OA

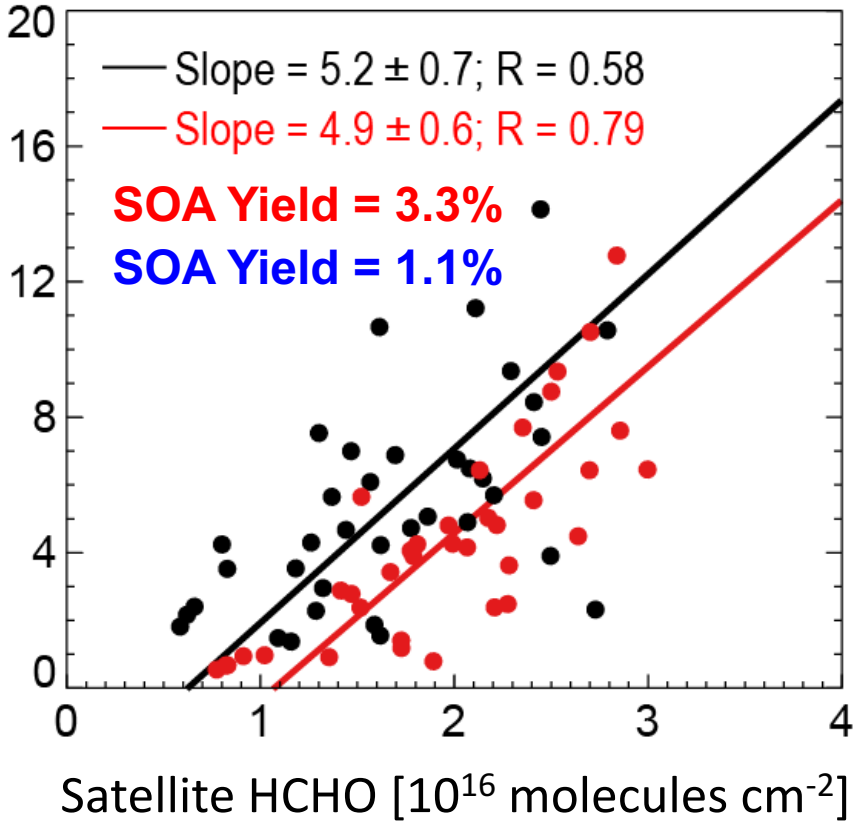


Adapted from Kim et al. [2015]

OA-HCHO Relationship Constrains Isoprene SOA Yields

OA-HCHO Relationship during SEAC^{4}RS





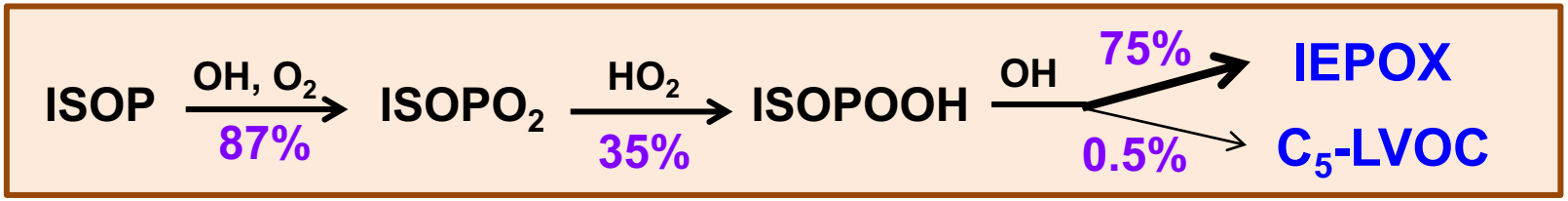
Slope is **sensitive** to underlying isoprene **SOA yields**

Equilibrium partitioning scheme underestimates the slope

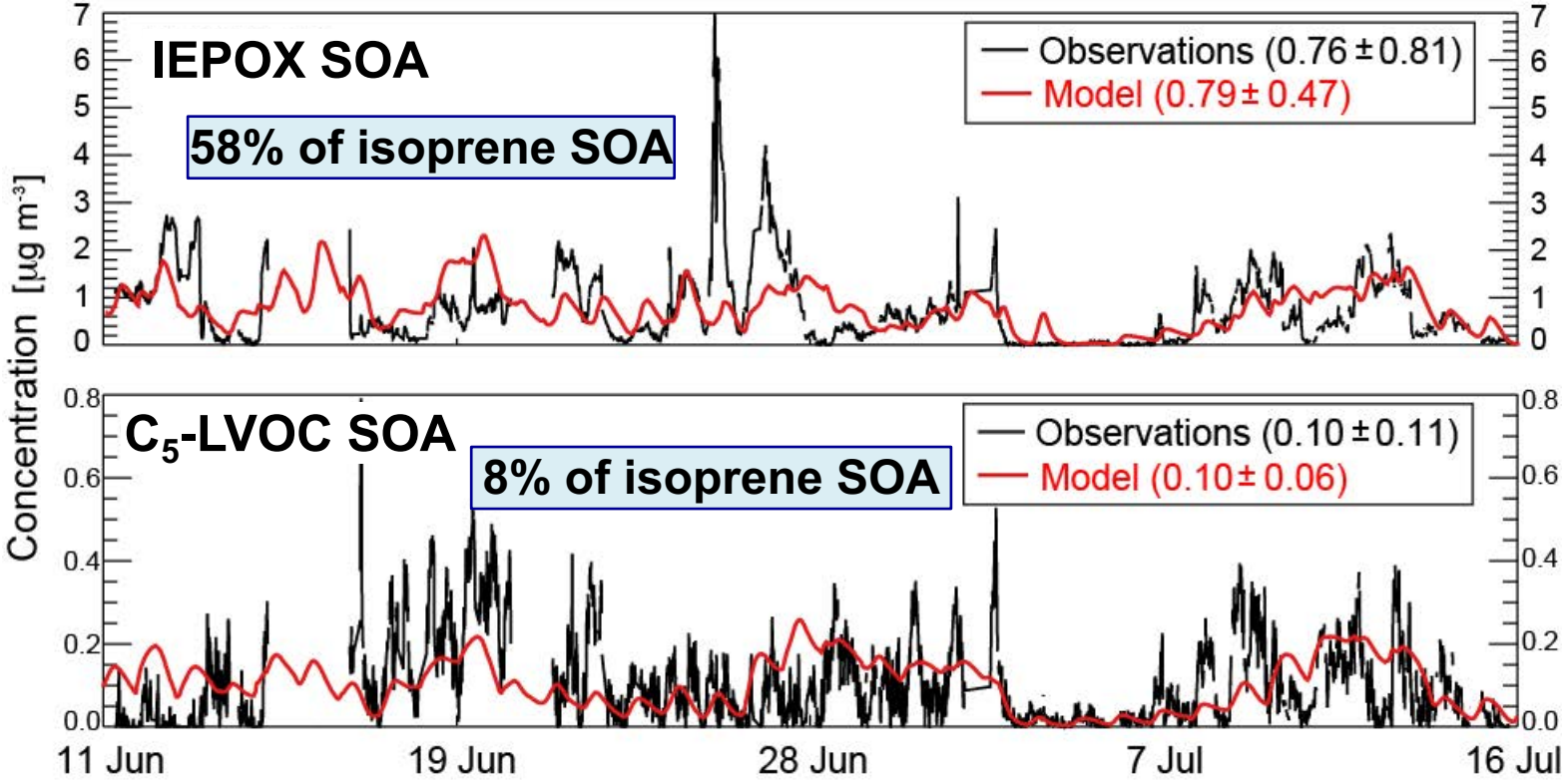
Reactive uptake scheme slope is similar to the observations

