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THE STATE UNIVERSITY OF NEW JERSEY

The Southern Oxidant and Aerosol Study

Annmarie G. Carlton

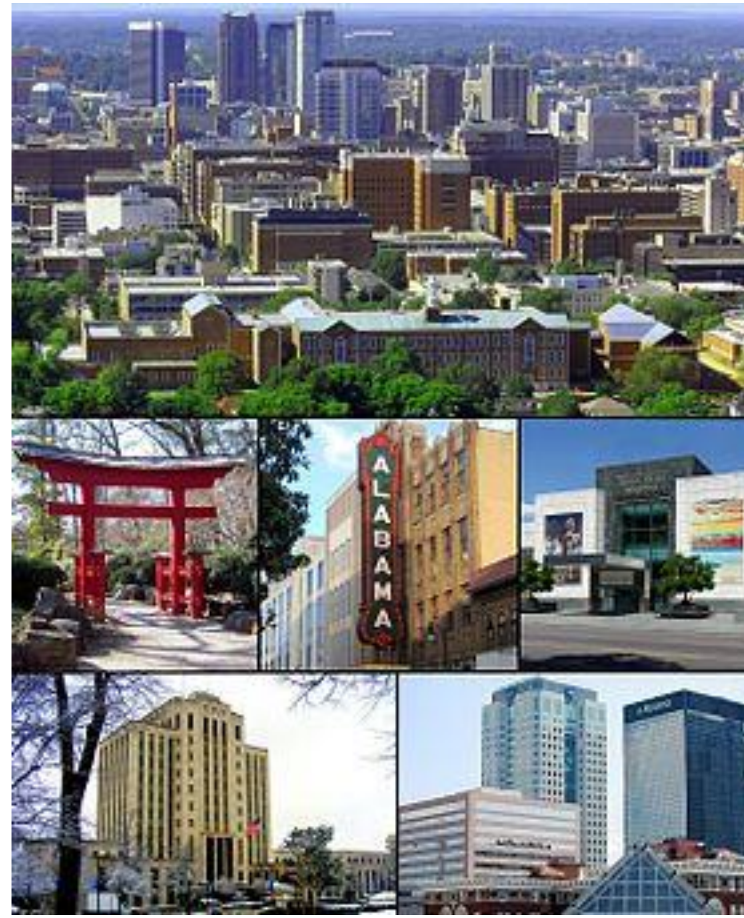
Southeast **A**tmosphere **S**tudies

June 1 - July 15, 2013

Additionally: EPA’s surface networks, NASA satellites, EPRI network

Stagnation event 1971

Smog over Birmingham, TSP ~700 μg m^{-3}. EPA's first implementation of the CAA's "emergency powers" provision. (The Birmingham News file/Dave Battle)



40 years later EPA proposed that Birmingham be certified as having attained the NAAQS.

Great Smoky Mountain National Park

Photo courtesy of CIRA

Southern **O**xidant and **A**erosol **S**tudy

SOAS
Southern Oxidant & Aerosol Study

June 1 - July 15, 2013

SOAS + SENEX + TropHONO + NAAMEX = Southeast Atmosphere Studies (SAS)

C130 portion of SOAS + TropHONO + NAAMEX = NOMADSS

NSF, NOAA, EPA, EPRI, NCAR, U.S. and European Universities, private companies worked together during the sequester**(!).**

NSF OFAP request: 160 hours on C130, 2 towers, 110 release sondes and individual investigator proposals

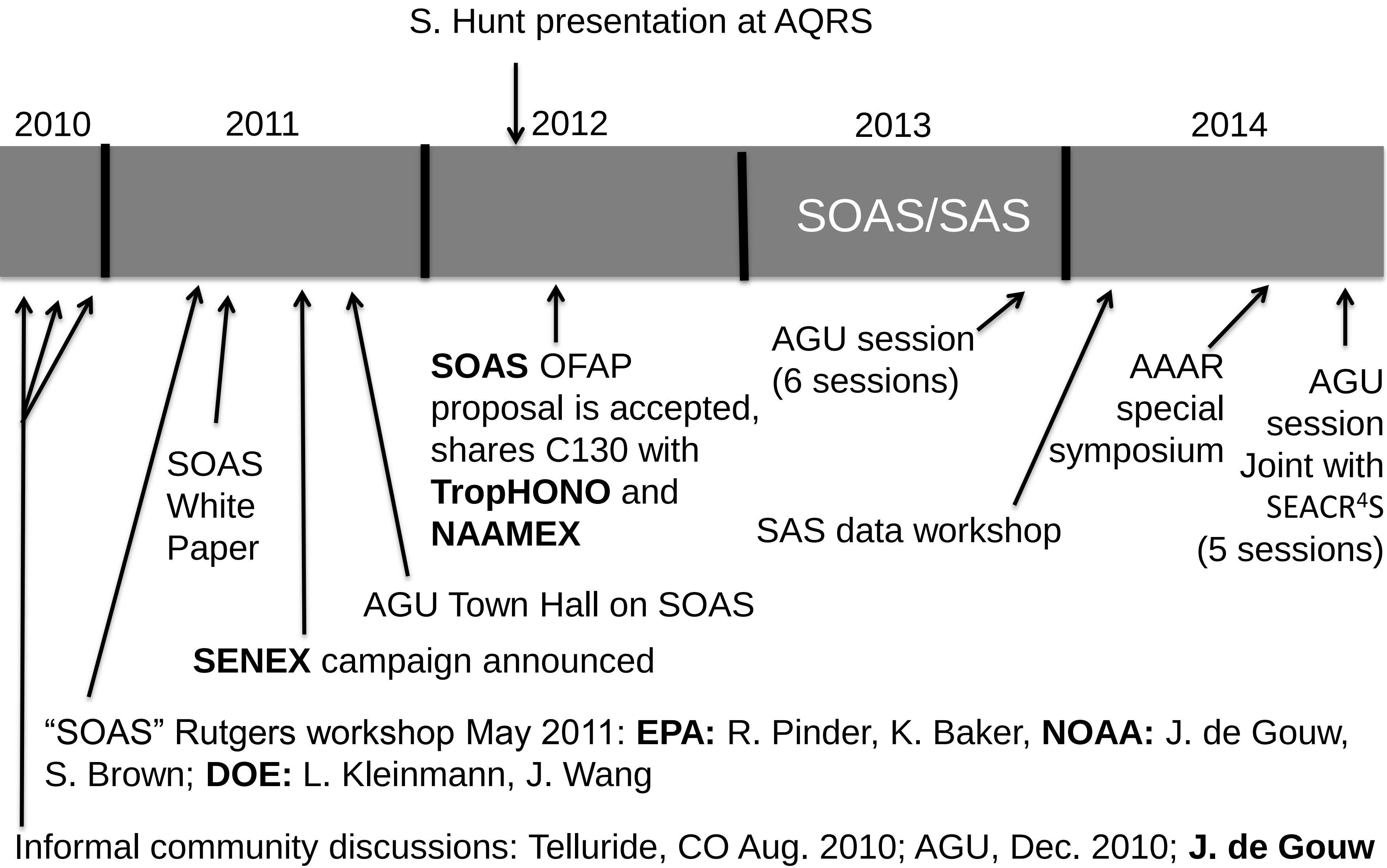
NOAA's commitment to fly the P3 for SENEX was an early and important impetus

EPA's anthropogenic influence on PM in the Southeast STAR RFP supported of SOAS. *University scientist funded to fly on a NOAA plane*

Main ground site is EPRI's "CTR" SEARCH network site.

SEACR^{4}S campaign repeated some P3 and C130 flight tracks later in summer, extending the intensive period for chemical characterization of the troposphere

SAS timeline



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SOS Reminders

 +  = O_3

SOUTHERN OXIDANTS STUDY

Overwhelming majority of organic compounds in the atmosphere come from the biosphere. Biogenic hydrocarbons interact with anthropogenic pollution to form pollutants ozone, even resulting in non-attainment.

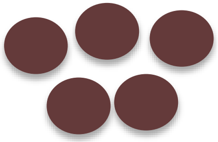
Last time our community converged on the Southeast U.S. AQ management redefined for O_3

- As late as 1988: literature describing how VOC controls are not working for Atlanta $O_{3:}$ NO_x-limited and VOC-limited
- Isoprene is 3% by mass of Atlanta’s VOC inventory, but >30% of the reactivity

SOAS
Southern Oxidant & Aerosol Study

+

=



Emissions from the biosphere interact with emissions from human activity to form particulate matter. Anthropogenic pollution facilitates biogenic **SOA** formation (Weber et al., 2007; Surratt et al., 2007; Lane et al., 2009; Jimenez and de Gouw, 2009; Carlton et al. 2010; Spracklen et al., 2011; Shilling et al., 2013).

Motivation behind SOAS in 2013.

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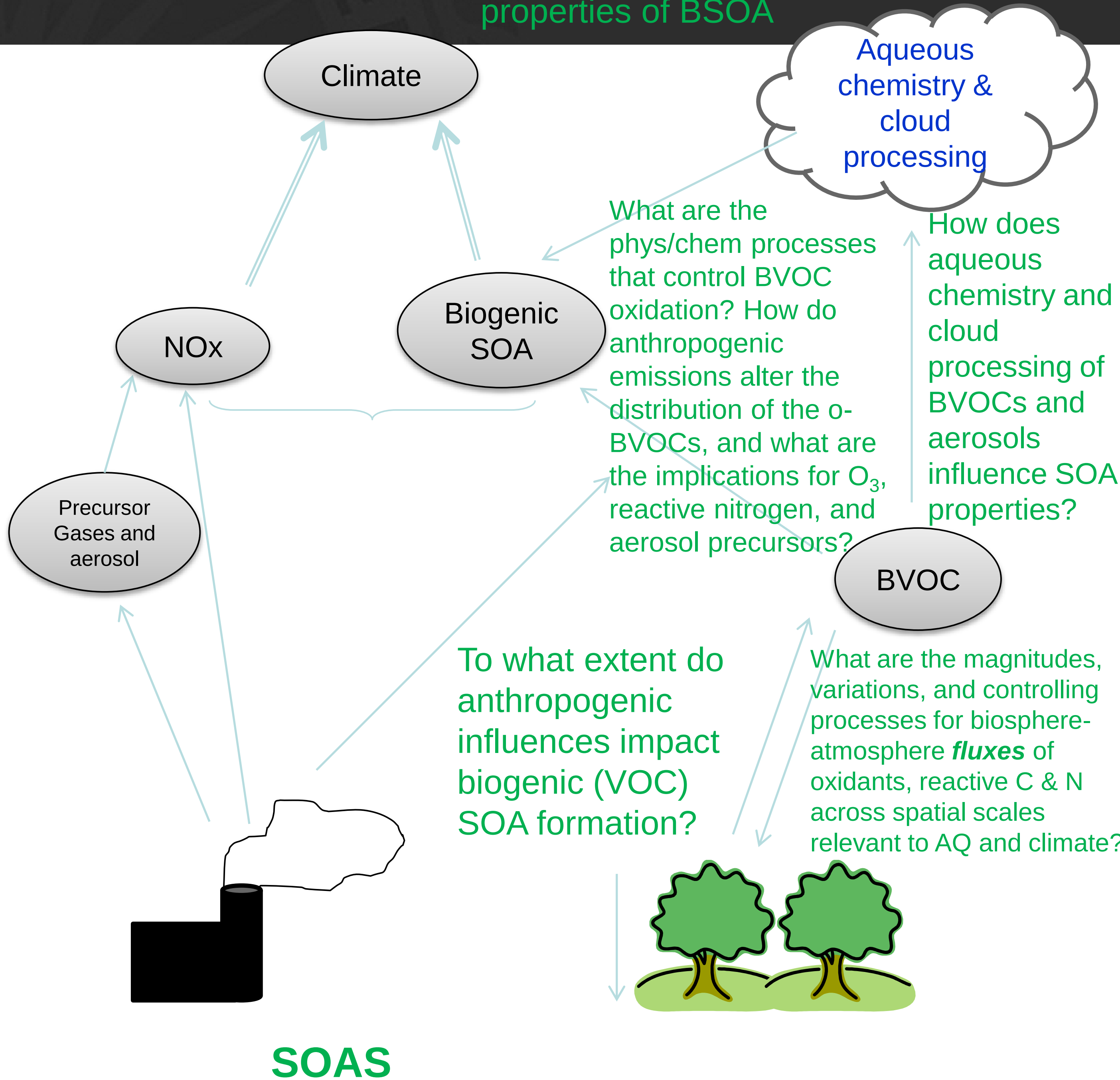
What are the climate-relevant properties of BSOA



