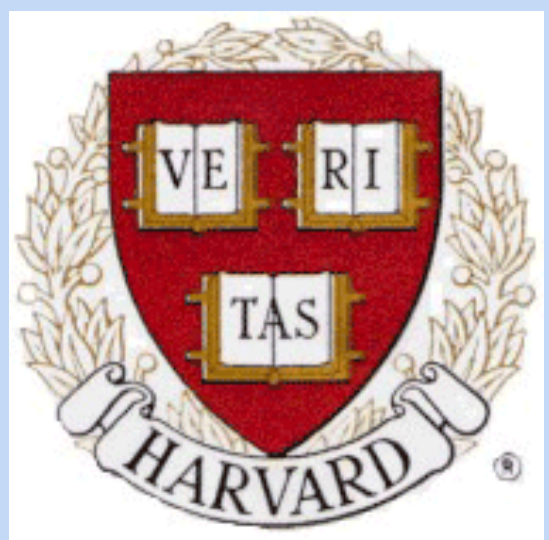# Evidence of 1991-2013 decrease in biogenic organic aerosol in response to SO_2 emission controls

Eloïse A. Marais (e.a.marais@bham.ac.uk)[1,*], Daniel J. Jacob[1], Jay R. Turner[2], Loretta J. Mickley[1]

[1]Harvard University, [2]Washington University, St Louis, *Now at: School of Geography, Earth and Environmental Sciences, University of Birmingham, UK

1. INTRODUCTION

Air quality policy to decrease fine particle mass concentrations ($PM_{2.5}$) has targeted sulfate with strict controls on sulfur dioxide (SO_2) sources. Organic aerosol (OA) instead of sulfate is now the dominant $PM_{2.5}$ component, but there is no clear strategy to regulate OA.

SO_2 emissions in the US have decreased by 3.3% a^{-1} (1991-2013)[1] leading to a nationwide decline in sulfate of 2.7% a^{-1} (1992-2010).[2] In the Southeast US summertime (Jun-Aug) OA has also decreased by 0.9% a^{-1} over 1992-2013 and 1.5% a^{-1} over 1998-2013, but the cause for this trend is uncertain.[3] In summer OA is predominantly secondary (SOA),[4] dominated by biogenic isoprene oxidation products, mostly epoxydiols (IEPOX) and glyoxal, that condense to aqueous aerosol.[5,6]

We use the GEOS-Chem chemical transport model, with a new mechanism for aqueous-phase isoprene SOA formation,[6] to demonstrate that the observed decline in total summertime OA is due to decline in sulfate that drives down aqueous aerosol acidity and aqueous aerosol volume mass concentrations.