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

Observational Constraints on Isoprene SOA Components



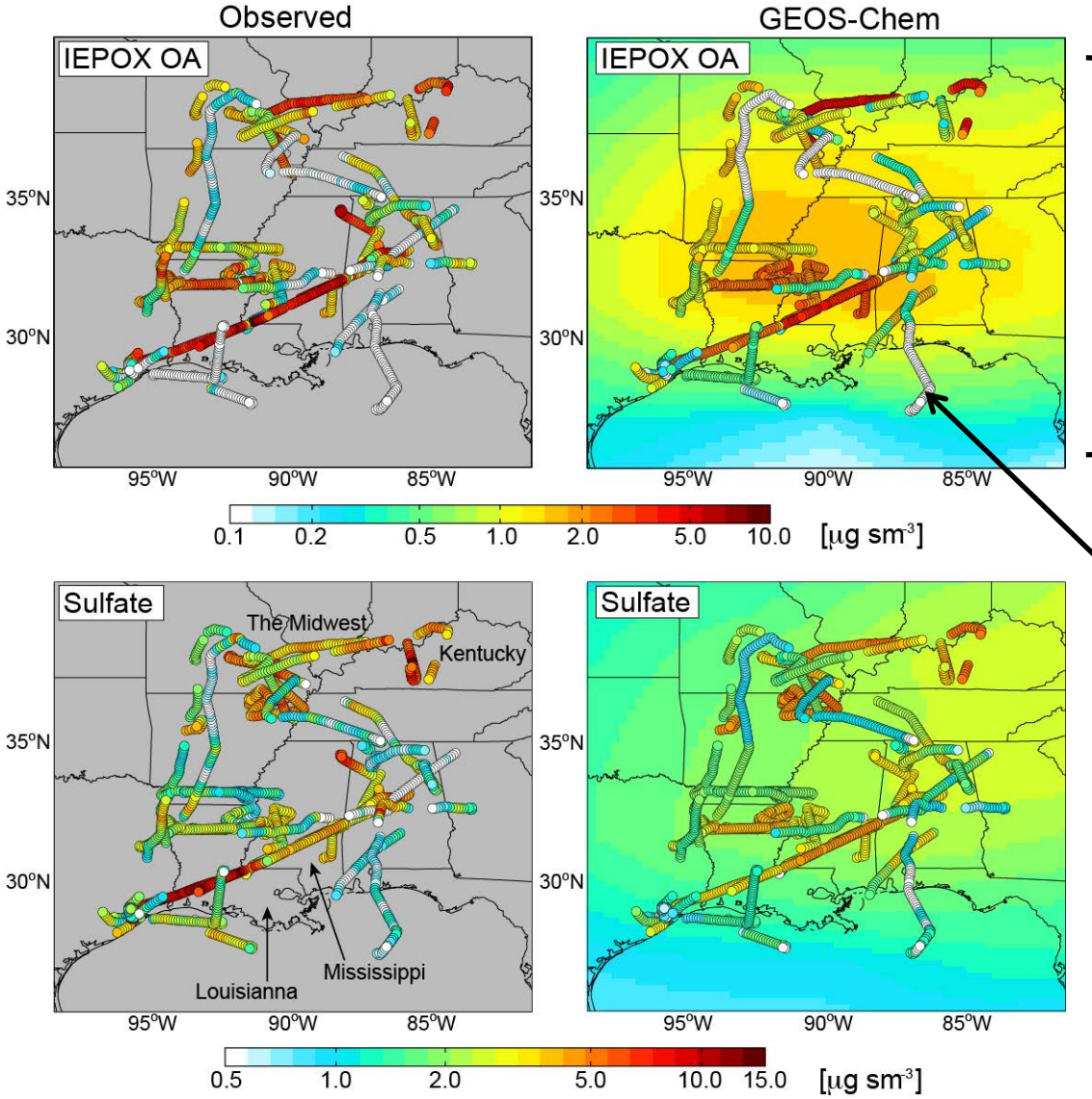
Secondary organic aerosol from IEPOX and C_5-LVOC at Centreville, AL (SOAS campaign; Jun-Jul 2013)



[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



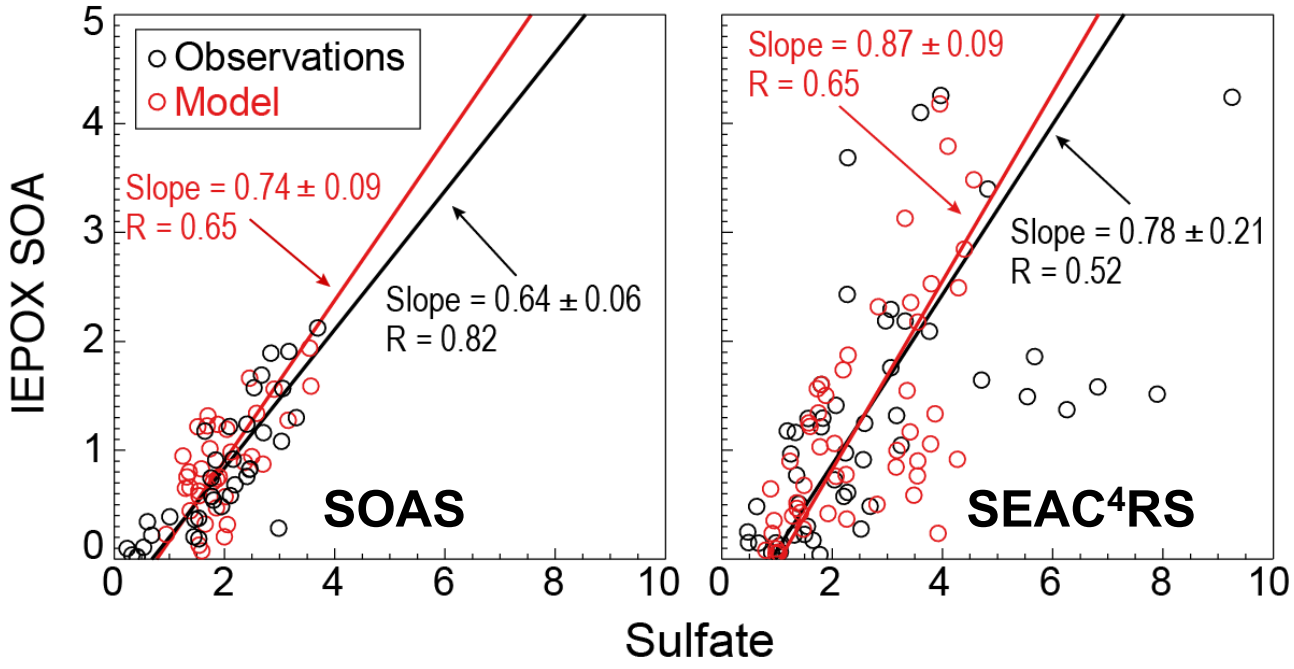
Background is daytime mean during SEAC⁴RS