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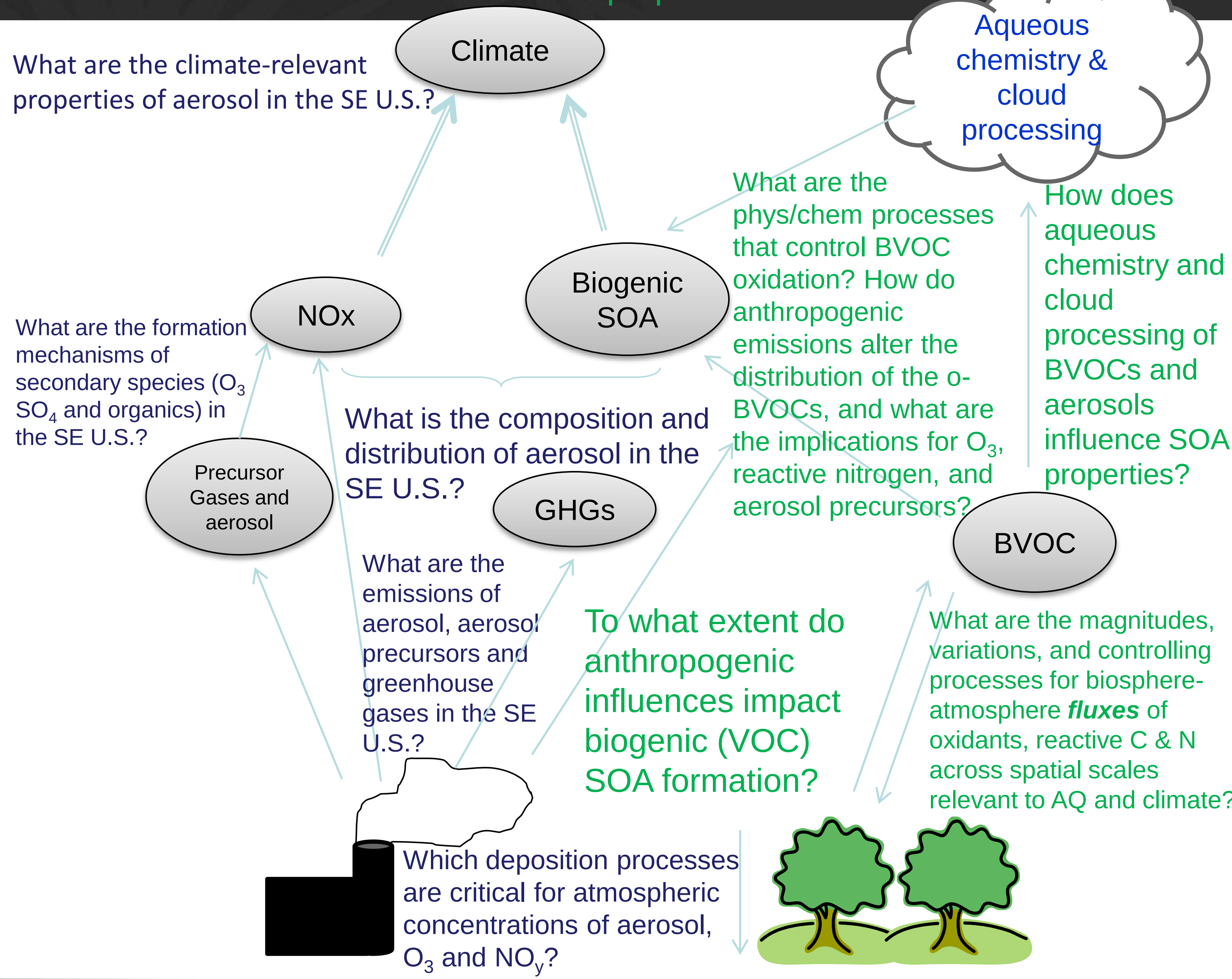
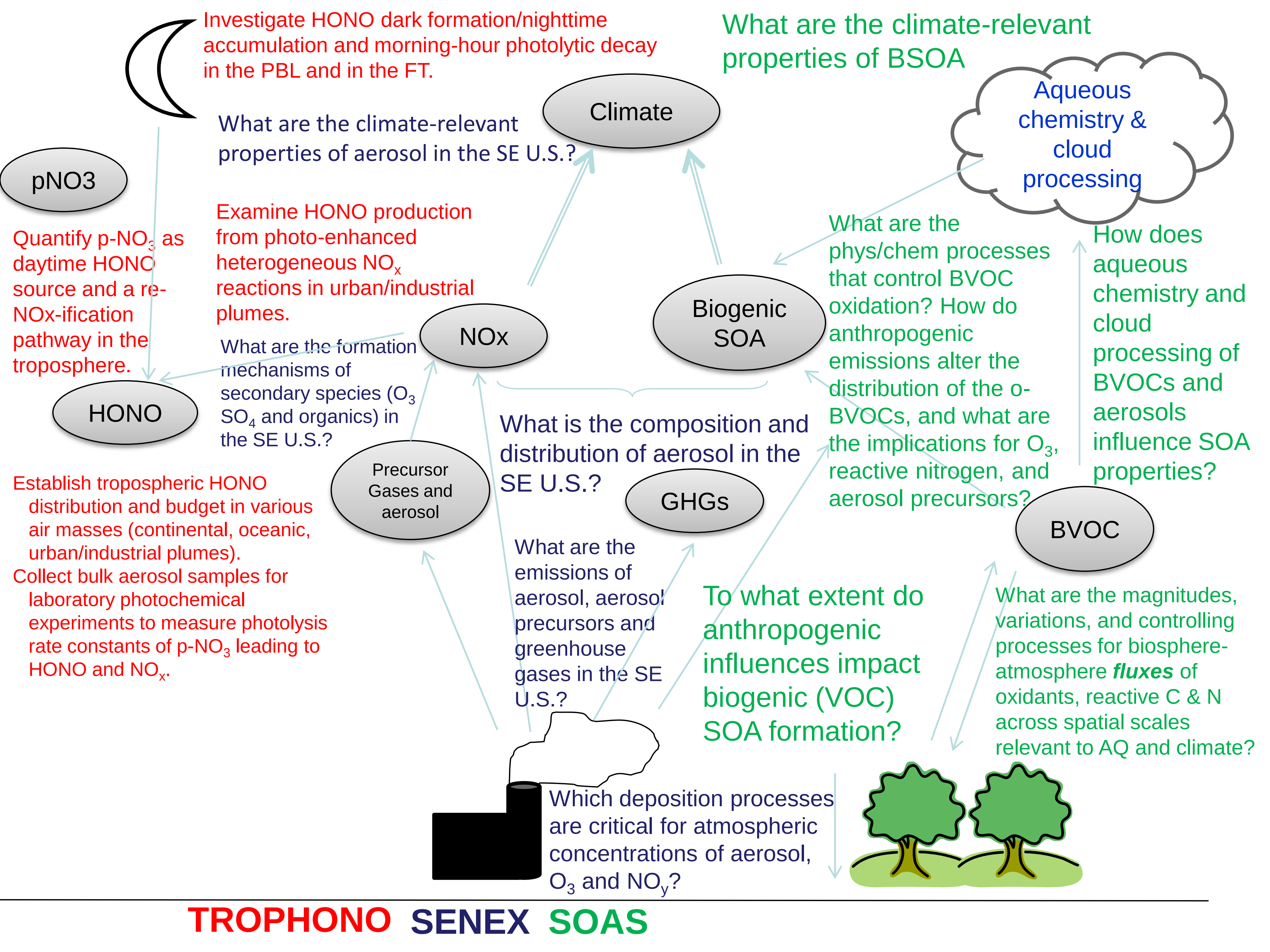
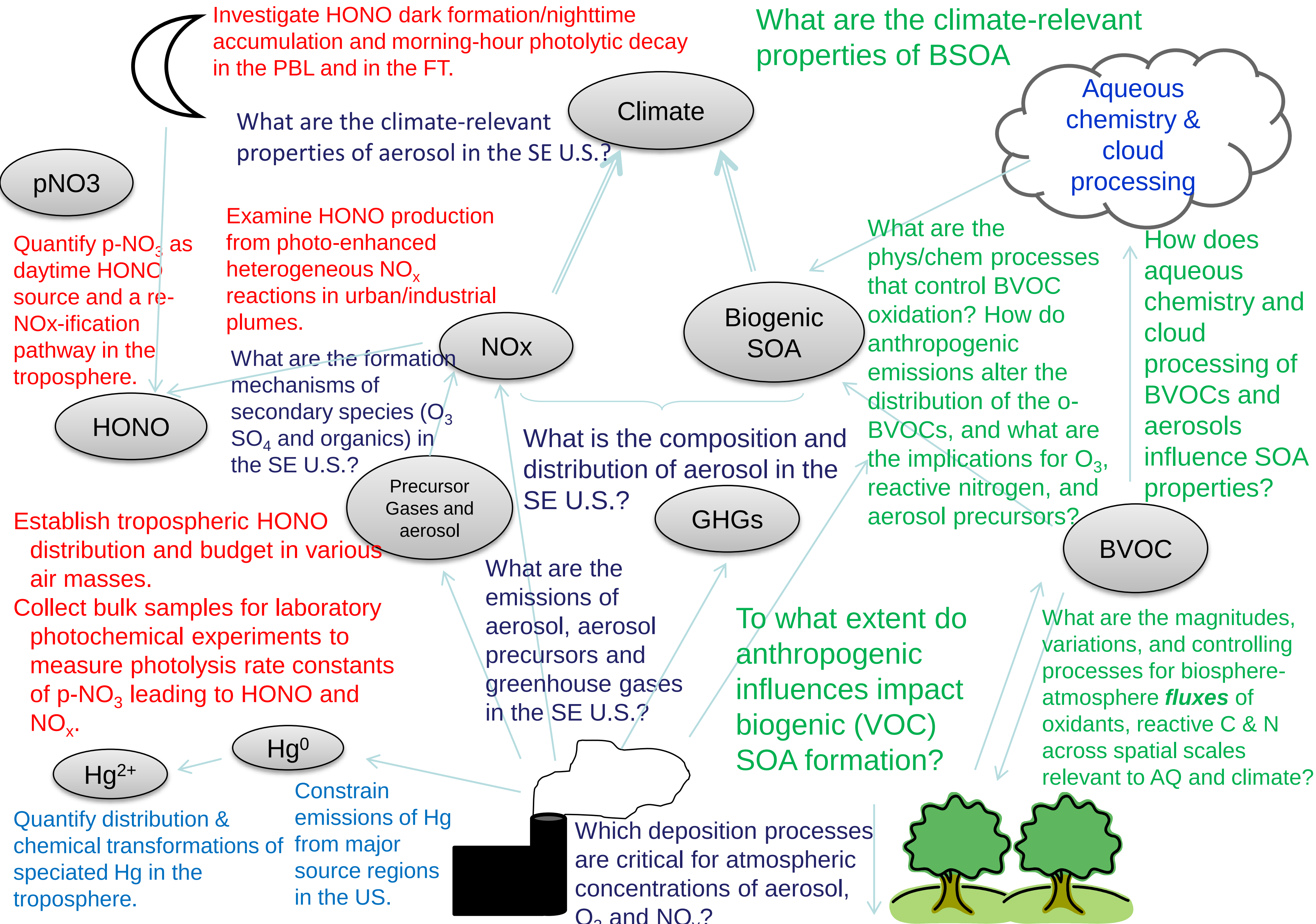
What are the climate-relevant properties of BSOA



