DO YOU KNOW THE WAY TO SOA?

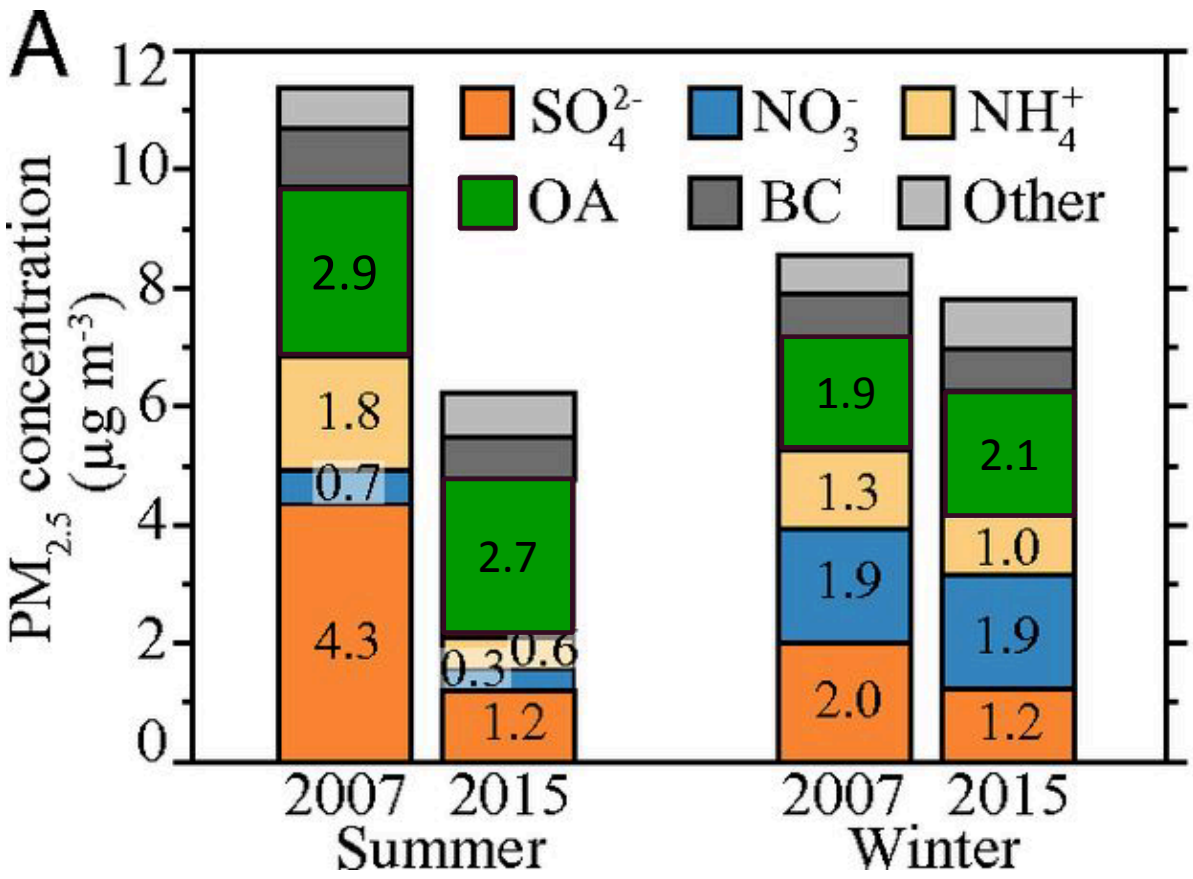
(1) WINTER ANTHROPOGENIC SOA (2) SUMMER BIOGENIC SOA
(3) ANTHROPOGENIC EFFECTS ON BIOGENIC SOA