Points are data along the SEAC⁴RS flight tracks

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

What modulates IEPOX OA in the Southeast US?

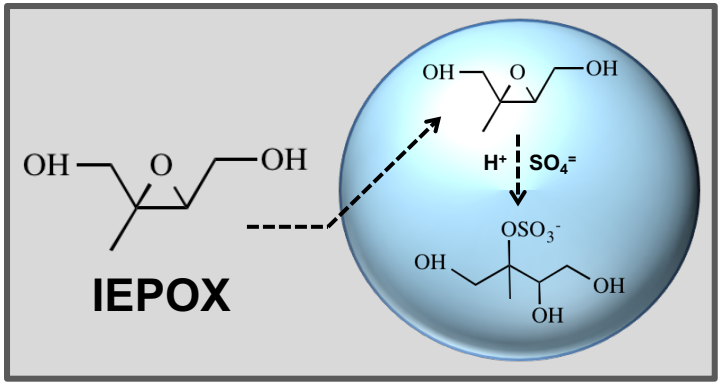
IEPOX SOA and Sulfate correlation during SOAS and SEAC⁴RS



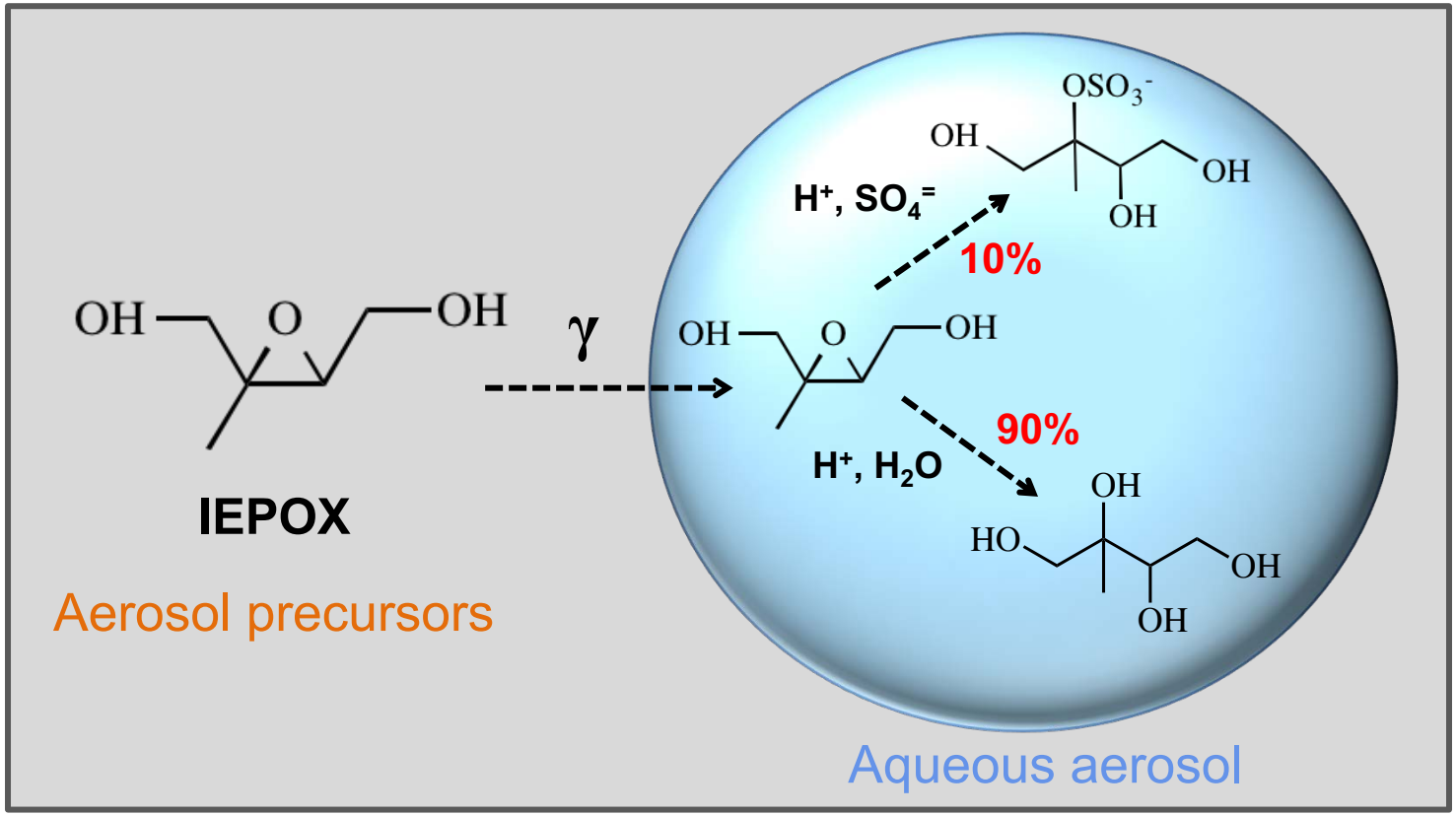
Similar relationship between sulfate and IEPOX OA in the observations and model