SENEX SOAS


Investigate HONO dark formation/nighttime accumulation and morning-hour photolytic decay in the PBL and in the FT.
What are the climate-relevant properties of BSOA
Aqueous chemistry & cloud processing
Climate
What are the climate-relevant properties of aerosol in the SE U.S.?
pNO3
Quantify p-NO_3 as daytime HONO source and a re-NOx-ification pathway in the troposphere.
Examine HONO production from photo-enhanced heterogeneous NO_x reactions in urban/industrial plumes.
What are the phys/chem processes that control BVOC oxidation? How do anthropogenic emissions alter the distribution of the o-BVOCs, and what are the implications for O_3, reactive nitrogen, and aerosol precursors?
How does aqueous chemistry and cloud processing of BVOCs and aerosols influence SOA properties?
Biogenic SOA
NOx
What are the formation mechanisms of secondary species (O_3 SO_4 and organics) in the SE U.S.?
HONO
What is the composition and distribution of aerosol in the SE U.S.?
Precursor Gases and aerosol
GHGs
BVOC
Establish tropospheric HONO distribution and budget in various air masses (continental, oceanic, urban/industrial plumes).
Collect bulk aerosol samples for laboratory photochemical experiments to measure photolysis rate constants of p-NO_3 leading to HONO and NO_x.
What are the emissions of aerosol, aerosol precursors and greenhouse gases in the SE U.S.?
To what extent do anthropogenic influences impact biogenic (VOC) SOA formation?
What are the magnitudes, variations, and controlling processes for biosphere-atmosphere ***fluxes*** of oxidants, reactive C & N across spatial scales relevant to AQ and climate?
Which deposition processes are critical for atmospheric concentrations of aerosol, O_3 and NO_y?
TROPHONO SENEX SOAS



NAAMEX + **TROPHONO** + **SENEX** + **SOAS** = Southeast Atmosphere Studies (**SAS**)

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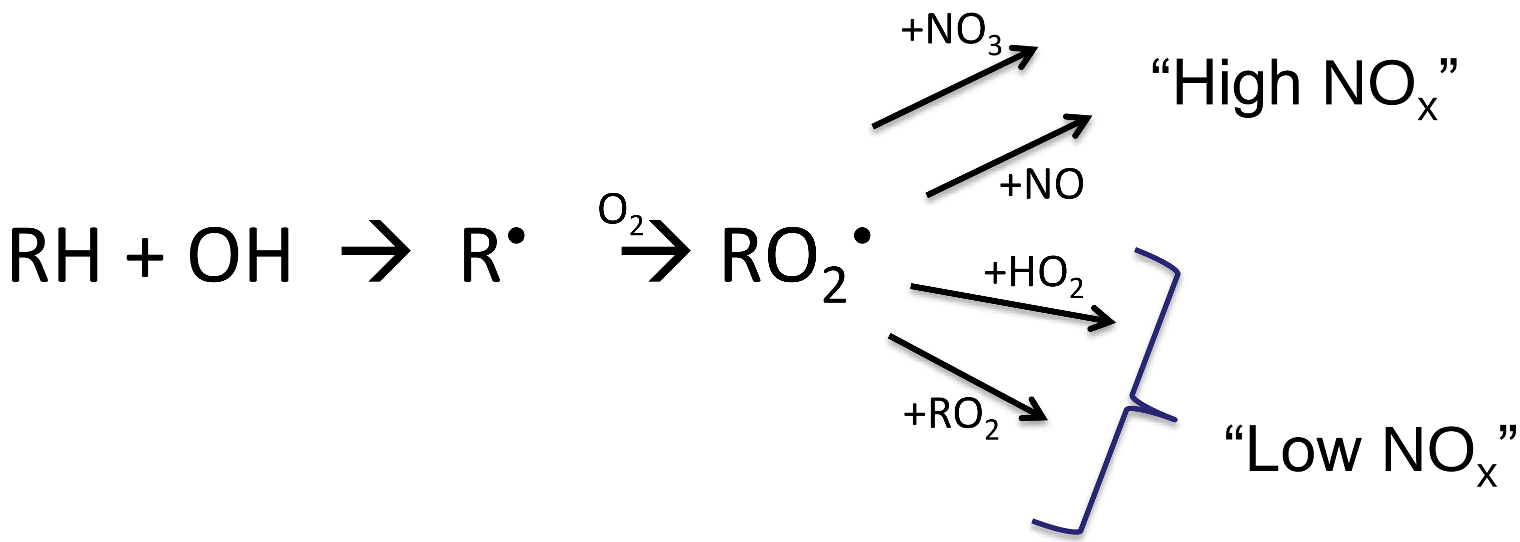
“Big” Picture

$$VOCs + NO_x + hv \rightarrow O_3 + particles + \ldots$$



Model predictions must **correctly predict** concentrations for the **right reasons**. This is **essential** to ensure **appropriate model response** to simulated control strategies and is critical to development **of cost-effective air quality management plans**.

Moving Forward

Reaching across scientific discipline workhsop at GFDL: “Southeast Atmosphere Studies Workshop: Intensive Observation Period Modeling to Improve Mechanistic Representation of Trends”

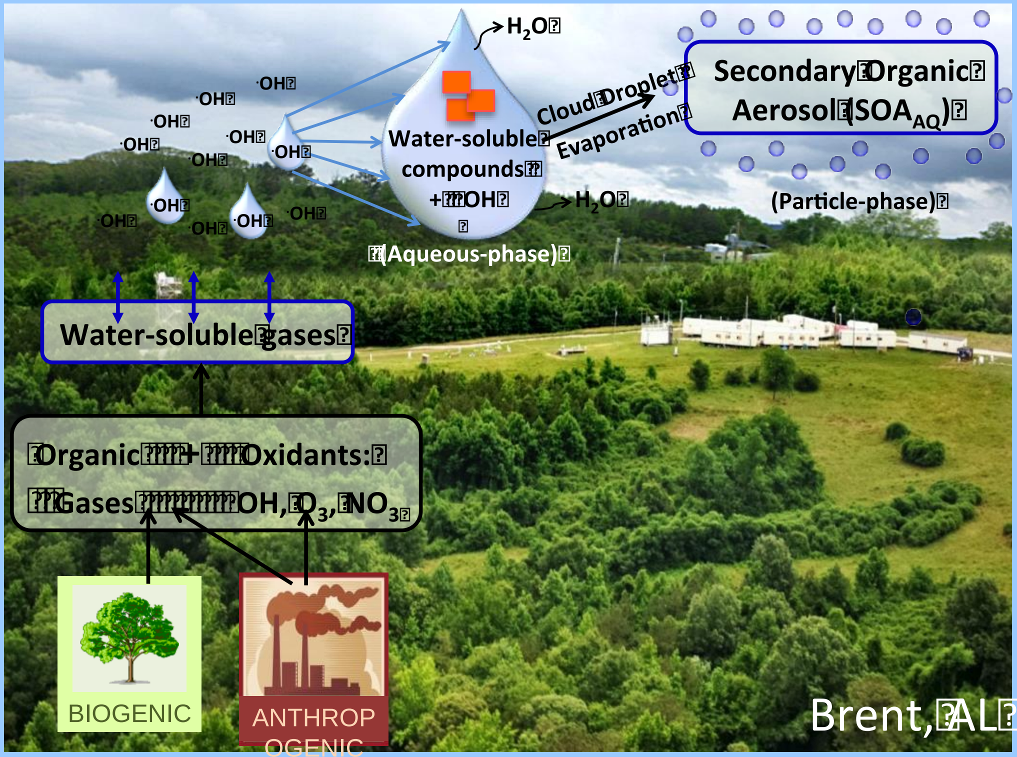
Are we still asking the most critical and open important science questions?

What are high level questions we can answer with our robust data set? Are we getting the most out of this resource?

What are the important scientific details can we “finally figure out” and “nail down”?

How do we impact future the development of ***effective*** air quality management strategies?