Interaction between anthropogenic sulfate and biogenic isoprene SOA
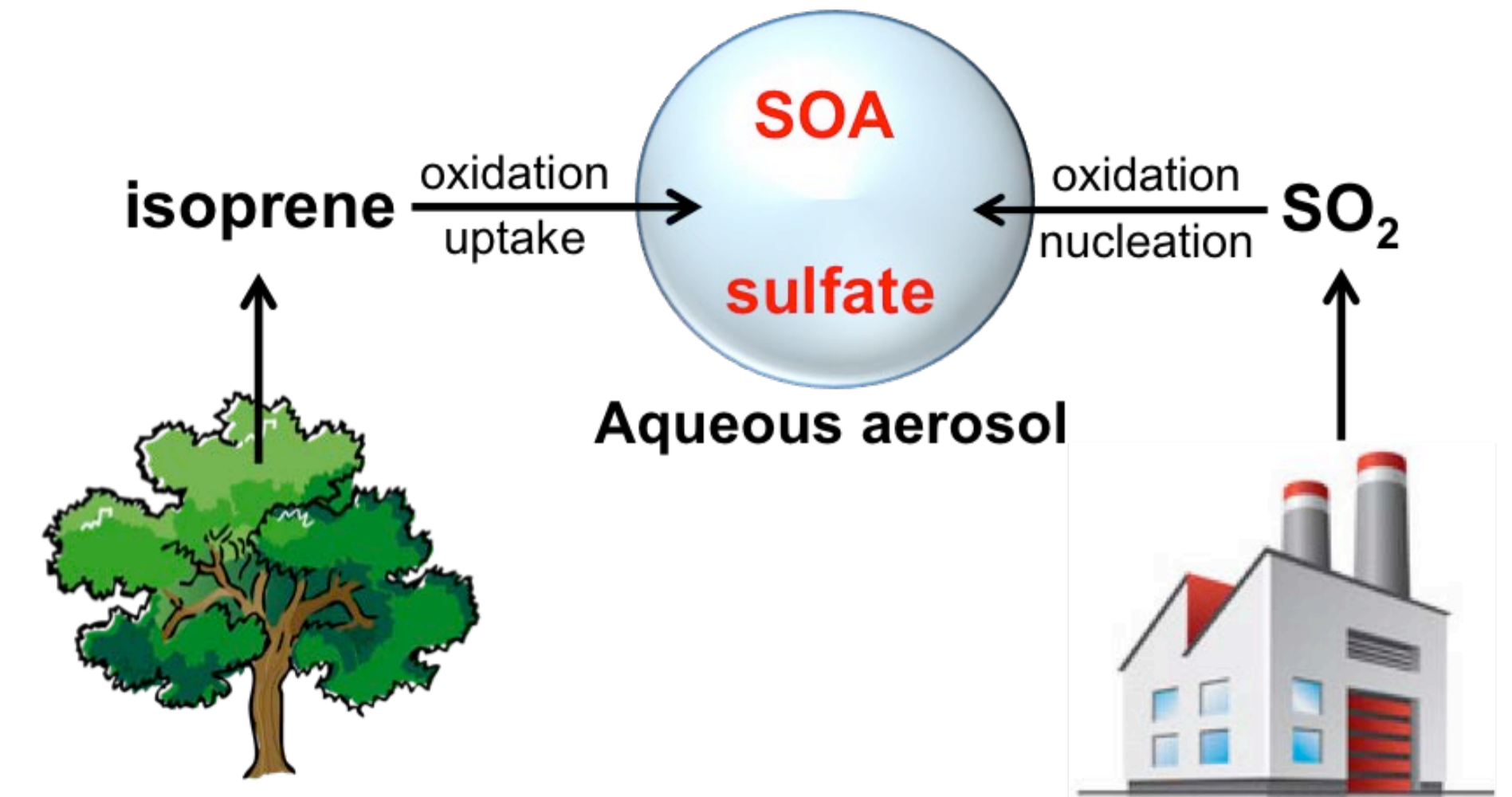
Mechanistic relationship between anthropogenic sulfate and biogenic isoprene SOA

↓ SO_2 ⟶ ↑ Aerosol pH ↓ Aerosol water ⟶ ↓ Isoprene SOA

2. 1991-2013 TRENDS IN SOUTHEAST US ORGANIC AEROSOL AND SULFATE

2a. OBSERVATIONS

SEARCH sites (1998-2013) are a mix of urban, suburban and rural. IMPROVE sites (1991-2013) are mostly rural.

Measurements, reported as organic carbon (OC), are converted to organic aerosol (OA) using a conversion factor of 2.2 (OA/OC = 2.2).

Observed trends (obtained with the Theil-Sen estimator[7]) are significant at the 95% confidence level.

Decline in sulfate is steeper at SEARCH than IMPROVE due to greater urban influence. Similar OA trends at SEARCH and IMPROVE sites supports biogenic SOA driving the OA trend.

OA instead of sulfate is now the dominant $PM_{2.5}$ component.