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 nucleophillic addition

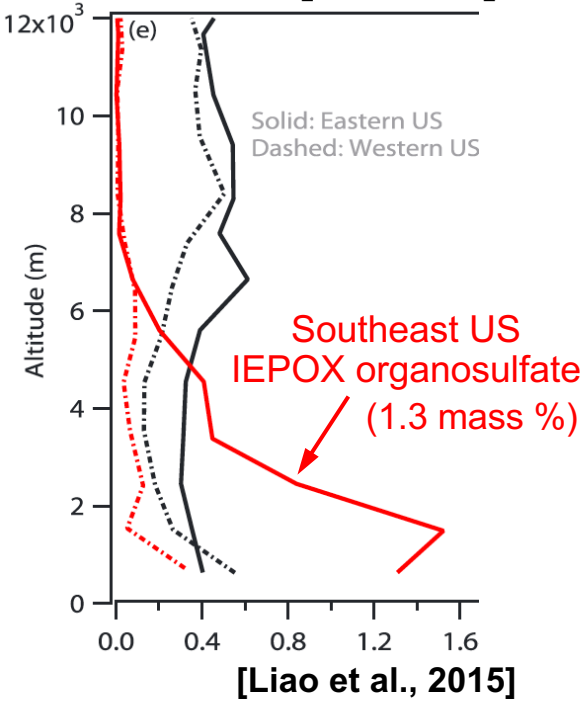


In our mechanism acid-catalyzed **sulfate addition is 10%** and acid-catalyzed **H_2O addition is 90%** of the fate of IEPOX

Sulfate has indirect effect on aerosol acidity and volume

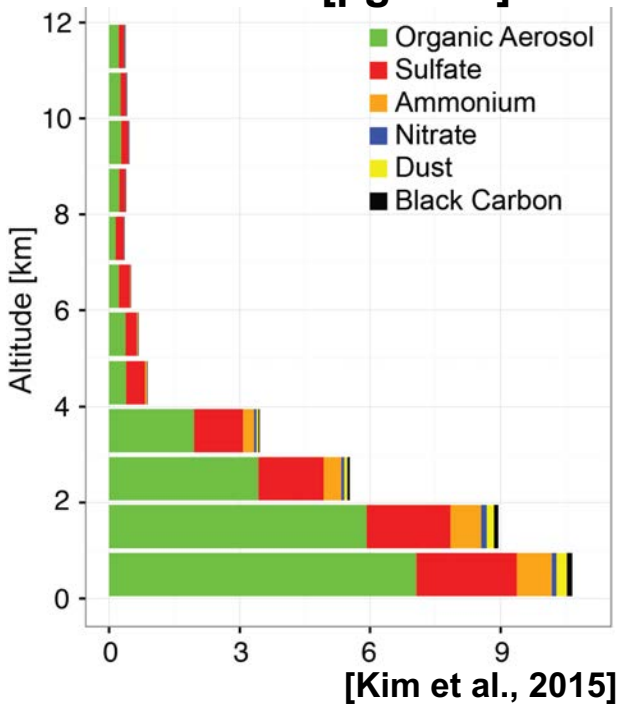
Additional support for limited role of sulfate channel from SEAC^{4}RS PALMS **IEPOX-organosulfate observations:**

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)

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

Sulfate impacts **aerosol acidity** and **aerosol volume:**

$$\gamma \sim [H^+] \times V$$

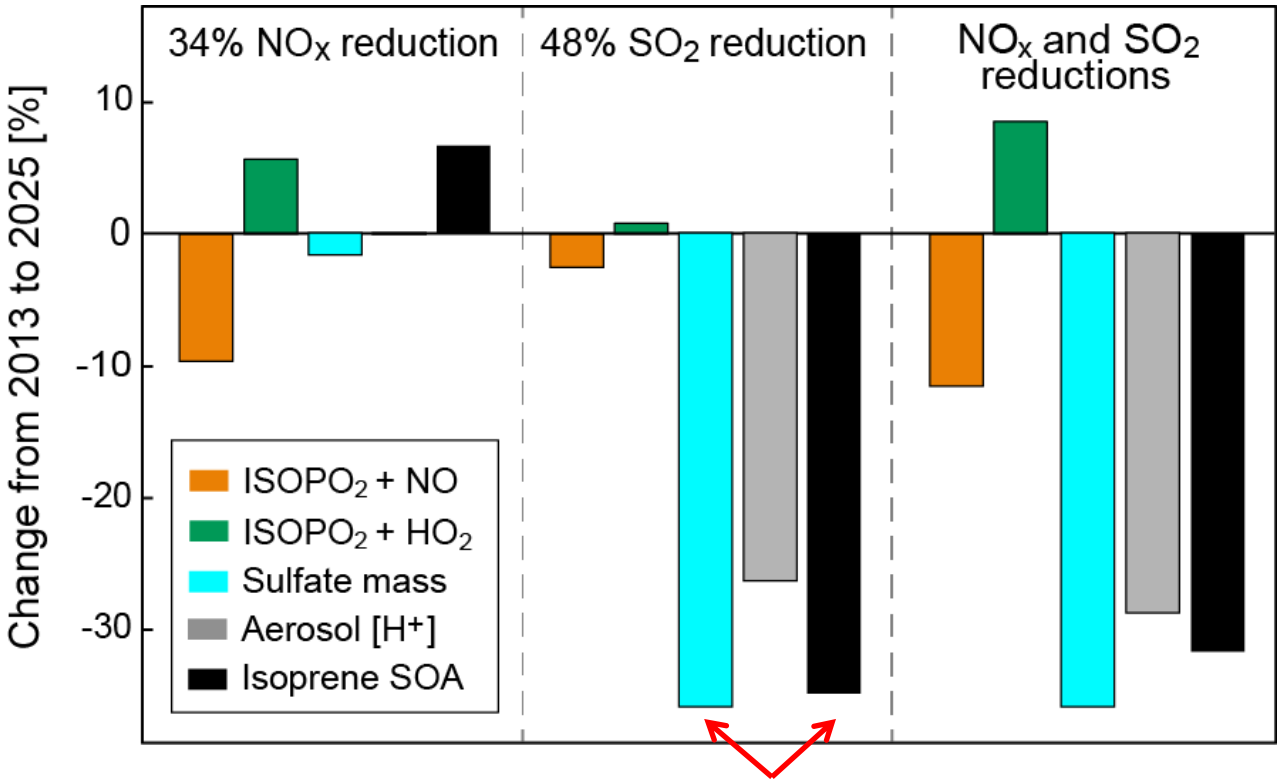
Effect of Anthropogenic Emission Reductions

US EPA Anthropogenic Emission Reduction Projections (2013-2025):

NO_x: 34%
SO_2: 48%

} Use **GEOS-Chem** to test the effect on isoprene SOA

Effect of Emission Reductions on the fate of $ISOPO_2$, sulfate mass, aerosol pH, and isoprene SOA