Joel Thornton
Department of Atmospheric Sciences
University of Washington

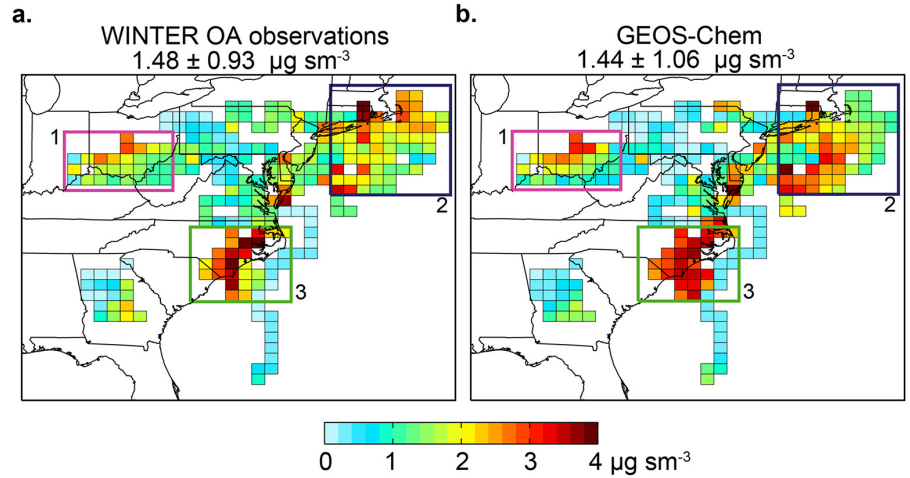
Funding: NSF-AGS, DOE ASR, NOAA CGC PF

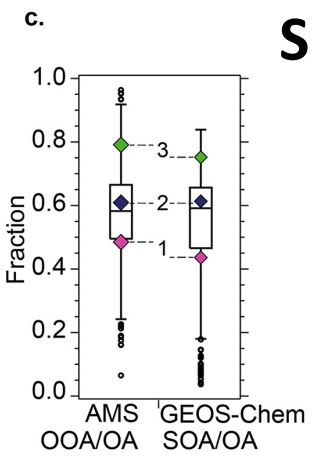
joelt@uw.edu

OA CONTRIBUTION TO E. U.S. SURFACE PM2.5

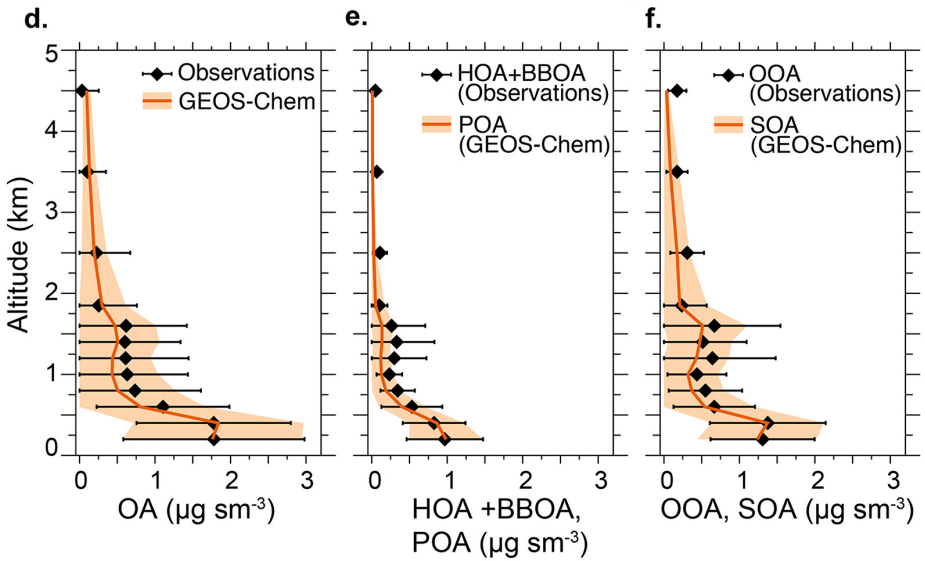


WHAT DRIVES WINTERTIME OA OVER EASTERN U.S.?