Organic Aerosol Formation in the Humid, Photochemically-Active Southeastern US: SOAS Experiments and Simulations



Barbara Turpin[t], Annmarie Carlton, Neha Sareen

Rutgers University – New Brunswick

[t]now at University of North Carolina – Chapel Hill

Turpin–Carlton Specific Aims - SOAS:

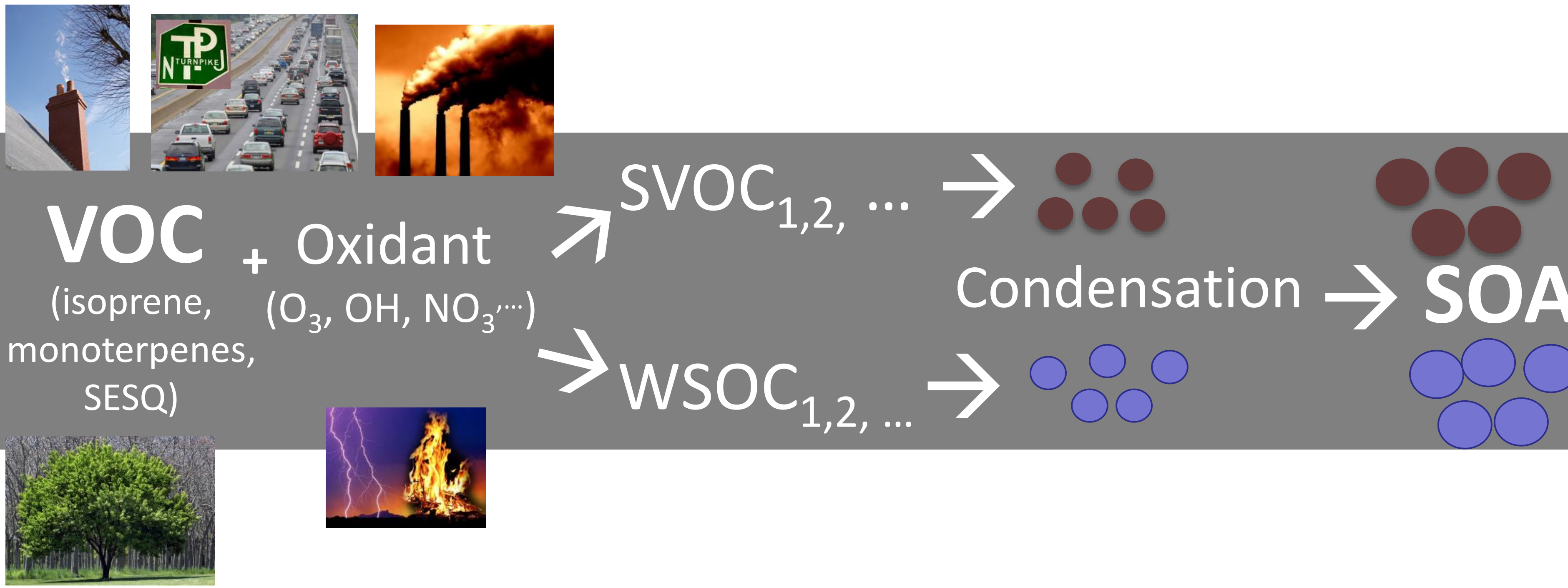
1) Model aerosol liquid water concentrations

2) Model water-soluble gases

3) Conduct aqueous OH oxidation experiments with ambient SOAS mixtures of water-soluble gases (WSOG) to identify precursors/products

4) Collaborate, provide intellectual leadership and share data to achieve the SOAS science goals

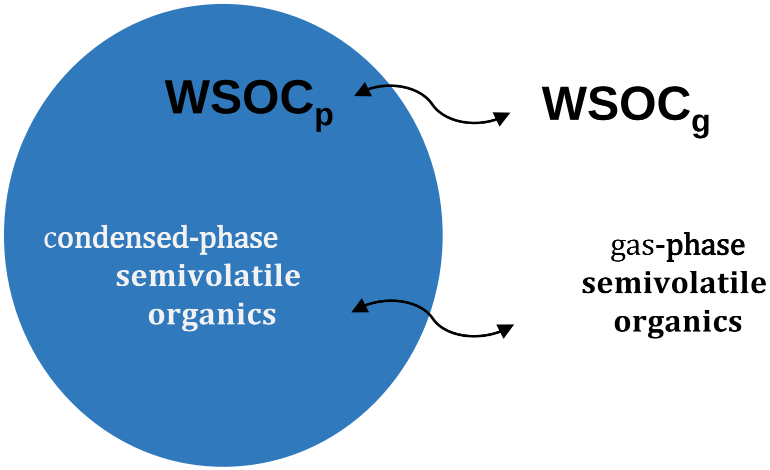
VOCs + NOx + hv → O_3 + particles + …



Polar gases also partition to **polar** solvents → water → **SOA_{aq}**

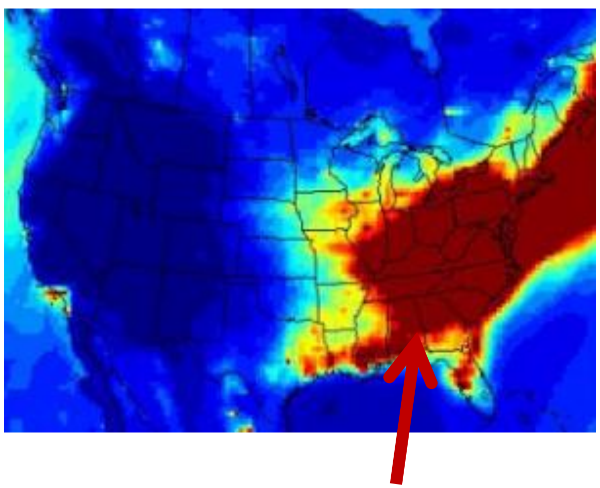
Majority of partitionable atmospheric organic compounds are small, **water-soluble gases** (Grosjean et al., 1996; Nolte et al., 2001: Zhang et al., 2007) and globally, **particle phase liquid water mass >>2-3x organic aerosol** mass (Liao and Seinfeld, 2007).

Why is Southeastern U.S. the ideal region for this study?

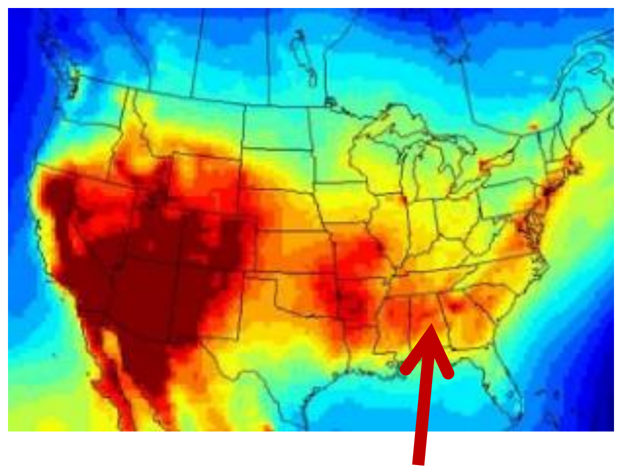


CMAQ used in site selection

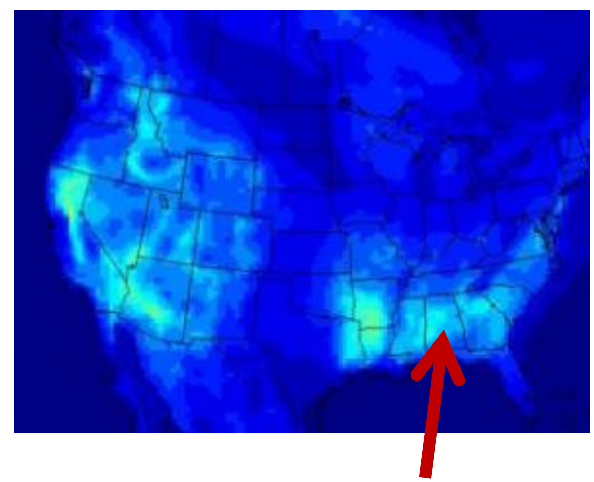
CMAQ predictions for all of the ground sites extracted and uploaded to ftp in ICARTT format



Lots of aerosol water



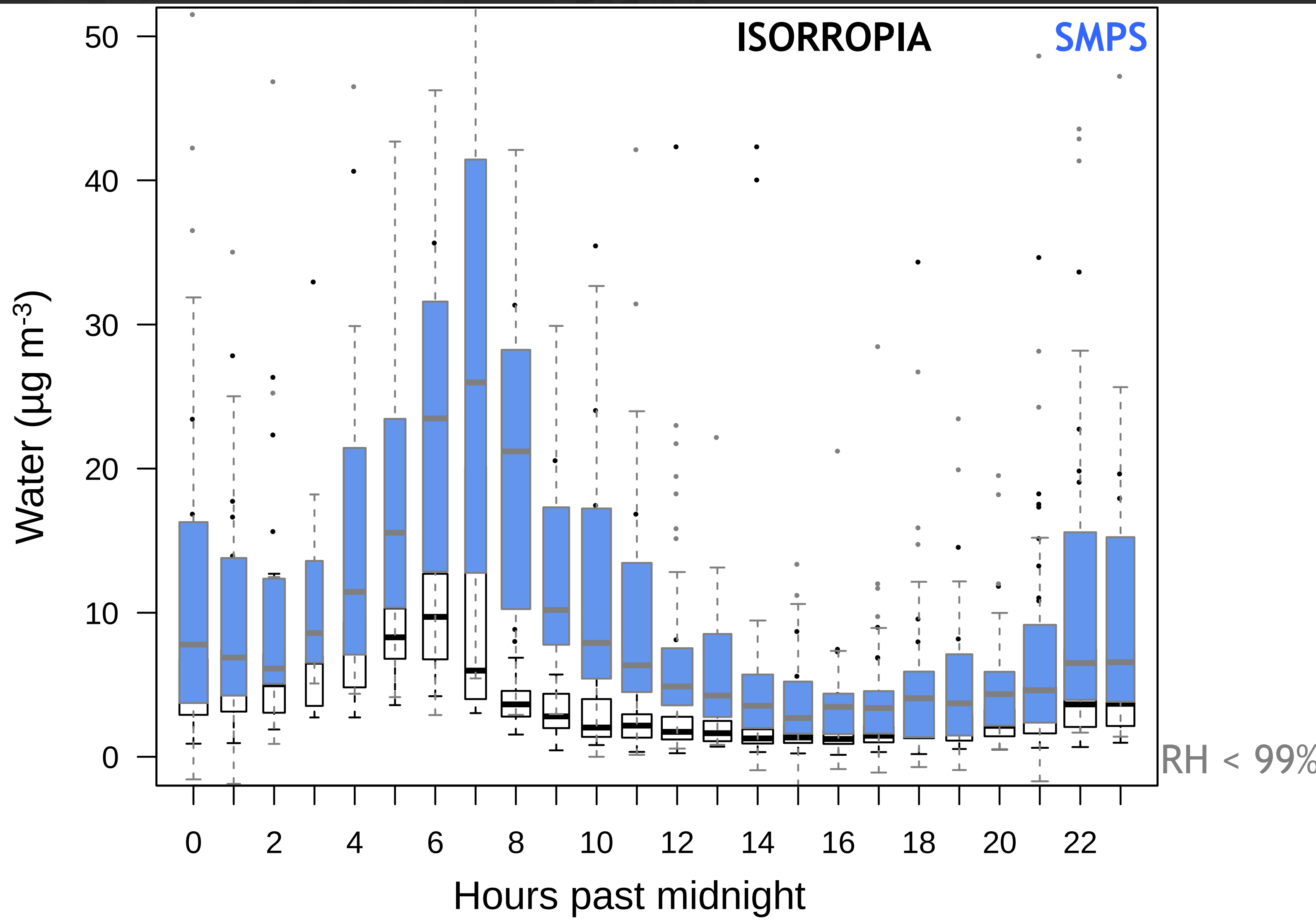
Lots of $WSOC_g$ (glyoxal …)