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

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

Concluding Remarks

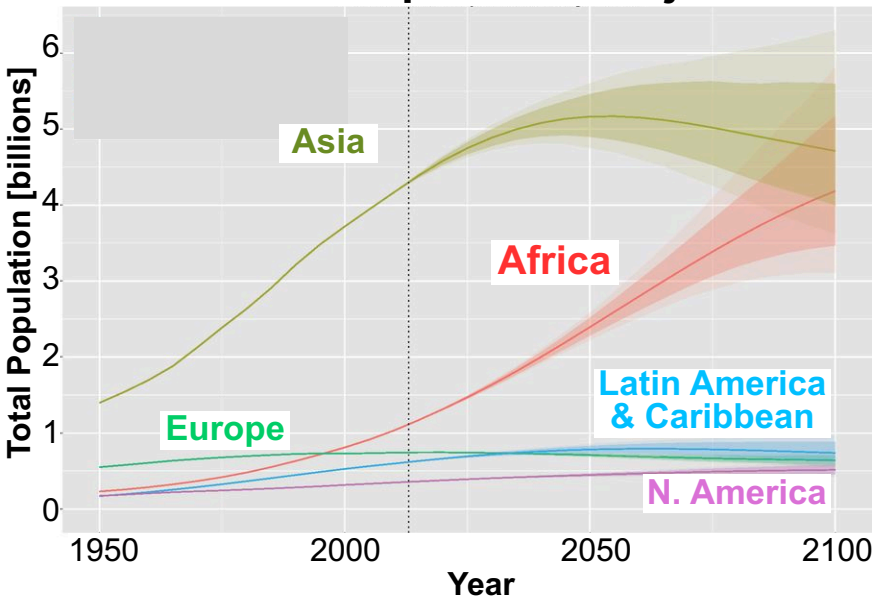
- Don't need complicated schemes to model isoprene SOA in the Southeast US
  - 2 precursors, **IEPOX and glyoxal**, are **86%** of isoprene SOA.
- The low-NO_x pathway (**$ISOPO_2$ + HO_2**) is the dominant (**73%**) contributor to isoprene SOA in the Southeast US.
- Equivalent reduction in isoprene SOA and sulfate provides additional support for **SO_2 emission controls**
- **Biogenic SOA** is typically termed **natural**, but we should distinguish the natural component and the **anthropogenic** component influenced by SO_2 (and NO_x) emissions.

[Marais et al., *submitted to* ACPD]

Air Quality in Africa: A View from Space

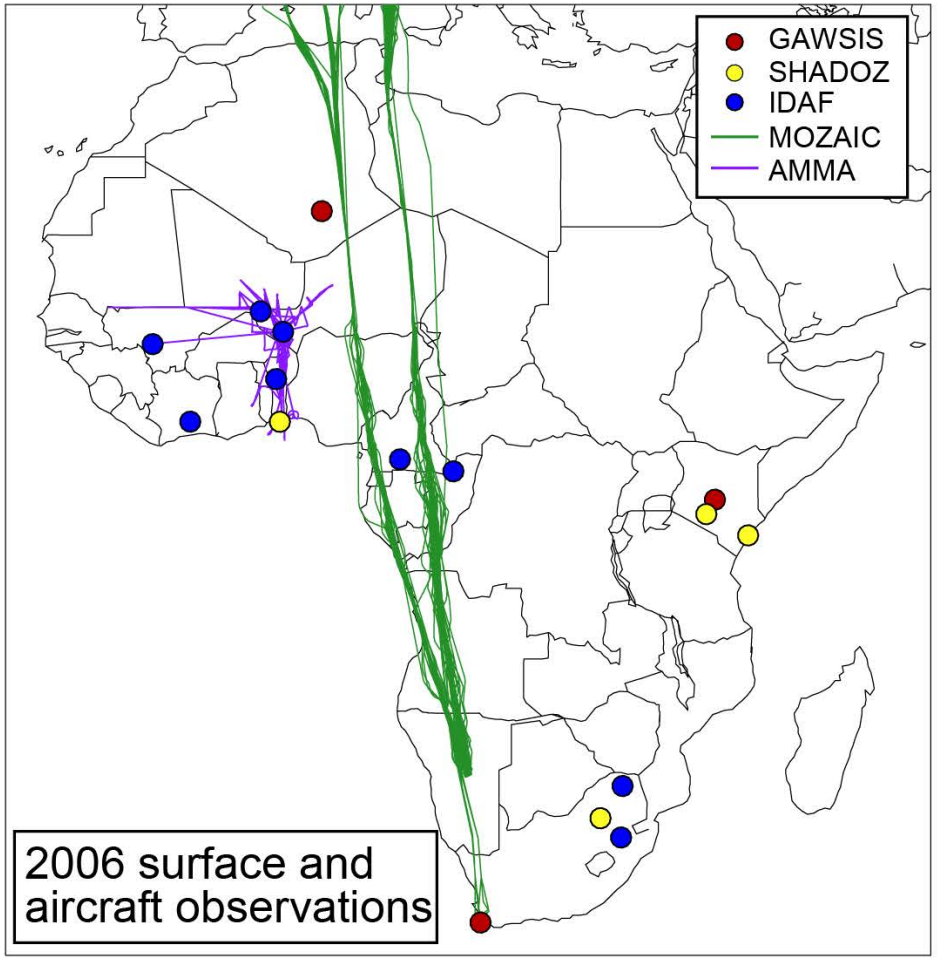
Africa is experiencing **population and economic growth rates** similar to that in India and China.

Continental Population Projections



Gerland et al., 2014

Surface and aircraft observations limited to a few international campaigns and networks