Shah et al GRL 2019



Implement SIMPLE SOA Scheme

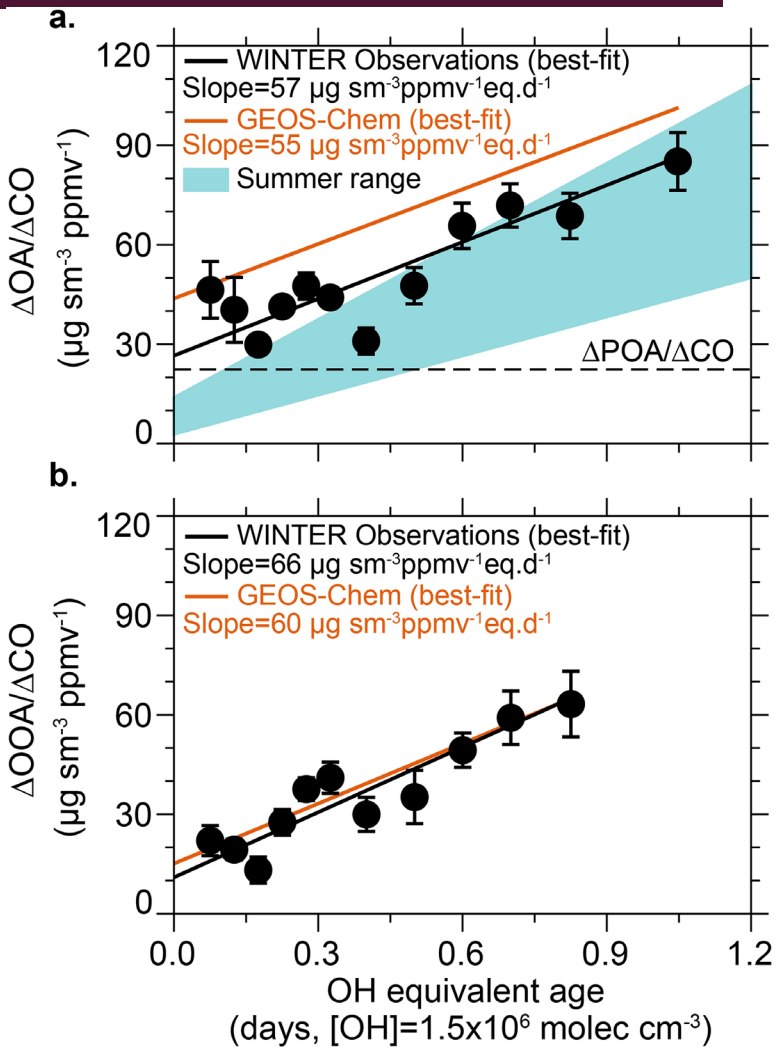
AVOC co-emitted w/CO (80 g/kg)

AVOC + OH → ASOA

Hodzic & Jimenez 2011

WHAT DRIVES WINTERTIME OA OVER EASTERN U.S.?

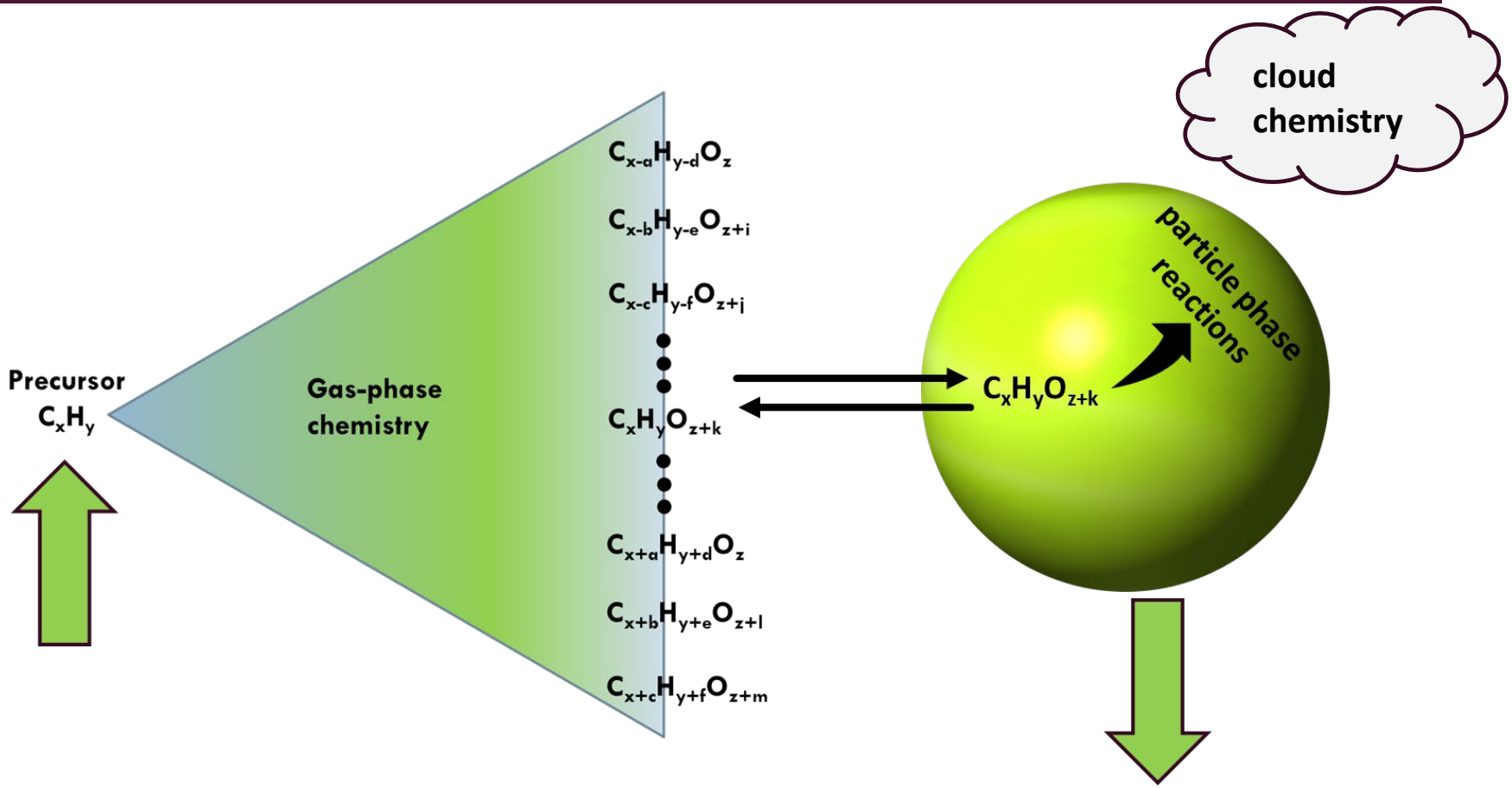
- Net OA growth downwind of emissions due to anthropogenic SOA (ASOA) formation
- Winter SOA rate of growth remarkably similar to observed summer time values
- Simple scheme does quite well at reproducing near-surface SOA abundance and distribution