Lots of semi-volatile organic compounds

[*Carlton and Turpin*, 2013, ACP]

Water model comparison for SOAS

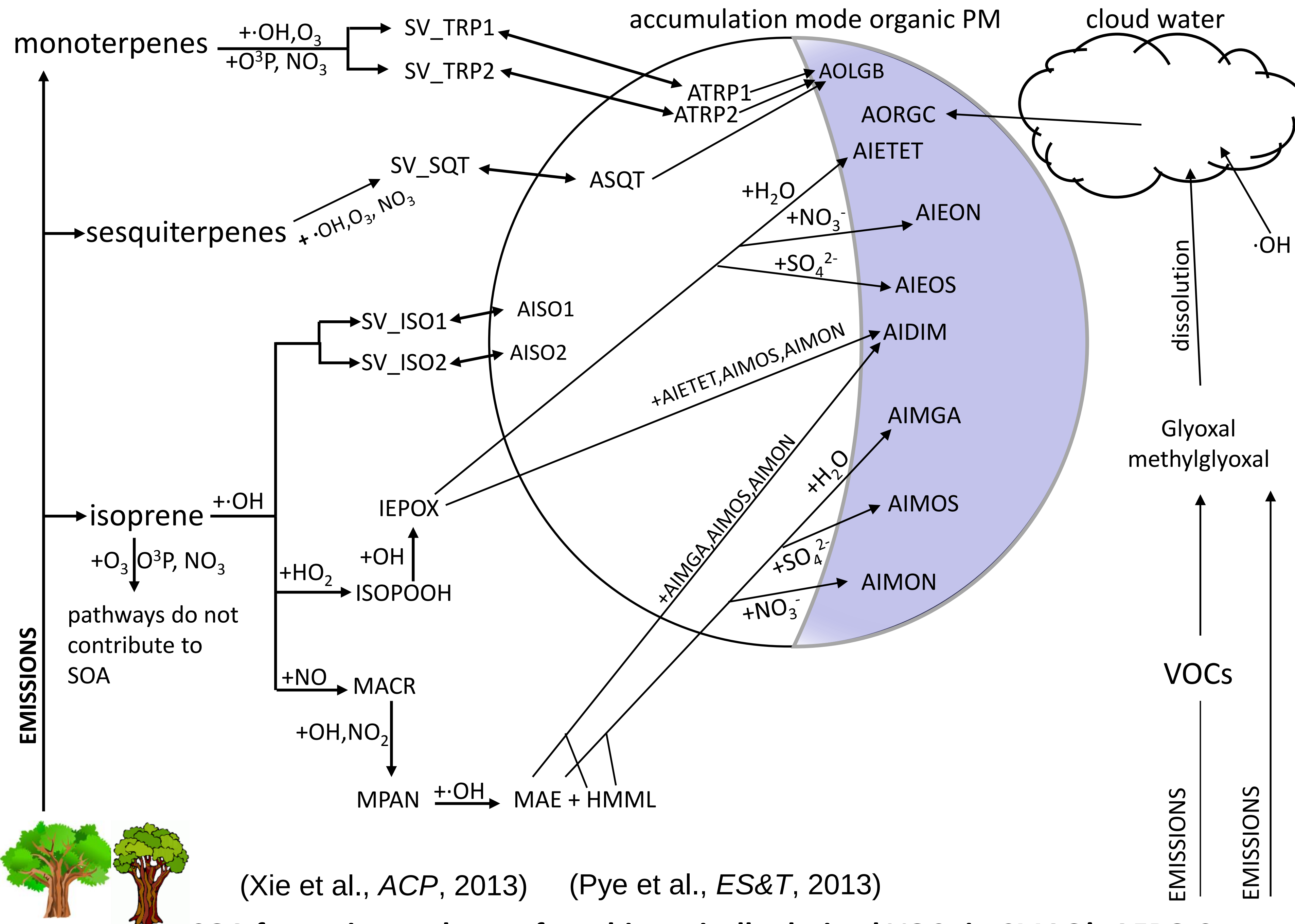


ISORROPIA ran with measured data input

SMPS data from Nguyen et al., 2014 adjusted to SEARCH RH using P&K eqn.

CMAQ Modeling

- CMAQv5.0.1
- June 6-June 15 2013
- SAPRC07 updated with “explicit” isoprene gas phase oxidation chemistry (Xie et al., *ACP*, 2013)
- Heterogeneous organic chemistry (Pye et al., *ES&T*, 2013)
- WRFv3.4
- BEISv3.14
- Point and other anthropogenic species based on NEI2008v3.1 and “grown” (forecasting ‘runs’)
- 12km x 12km grid for the ConUS



SOA formation pathways from biogenically-derived VOCs in CMAQ's AERO 6

WSOG species

- Formaldehyde (HCHO)
- Acetone (ACETONE)
- Acetaldehyde (CCHO)
- Methyl ethyl ketone (MEK)
- Methyl vinyl ketone (MVK)
- Methacrolein (MACR)
- Glyoxal (GLY)
- Methylglyoxal (MGLY)
- Acetic acid (CCOOH)
- Methanol (MEOH)
- Isoprene epoxydiol (IEPOX)
- Methacrylic acid epoxide (MAE)
- Hydroxymethylmethyl-α-lactone (HMML)

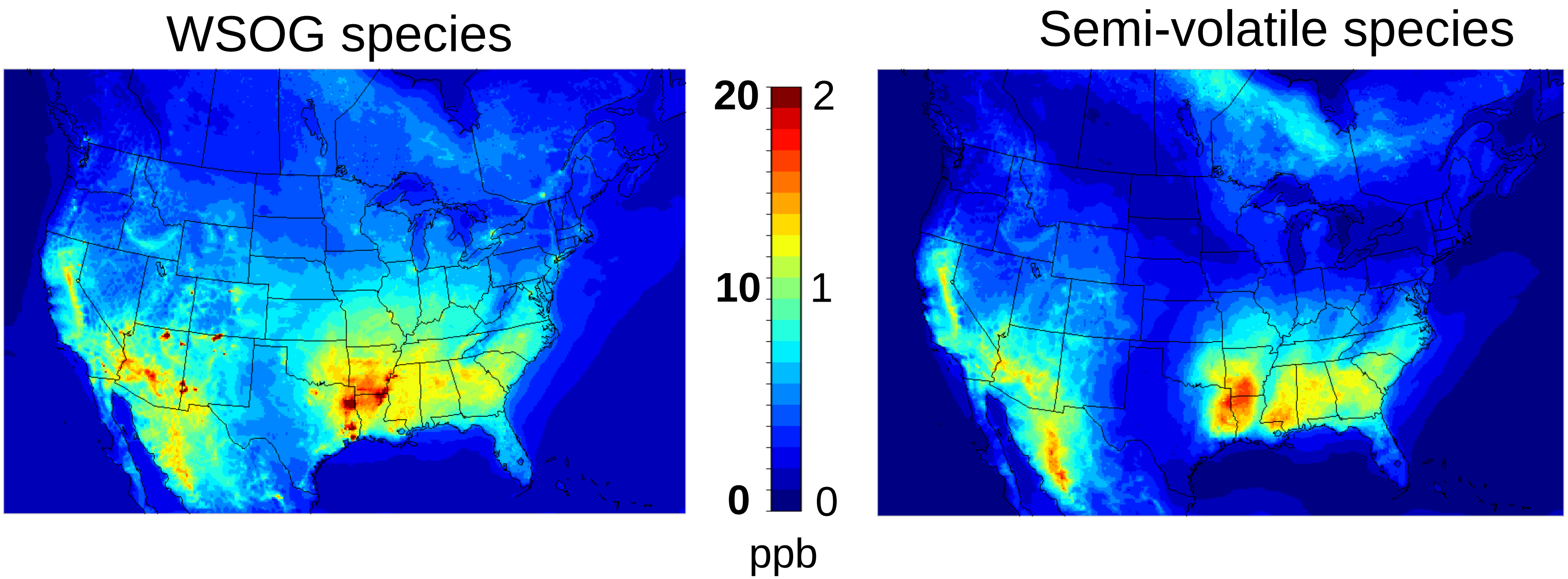
SV species

- Alkane (SV_ALK)
- Xylene (SV_XYL*)
- Toluene (SV_TOL*)
- Benzene (SV_BNZ*)
- Terpene (SV_TRP*)
- Isoprene (SV_ISO*)
- Sesquiterpene (SV_SQT)