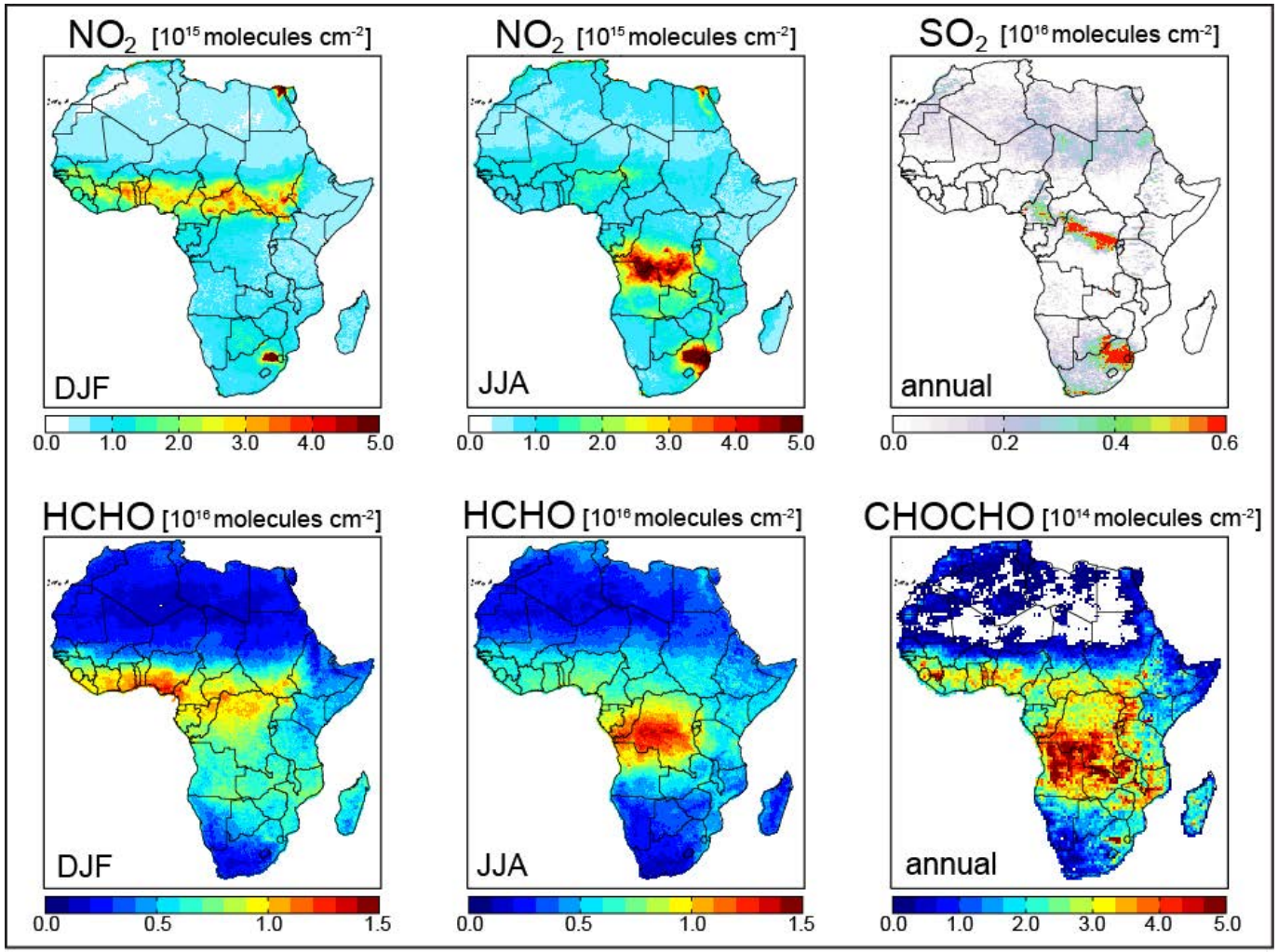


Not shown: AERONET

Country-level air quality monitoring and environmental regulation limited to South Africa

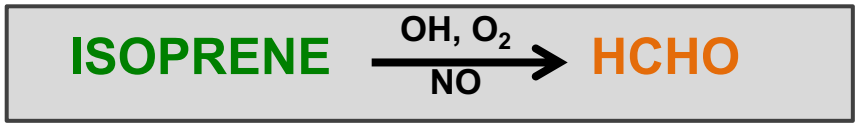
Satellite Observations Fill Substantial Data Gaps

Tropospheric Composition Observed with the Ozone Monitoring Instrument (2006-2007)

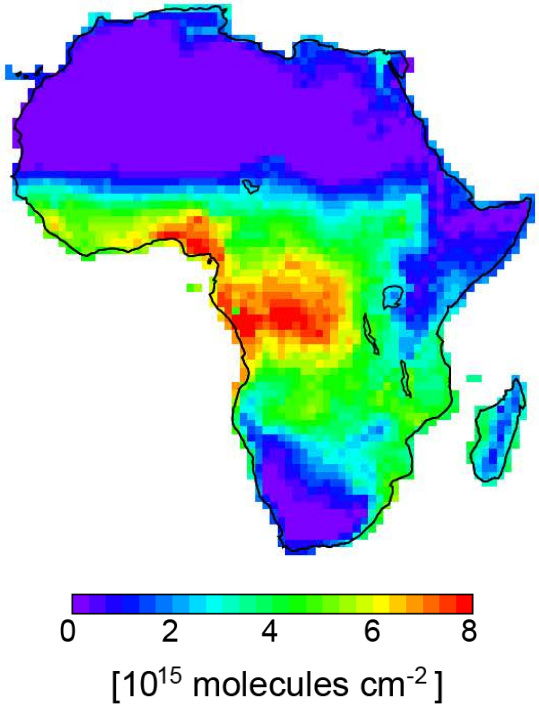


Identify **natural** (forests, volcanoes), **anthropogenic** (power plants, inefficient combustion), and **biomass burning** (savannahs, croplands) emission sources.

OMI-derived Isoprene Emissions



OMI Slant Column HCHO
(background removed)



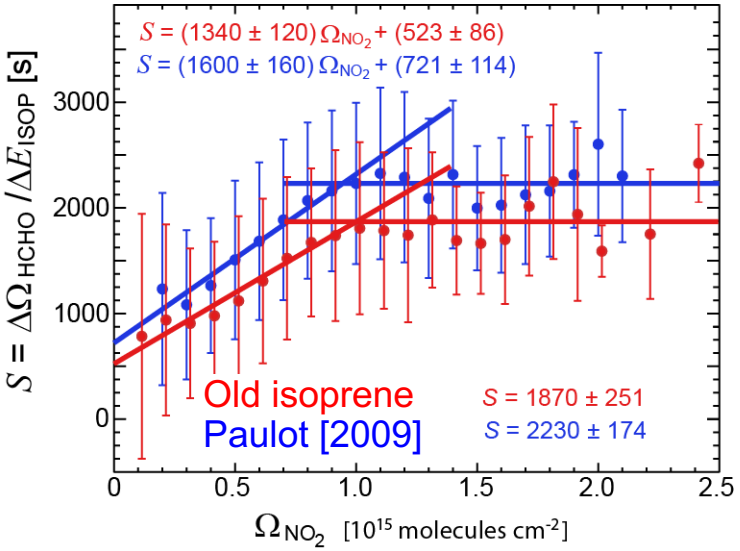
Active fires

Absorbing AOD

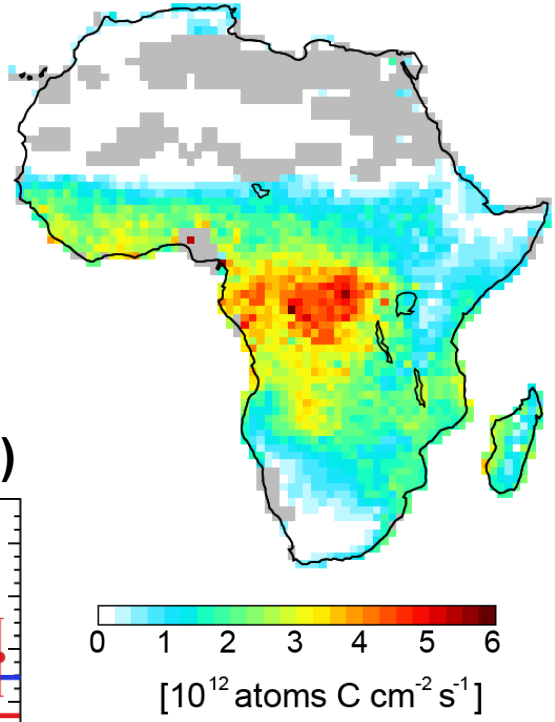
Remove biomass burning HCHO

Apply NO_x-dependent yields of HCHO from isoprene

HCHO yield (S) vs NO_2 (Ω_{NO2})