Observed 1991-2013 trends in summertime organic aerosol and sulfate mass concentrations. Maps show site locations.
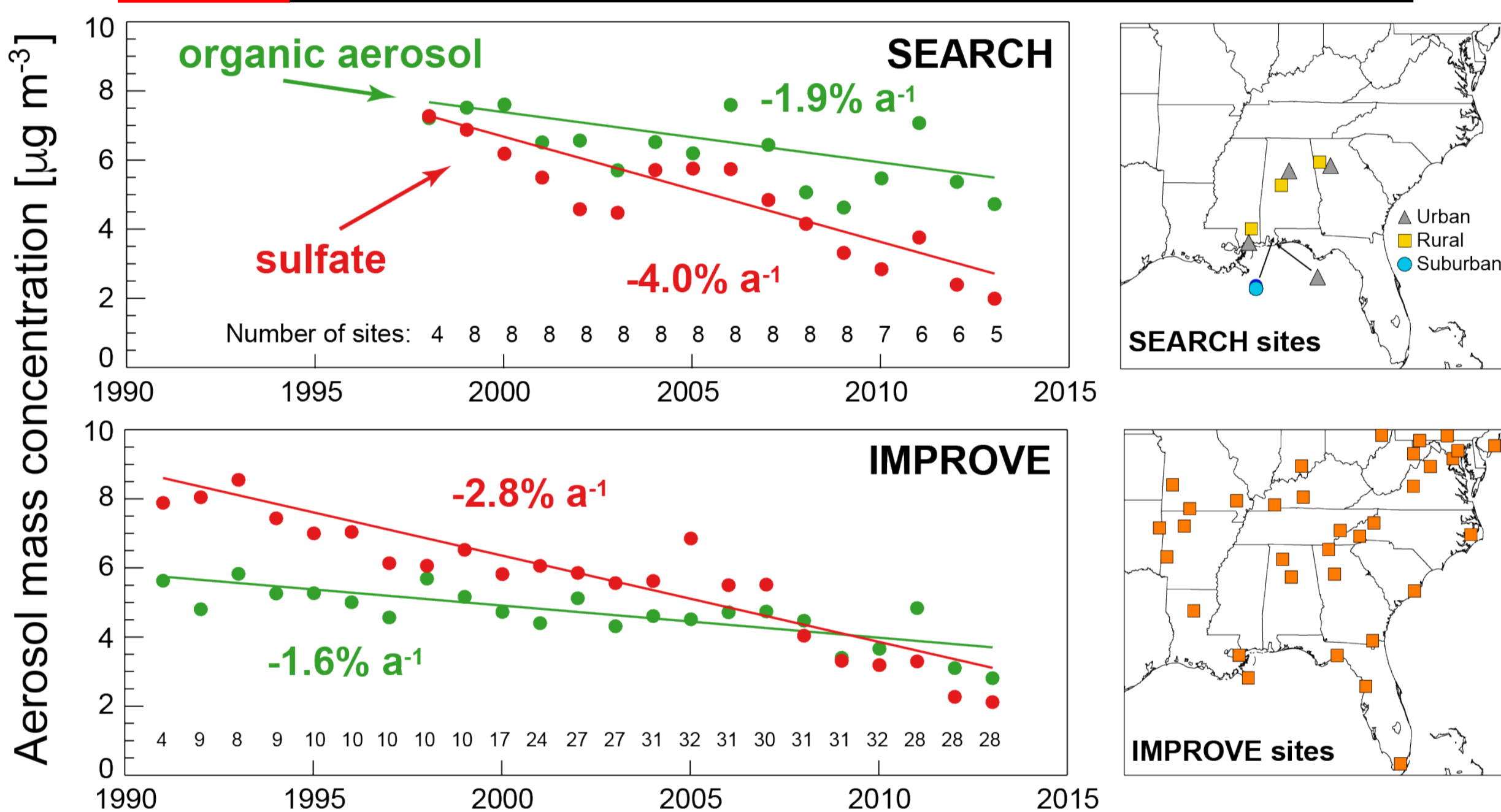

2b. MODEL

GEOS-Chem is driven with consistent reanalysis meteorology and sampled in Jun-Aug 1991-2013 following a 1-month spin up. Annual anthropogenic emission trends of NO_x (3.3% a^{-1}), SO_2 (2.1% a^{-1}), and VOCs (1.6% a^{-1}) are from the EPA.[1] Isoprene emissions are from MEGAN and include year-to-year variability dominated by changes in temperature. Aerosol acidity is calculated with the ISORROPIA thermodynamic equilibrium model and aerosol water is estimated with look-up tables of relative humidity dependent hygroscopic growth factors.[6]

Isoprene SOA formation is by reactive uptake of oxidation products to aqueous aerosol. Reactive uptake rates depend on aqueous aerosol volume and, for IEPOX, aerosol acidity.[6]