* multiple species

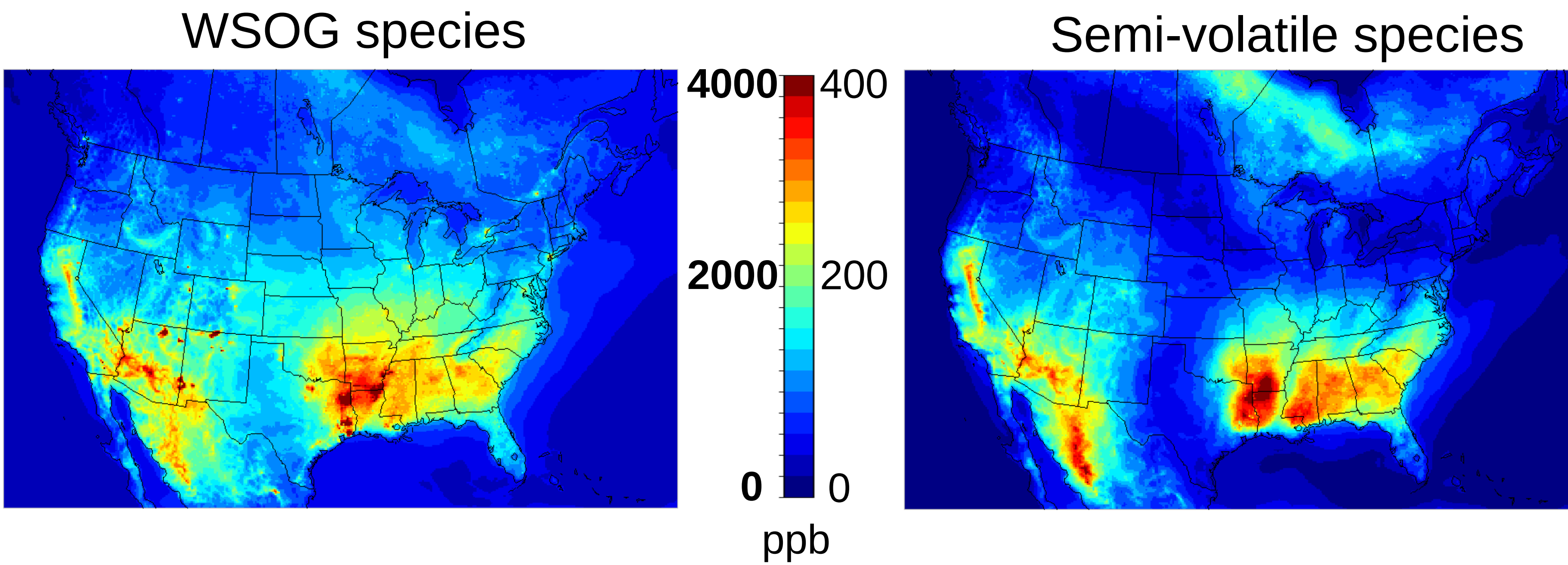
CMAQ modeling

Surface layer

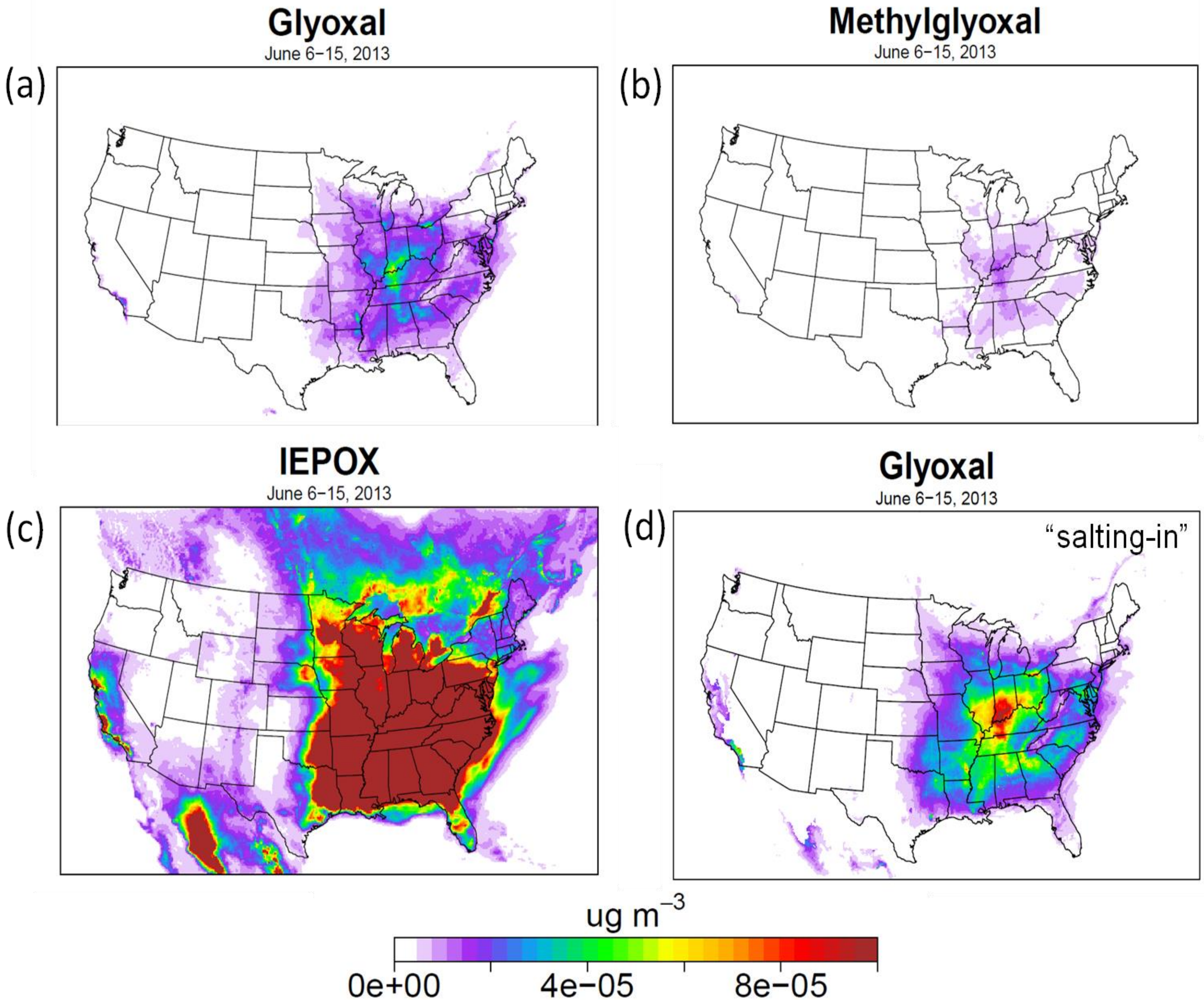


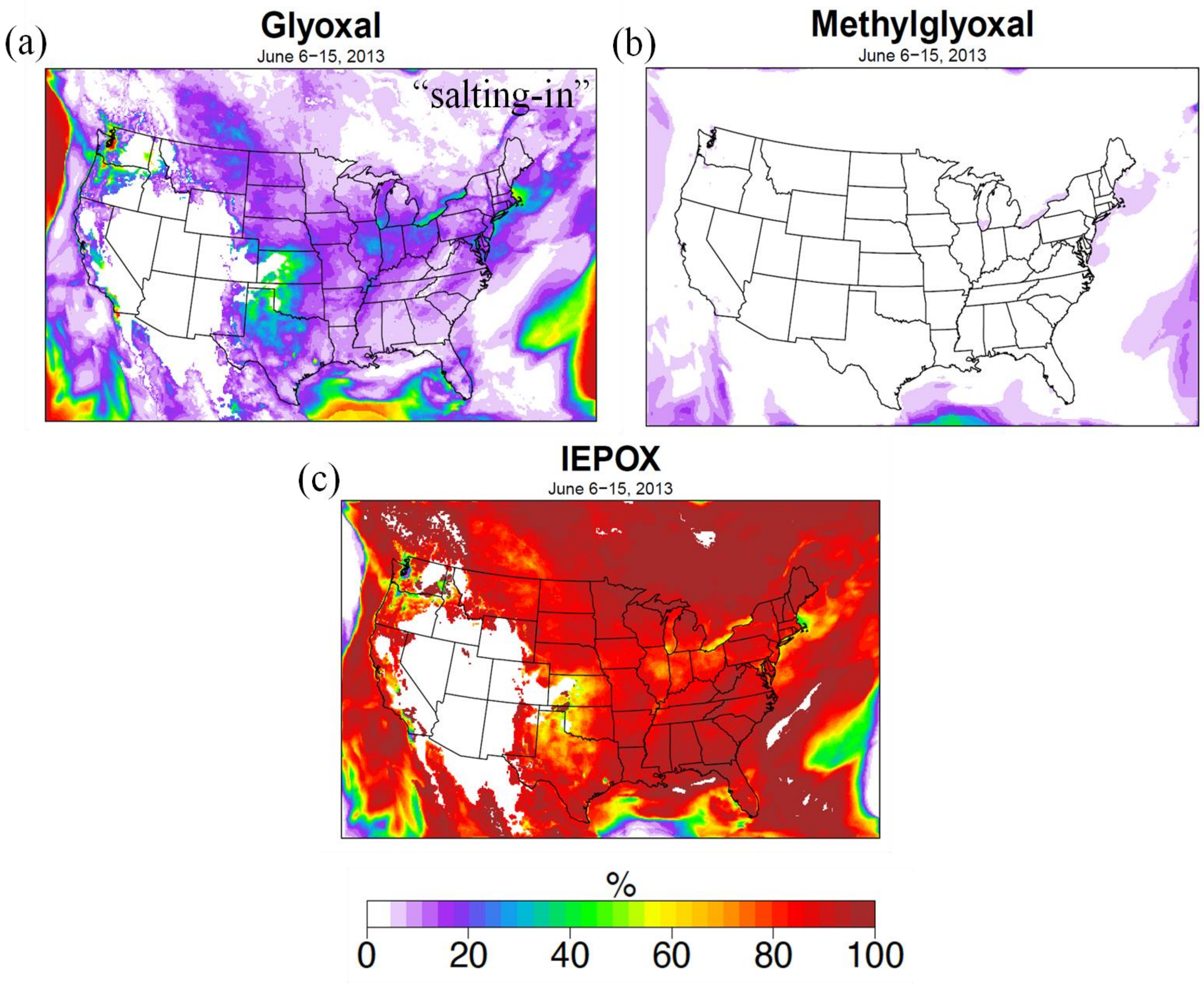
CMAQ modeling

Vertical total

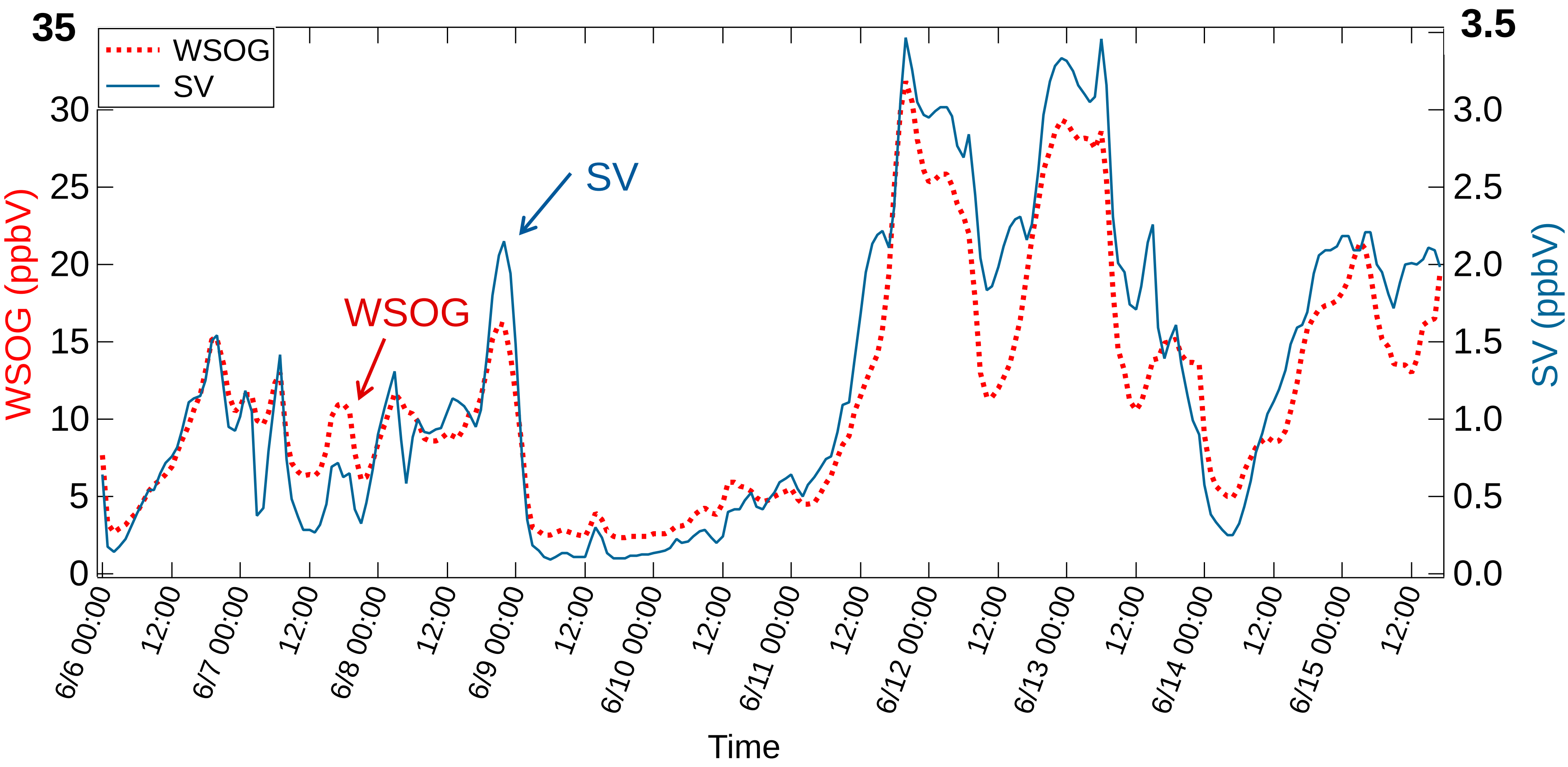


$[C_i]_p = H_i RTLC_{i(g)}$




(a)
Glyoxal
June 6−15, 2013
"salting-in"
(b)
Methylglyoxal
June 6−15, 2013
(c)
IEPOX
June 6−15, 2013
%
0
20
40
60
80
100

At surface layer, model predicts **WSOG** an order of magnitude **greater** than **semi-volatile** species at Brent ground site



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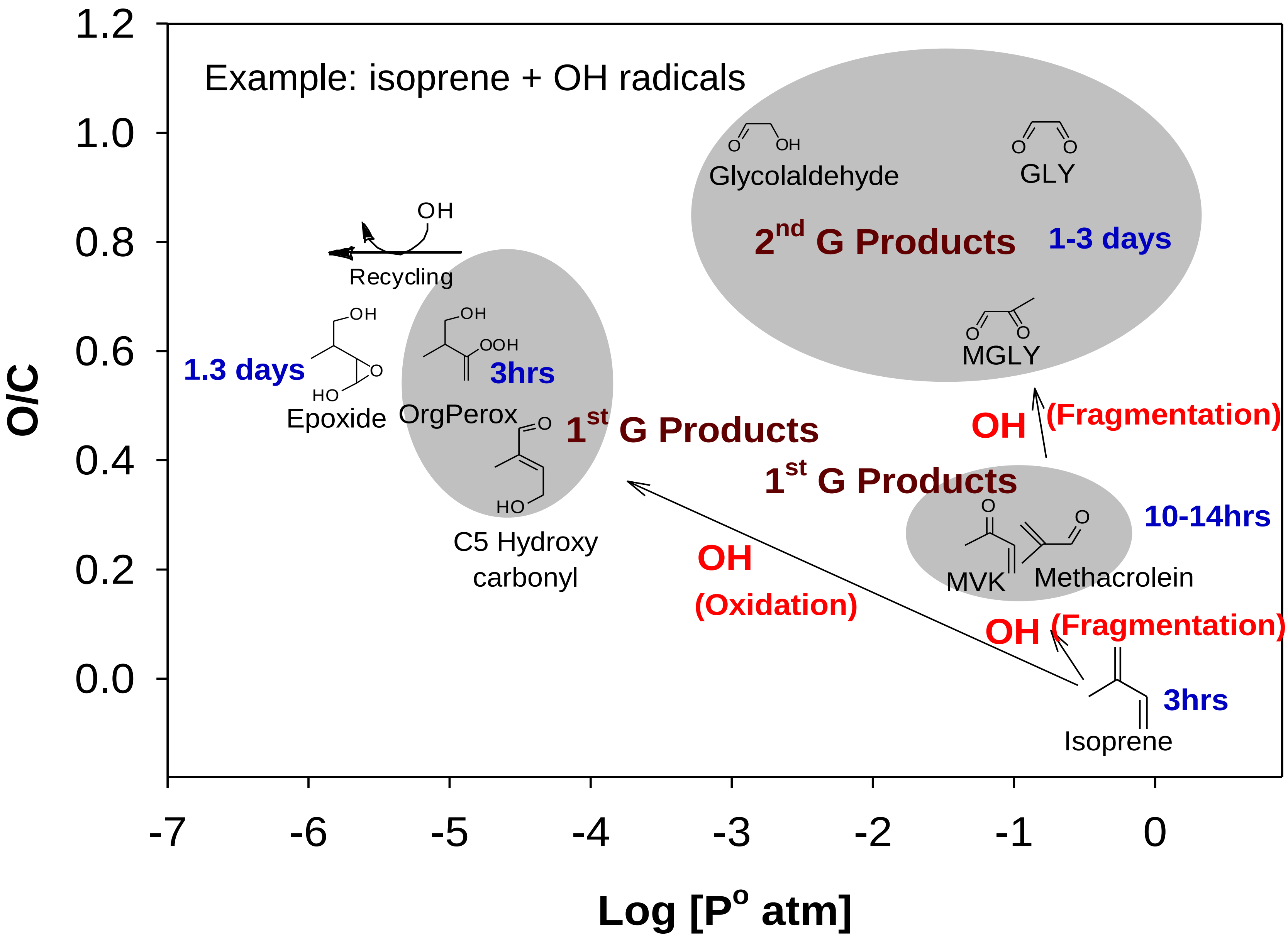
Modeling Summar

IEPOX is only recently discovered in ambient PM and modeling results suggest it dominates the $WSOC_g$ in wet aerosols in the SEU.S.

Model estimates depend on organic gas ‘solubility’, the extent to which this is accurately predicted remains an open question.

What happens to the partitioned material → Barbara Turpin

Expect gas phase chemistry to produce WS gases



Lab experiments with selected precursors