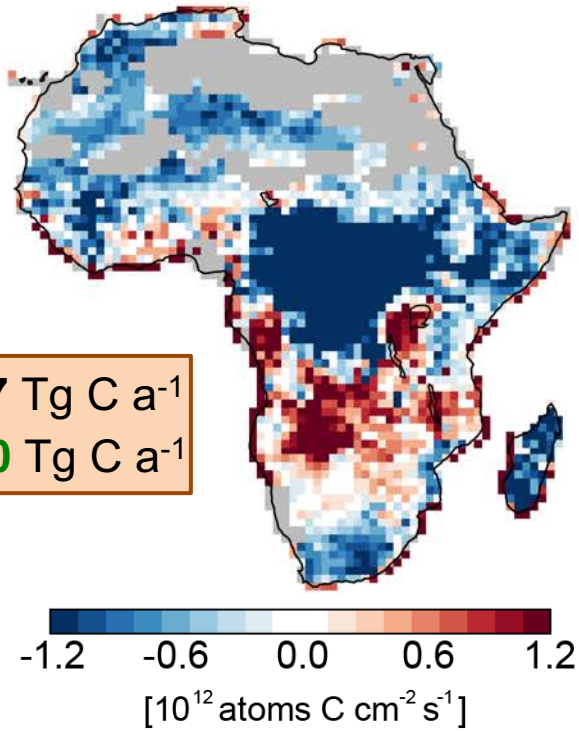
Above-canopy isoprene emissions



[Marais et al., ACP, 2012]

Reveal Discrepancies in Biogenic Emission Inventories

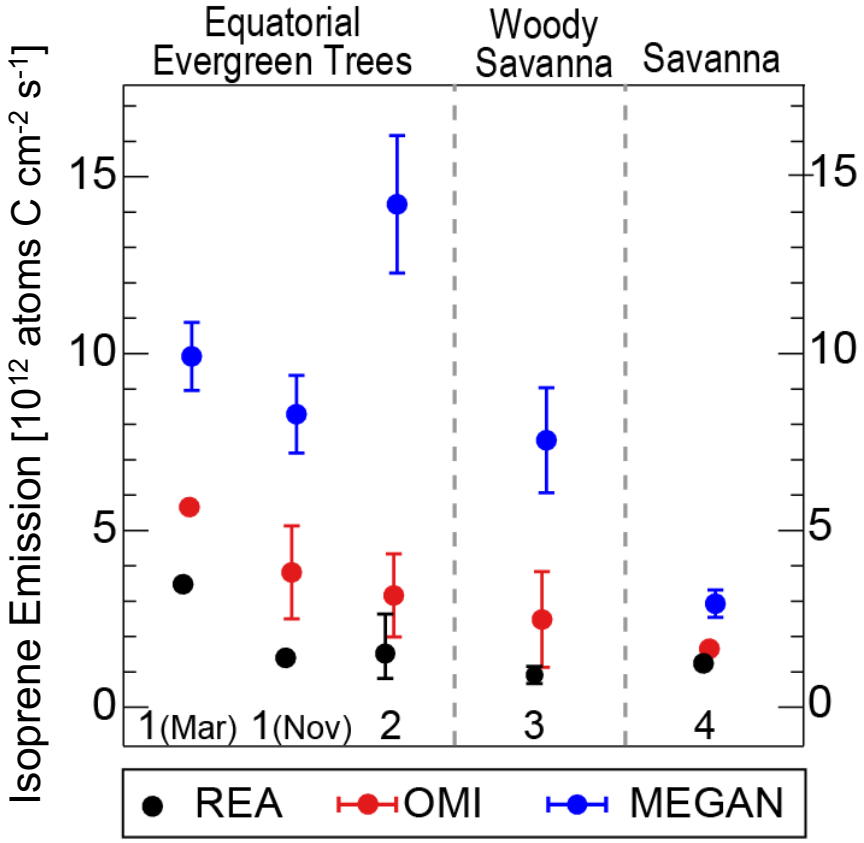
OMI minus MEGAN



MEGAN: **77** Tg C a^{-1}
OMI: **60** Tg C a^{-1}

[Marais et al., ACP, 2012]

Comparison of measured, OMI-derived, and MEGAN isoprene emissions



[Marais et al., ACP, 2014]

Annual totals are similar, but **regional discrepancies are large**

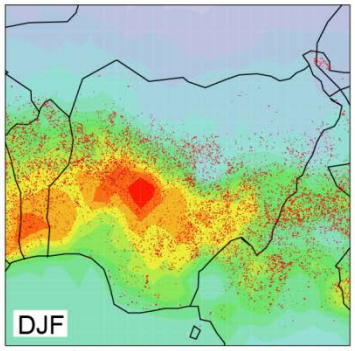
MEGAN isoprene emission overestimate in the tropics supported by flux measurements

Ozone Pollution Calamity in Populous Nigeria

Obtain observational constraints from satellite observations of pollutants from open fires, inefficient combustion, and extensive natural gas leakage and flaring