Model 1991-2013 trends in summertime organic aerosol and sulfate mass concentrations. Map shows domain sampled
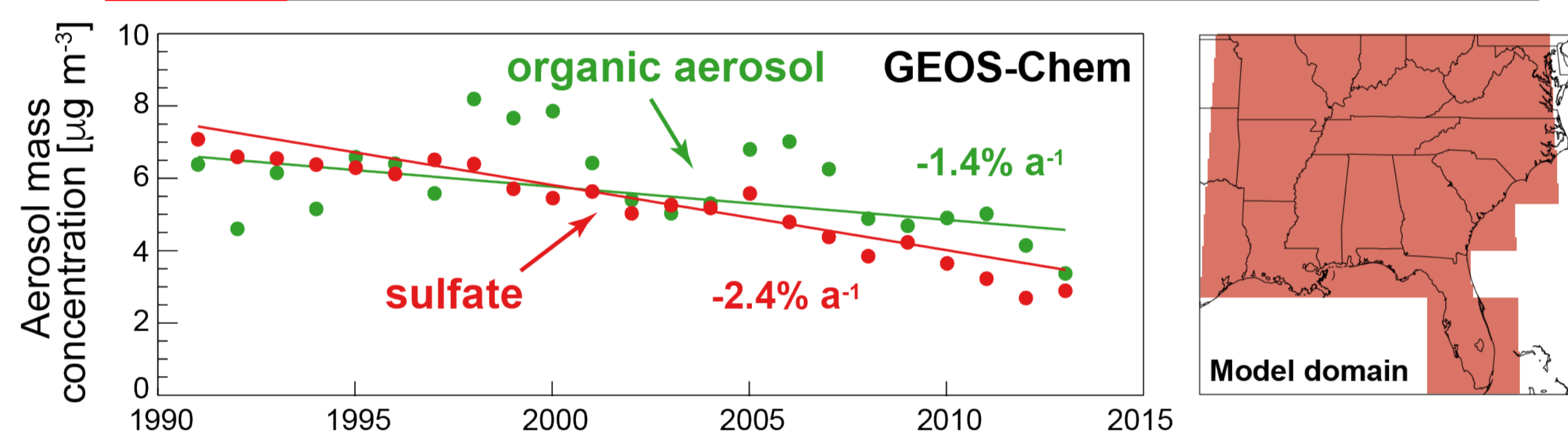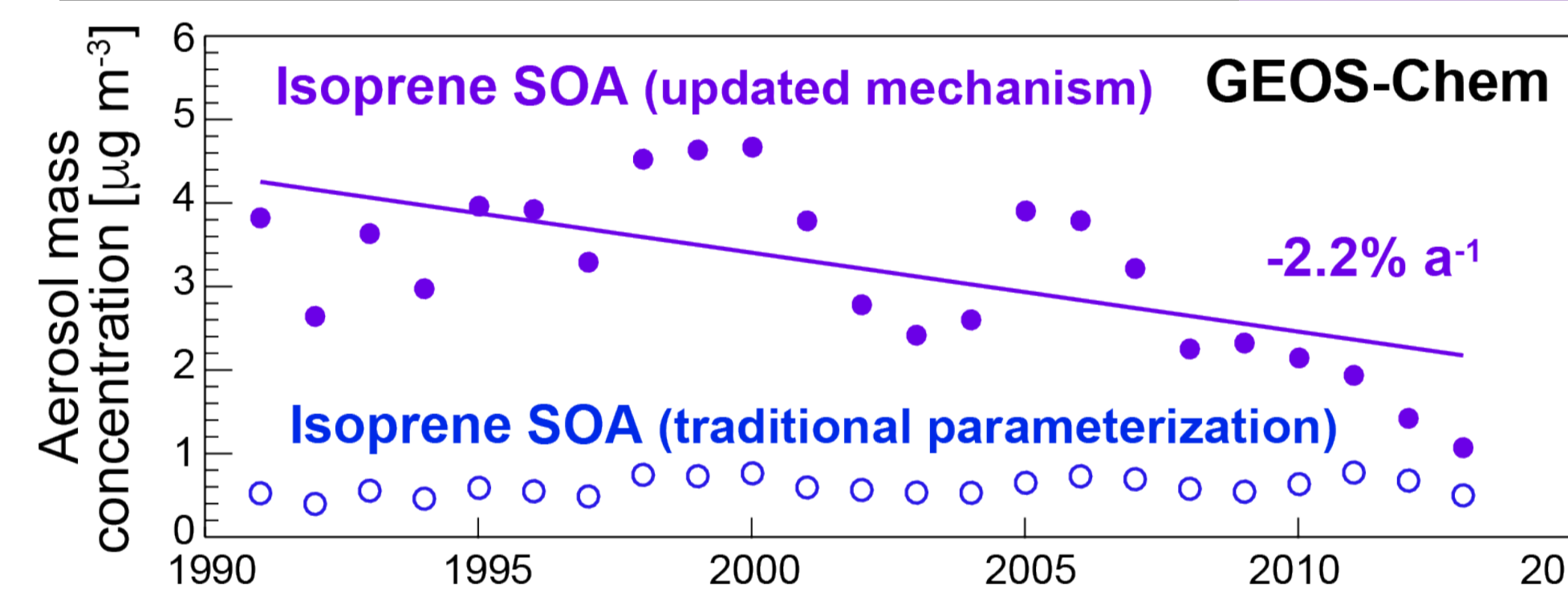

Model trends are significant at the 95% confidence level.