Shah et al GRL 2019

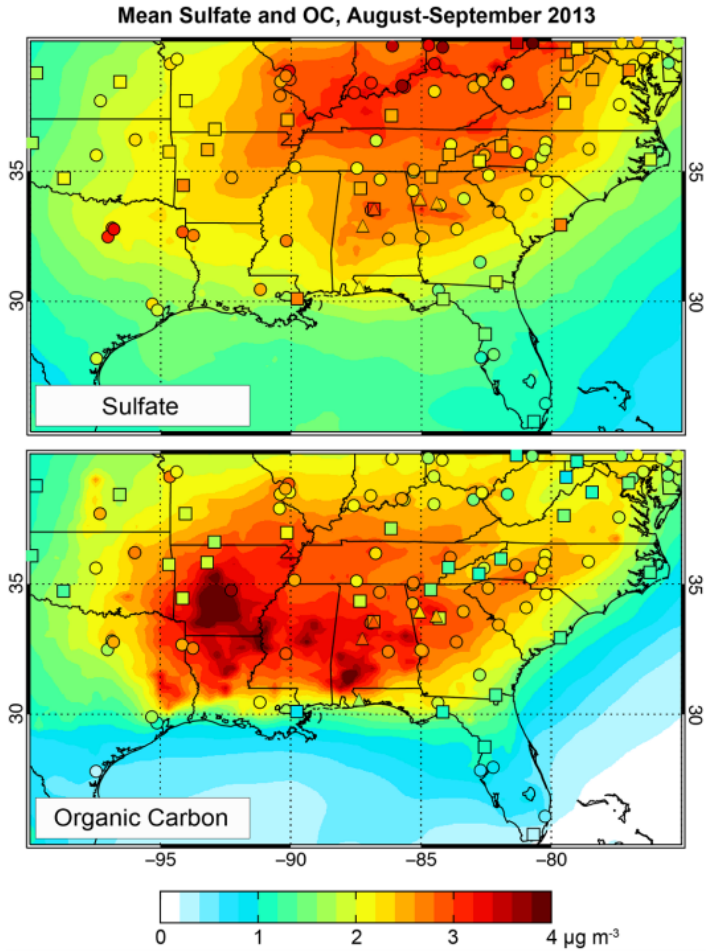
See also Schroeder et al JGR 2018

THE CHALLENGE: PRECURSORS-PATHWAYS-VOLATILITY

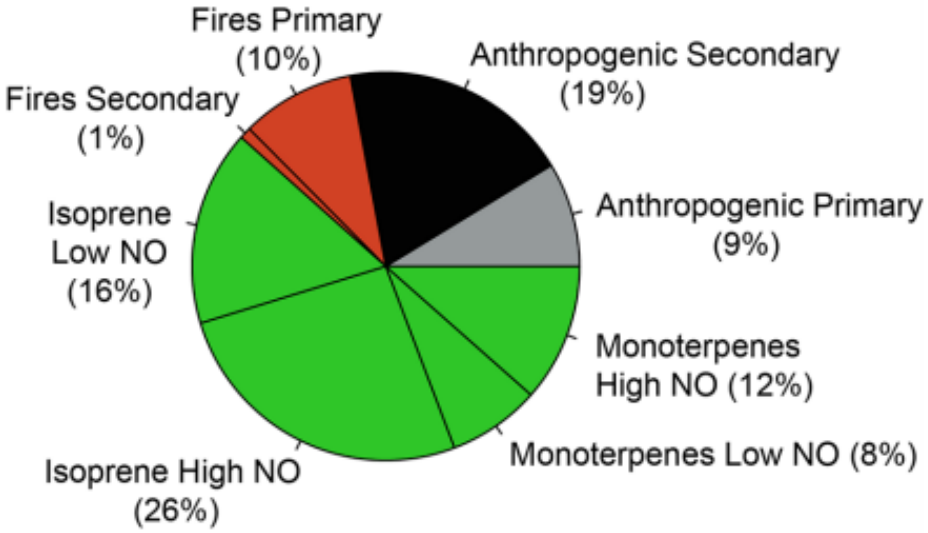


$$\frac{d[SOA]_{ox}}{dt} = Y_{ox}k[VOC][Ox] - \left(\frac{1}{\tau}\right)[SOA_{ox}] - U \cdot \nabla[SOA_{ox}]$$

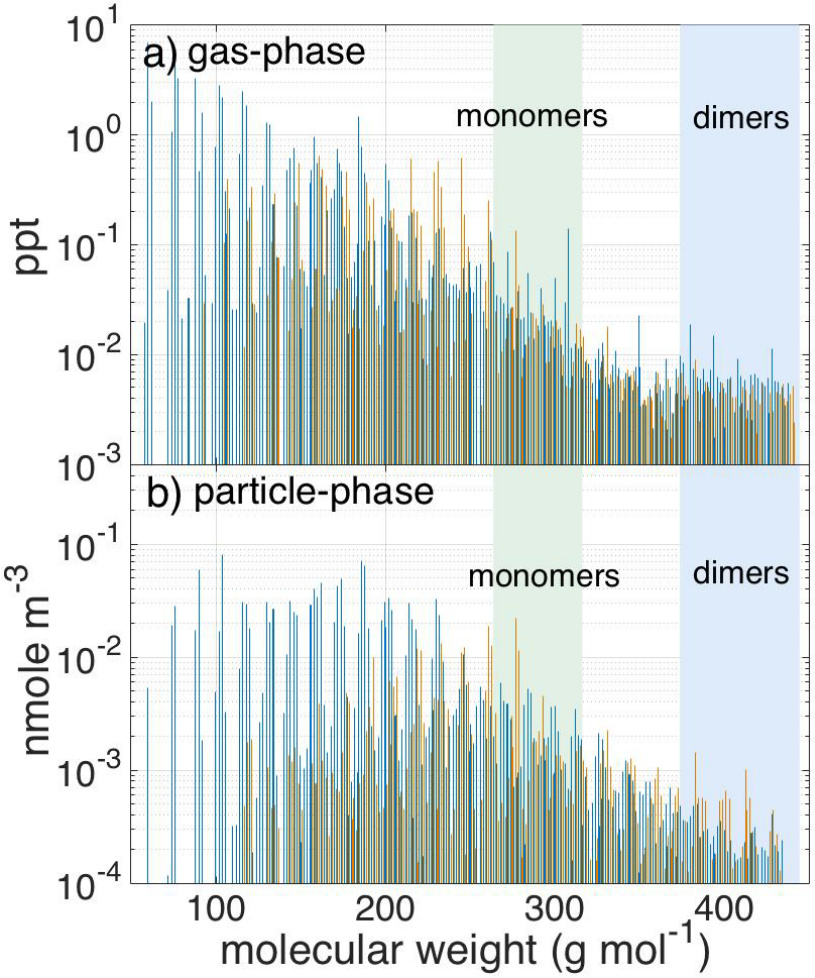
WHAT DRIVES SUMMERTIME OA IN THE SE U.S.?