<u>Wet aerosols:</u>

acid and ammonium catalyzed oligomerization
organosulfate formation
radical-radical reactions

<u>Dilute cloud chemistry:</u>

Oxidation – organic acid formation

<u>Droplet evaporation:</u>

e.g., amines and aldehydes

What are the important precursors in the real atmosphere? Can we identify more?

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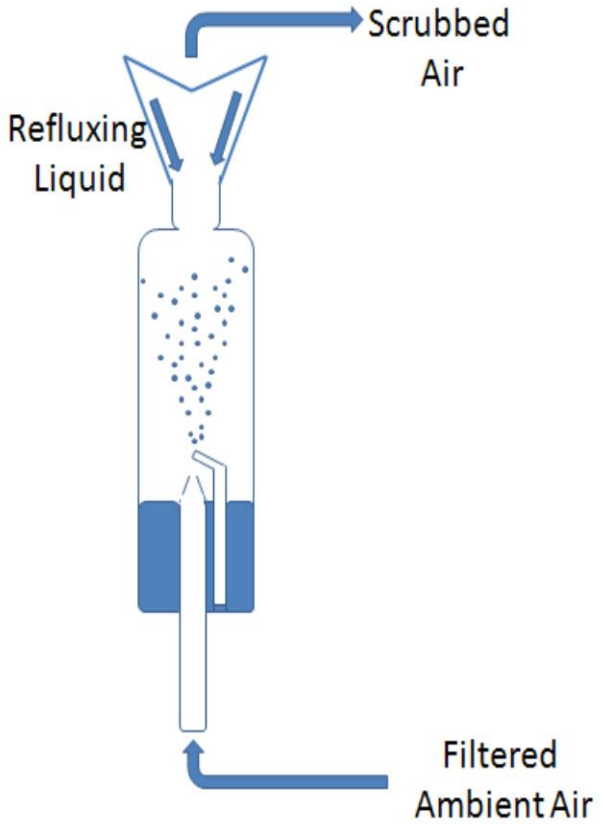
Mist Chamber Sampling at SOAS



4 mist chambers in parallel

- Water-soluble gases scrubbed from filtered ambient air
- 4 hr runs per day
- 3 runs composited daily between 7am-7pm
- 25 L-min^{-1} flow

WSOG mix close to Henry's law equilibrium based on WSOG vs collection time before campaign and 1 run with 2 in parallel (w/in 11%)

Aqueous photooxidation experiments using cuvette chamber

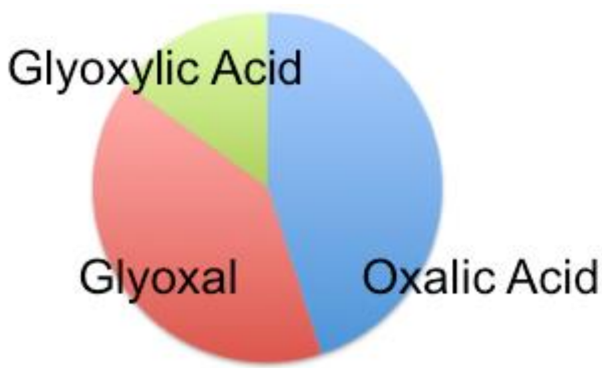
Experiments: Sample + OH

- 8 days in June 2013: 11,12,15,16,20,21,29,30
- TOC > 90 μM C

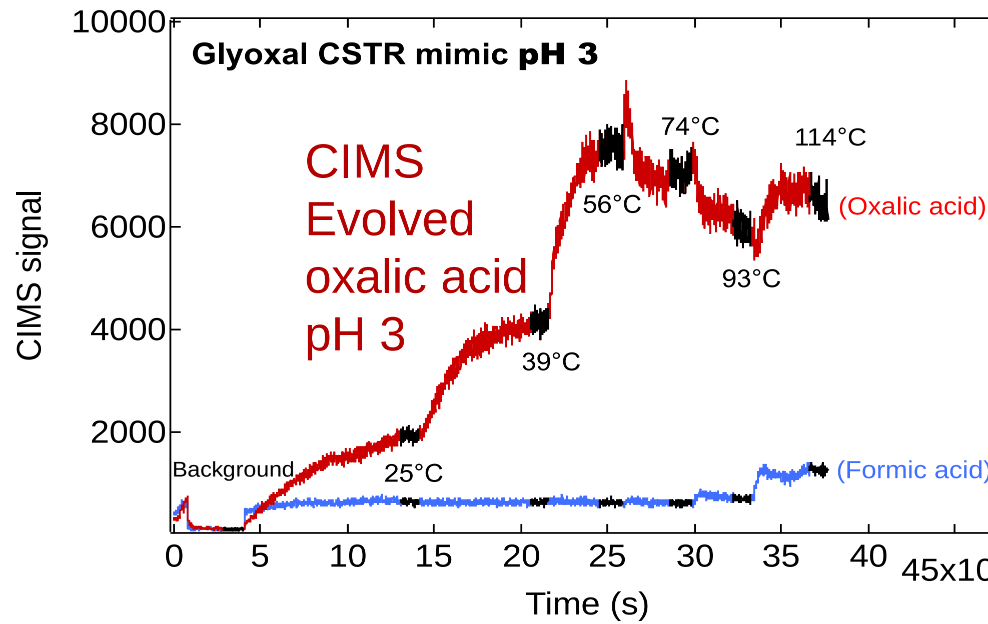
Controls: Sample + UV, Sample + H_2O_2, H_2O_2 + UV, field water blank + OH