The model reproduces the observed decline in OA and sulfate.

The majority of the decline in simulated OA is due to decline in isoprene SOA of 2.2% a^{-1} (see figure below).

#### Model 1991-2013 trend in summertime isoprene SOA

Isoprene SOA mass yields decline from 13% in 1991 to 3.5% in 2013. Contribution of isoprene SOA to total OA decreases from 59% in 1991-1995 to 40% in 2009-2013 (see table in Discussion Section).

There is no trend in isoprene SOA with the traditional volatility-based approach and mass concentrations remain low (<1 $\mu g\ m^{-3}$).

3. DISCUSSION

Spatial distribution of summertime mean organic aerosol
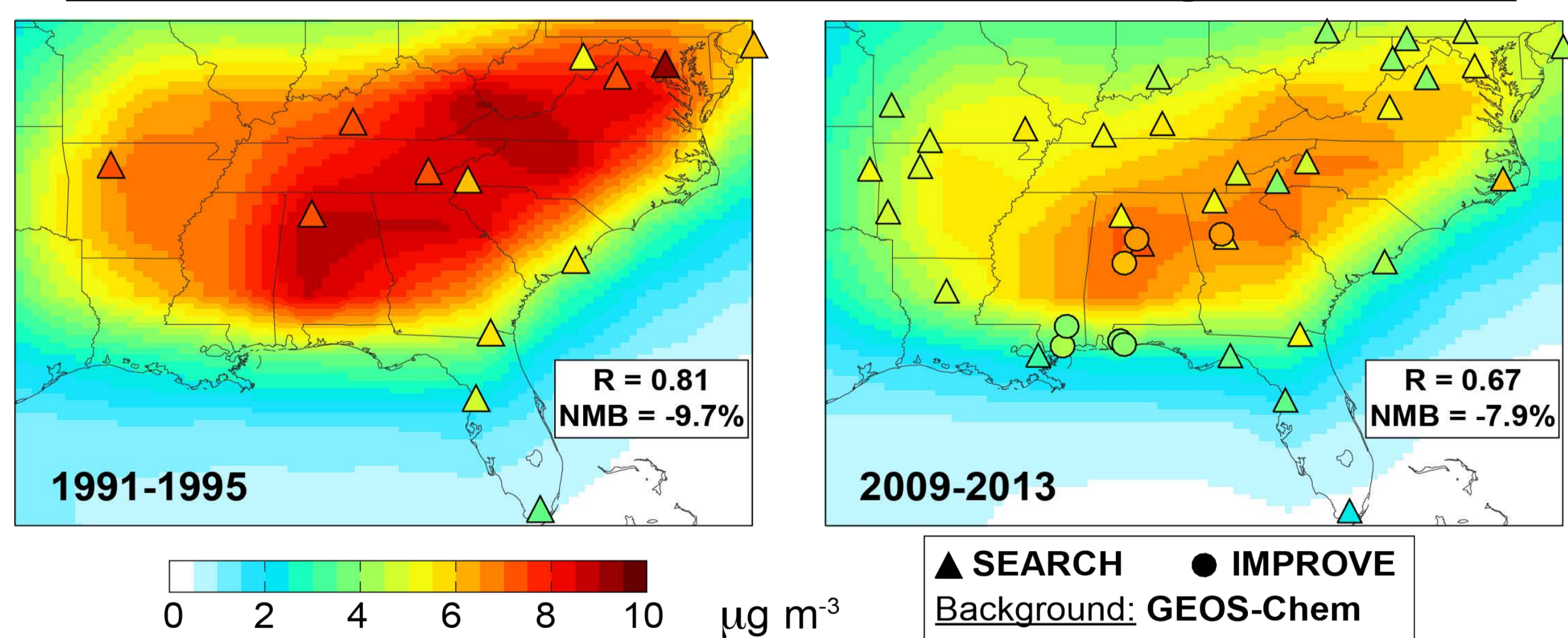
There is no significant change in OA spatial distribution in the observations or model from 1991-1995 to 2009-2013, supporting biogenic SOA driving the OA trend.

The model normalized mean bias (NMB) is small (<-10%) and decrease in OA from 1991-1995 to 2009-2013 is similar in the observations (25%) and the model (23%).