Seasonal open fires

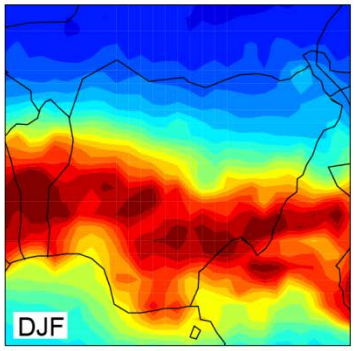
AIRS CO + MODIS fires



1.5 1.8 2.1 2.4 2.7 3.0

10^{18} molecules cm^{-2}

OMI NO_2

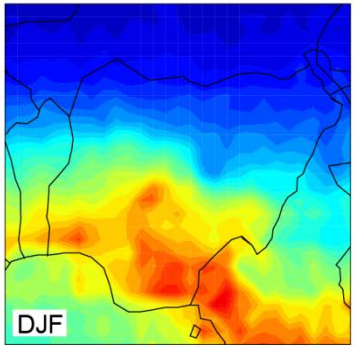


0 1 2 3 4

10^{15} molecules cm^{-2}

Anthropogenic Volatile Organic Compounds

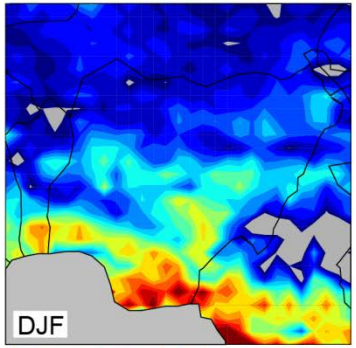
OMI HCHO



0.0 0.5 1.0 1.5 2.0

10^{16} molecules cm^{-2}

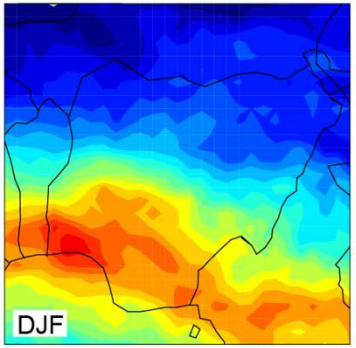
SCIAMACHY CH_4



1725 1750 1775

ppbv

GOME-2 CHOCHO

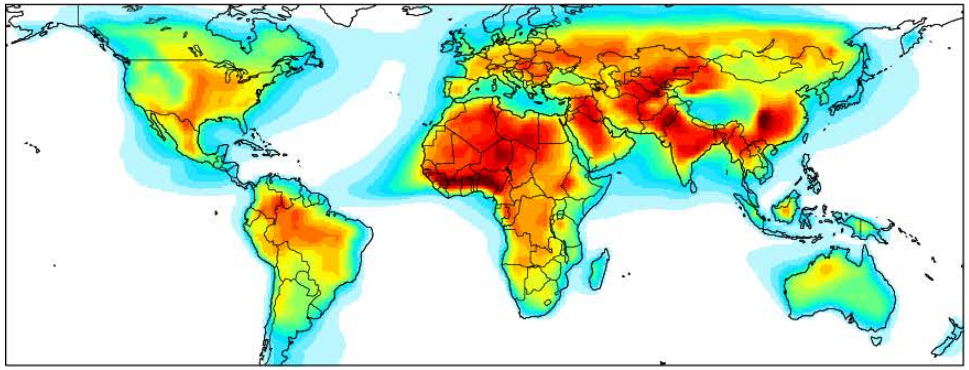


0 2.5 5.0 7.5 10.0

10^{14} molecules cm^{-2}

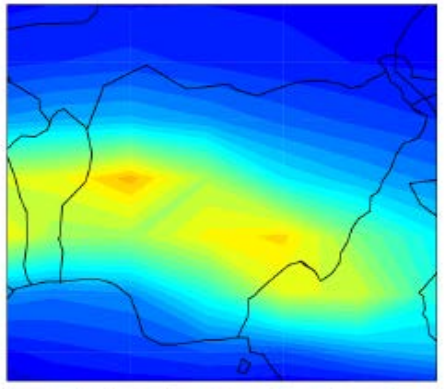
Evaluate the implications for ozone pollution using GEOS-Chem

Persistent stagnation in DJF (GEOS-Chem ^{222}Rn)



0 1 2 3 4 5 6 7 Bq/SCM

DJF MDA8 ozone [ppbv]

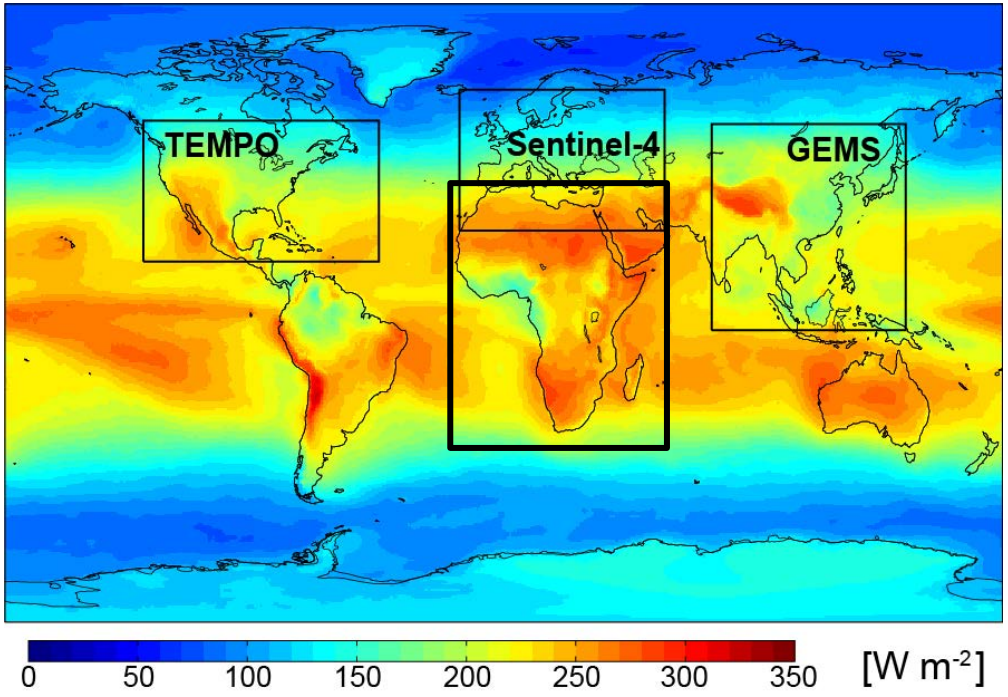


30 40 50 60 70 80 90 100 110

[Marais et al., AE, 2014]

Geostationary (GEO) Satellite to Monitor African Air Quality

N. Hemisphere GEO Satellite Constellation and MERRA All-sky Incident Solar Radiation



High temporal (**hourly**) and spatial (**~4 km²**) resolution

What About Africa?

Africa has exceptional viewing conditions for UV/vis instruments

Northern hemisphere satellites go dark in boreal winter

South Africa Clean Air Journal Article:

Demonstrate **merit of satellite observations**

Advocate for **air quality monitoring from space**

A Geostationary Air Quality Monitoring Platform for Africa

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Received: 15 March 2015 - **Reviewed:** 24 April 2015 - **Accepted:** 18 May 2015
http://dx.doi.org/10.17159/2410-972X/2015/v25n1a3

Africa Air Quality Summary

- OMI HCHO provides an improved estimate of isoprene emissions and reveals large discrepancies in the state-of-the-science MEGAN emission inventory.
- Nigeria has a severe ozone pollution problem that will worsen as the population expands (the UN projects Nigeria could be the 3rd largest population by 2050).
- Country-level air quality monitoring is almost non-existent in Africa. The best option to monitor adverse effects of rapid growth is to invest in a space-based monitoring platform.

Ongoing Africa Air Quality Research

- **Africa emission inventory** to account for diffuse inefficient residential and commercial pollution sources
- Understand the sources and factors that contribute to **deleterious effects of ozone on crop productivity and human health**