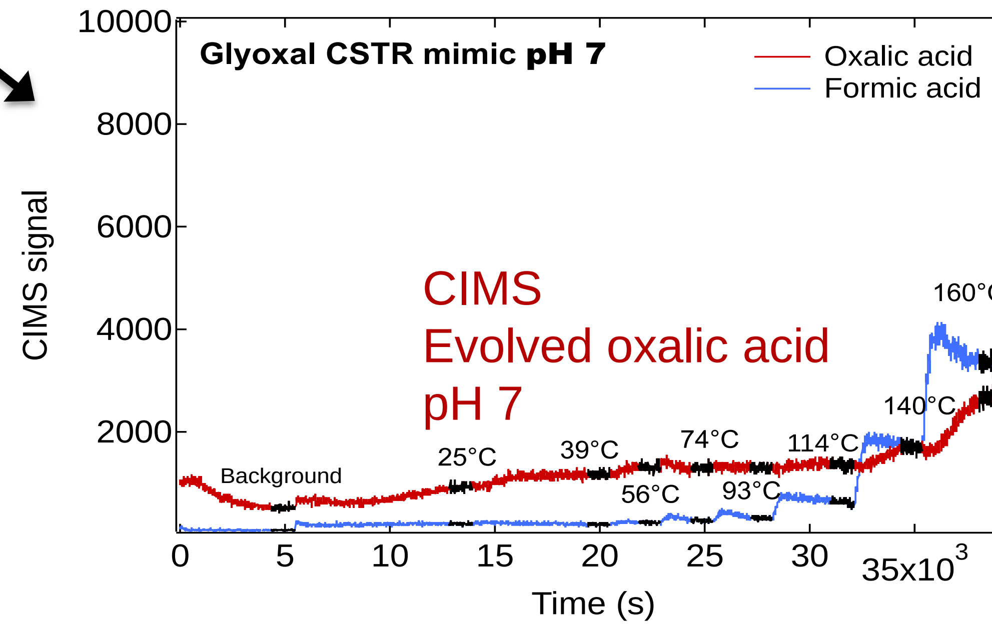
- $H_2O_2 + hv \rightarrow OH$ (1.25E-2 μM [OH] s^{-1})
- Catalase used to quench H_2O_2

Analyze using ESI-MS, IC, FT ICR MS-MS



$\pm NH_4OH$

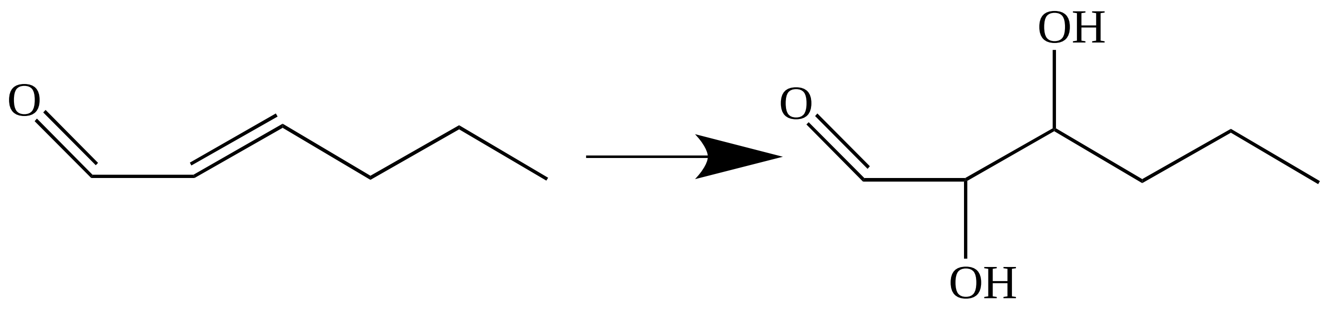




Oxalic acid likely to remain in gas phase at SOAS

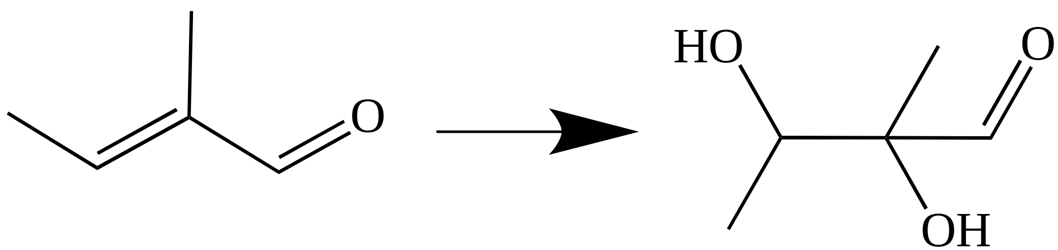
Ortiz-Montalvo et al., *ES&T* 2013

Gas-phase oxidation of 2-hexenal (or 3-hexenal)



O'Conner et al., *PCCP* 2006

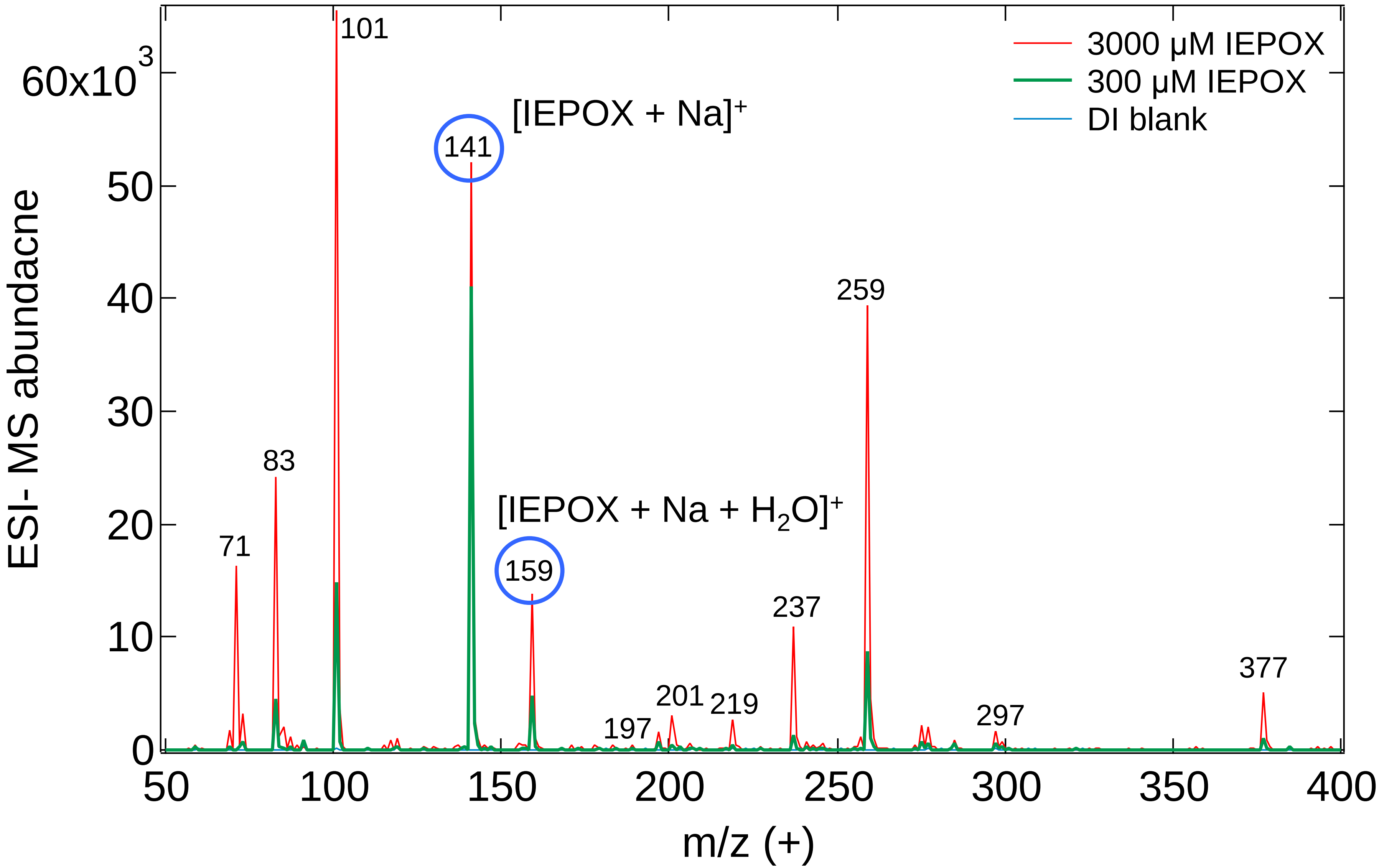
Gas-phase oxidation of (E)-2-methyl but-2-enal



Jimenez et al., *AE* 2009
Lanza et a.,, *CPL 2008*

IEPOX – signature peaks in ESI-MS(+)

IEPOX not seen in SOAS mist chamber samples – but is seen by ESI-MS



We conclude:

- Tentatively identified OH-reactive water soluble polyols, possible oxidation products of isoprene, green leaf volatiles
- IEPOX, ISOPOOH probably too reactive to be preserved in the mist chamber samples
- Complex WSOG mixtures produced oxalate, pyruvate
- Cloud-produced oxalate probably in gas phase at SOAS, in particle phase if a salt

EPA-STAR Publications

Carlton, ….Turpin et al. (2016) The Southeast Atmosphere Studies (SAS): Coordinated Investigation and Discovery to Answer Critical Questions about Fundamental Atmospheric Processes, *Bulletin of the American Meterological Society,* in preparation.

Sareen, N., Carlton, A.M.G., Felipe, H., Lopez-Hilfiker, D., Mohr, C., Thornton, J.A., Zhang, Z., Gold, A., Surratt, J.D., Lim, Y.B., **Turpin, B.J**. (2015) Identifying precursors and aqueous organic aerosol formation pathways during the SOAS campaign, *Atmospheric Chemistry Physics Discussion,* submitted.

Sareen, N., Waxman, E.M., **Turpin, B.J.,** Volkamer, R., Carlton, A.G. (2015) Dominance of isoprene epoxydiol (IEPOX) as an aerosol precursor in the Southeastern United States: model simulations, *ES&T,* in preparation.

Acknowledgements

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