Contribution (%) of OA components to total OA at the start and end of the long-term record:

OA component	1991-1995	2009-2013
Isoprene SOA	59	40
Mono- & Sesquiterpene SOA	13	22
Non-biogenic primary OA (POA)	21	25
Non-biogenic SOA	7	13

Decline in isoprene SOA in the model is driven by decreases in aqueous aerosol volume (54% over 1991-2013) and acidity (83% over 1991-2013), both driven by decreasing SO_2 emissions.

Aerosol acidity and volume each contribute to half of the isoprene SOA trend.

Decline in NO_x to address ozone pollution increases formation of gas-phase IEPOX, but the effect is small compared to that of SO_2 emission controls.

Model 1991-2013 trends in summertime aqueous aerosol acidity and volume mass concentrations
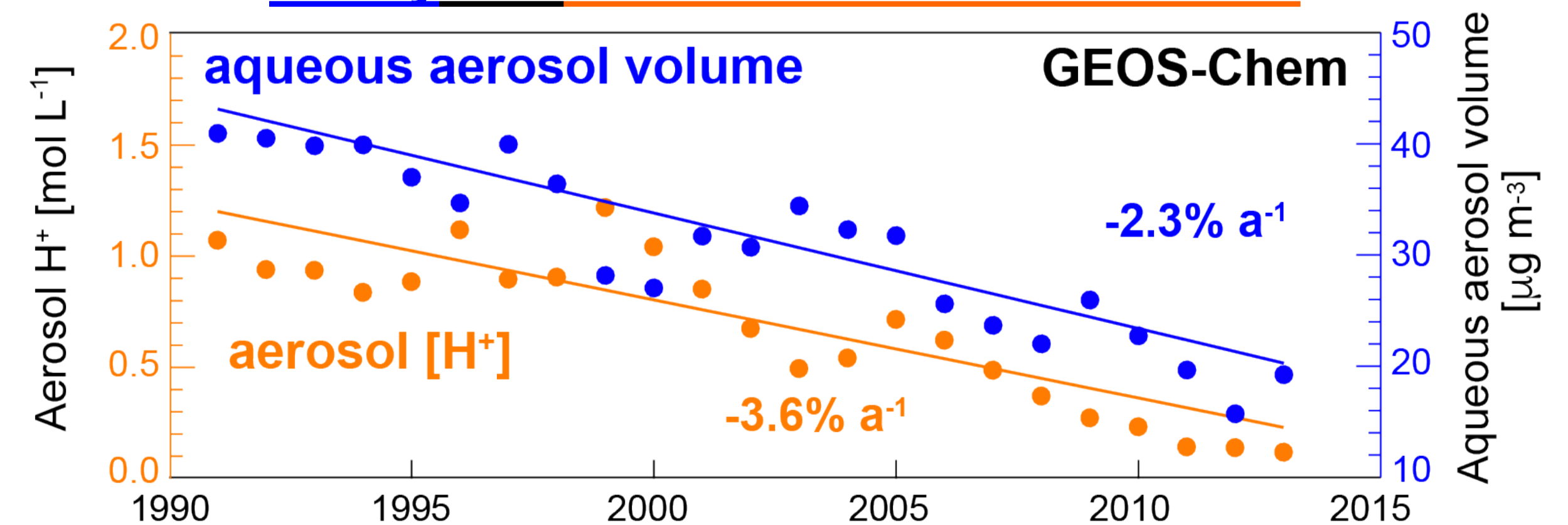
OA interannual variability (IAV) in the model, estimated as the relative departure from the long-term trend, is correlated with observed OA IAV (R = 0.49 with SEARCH and R = 0.55 with IMPROVE), confirming the important contribution of biogenic SOA to the long-term trend.

30 SECOND SUMMARY

- 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 secondary OA (SOA) formation from biogenic isoprene, 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).
- Thus SO_2 emission controls to decrease sulfate have had a large air quality co-benefit in the Southeast US by concurrently decreasing organic aerosol (OA).

ACKNOWLEDGEMENTS

REFERENCES

[1] EPA, 2015, http://bit.ly/2pAF7QS [Accessed Oct 5, 2015].
[2] Hand et al., ACP, doi: 10.5194/acp-12-10353-2012, 2012.
[3] Attwood et al., GRL, doi:10.1002/2014GL061669, 2014.
[4] Kleindienst et al., JAWMA, doi:10.3155/1047-3289.60.11.1388, 2010.
[5] Kim et al., ACP, doi:10.5194/acp-15-10411-2015, 2015.
[6] Marais et al., ACP, doi:10.5194/acp-16-1603-2016, 2016.
[7] Theil, Proc. Kon. Ned. Akad. V. Wetensch. A, 53 386-92, 1950.