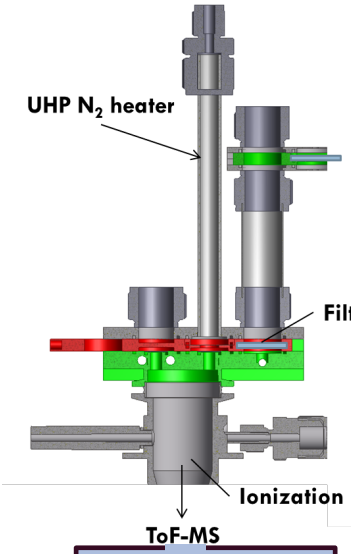


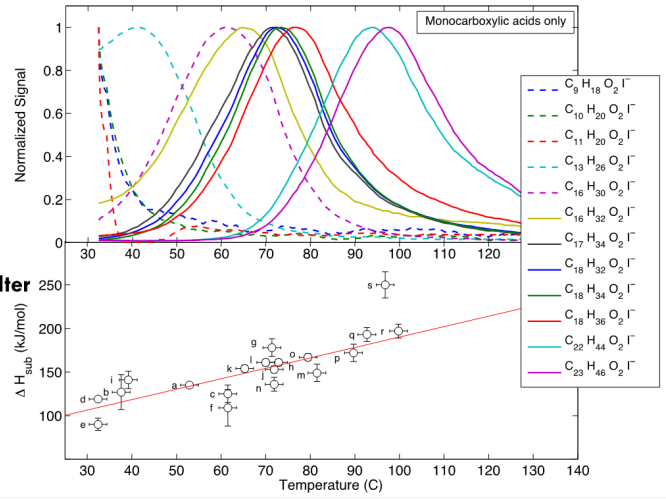
Kim et al ACP 2015



SOURCE APPORTIONMENT FROM ON-LINE SOA COMPOSITION







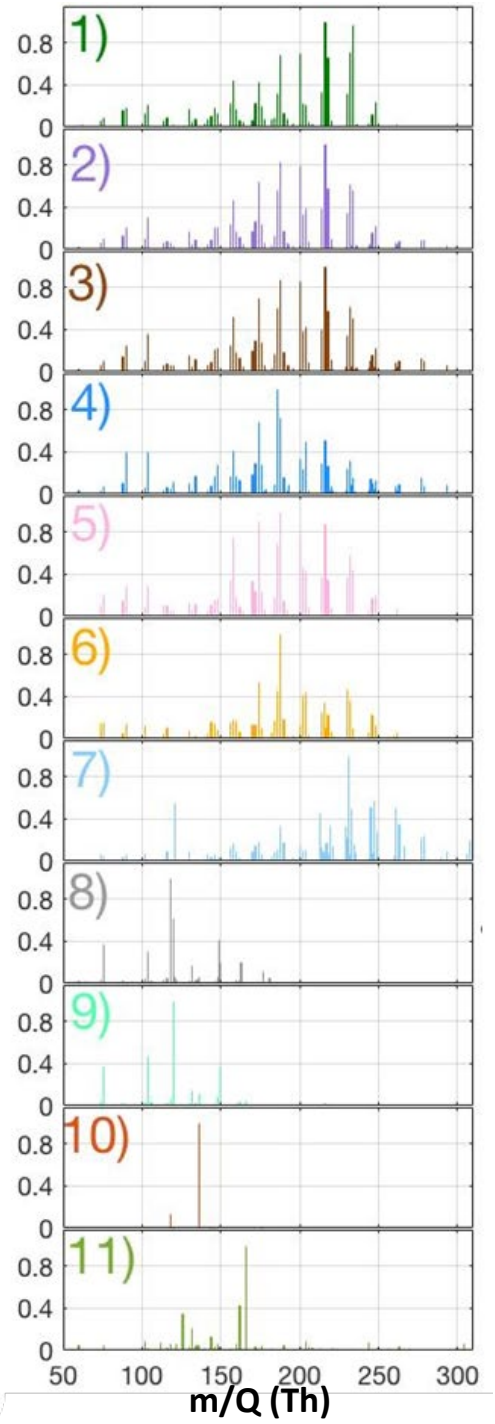
Lopez-Hilfiker et al AMT 2014

Tofwerk HRToF-CIMS

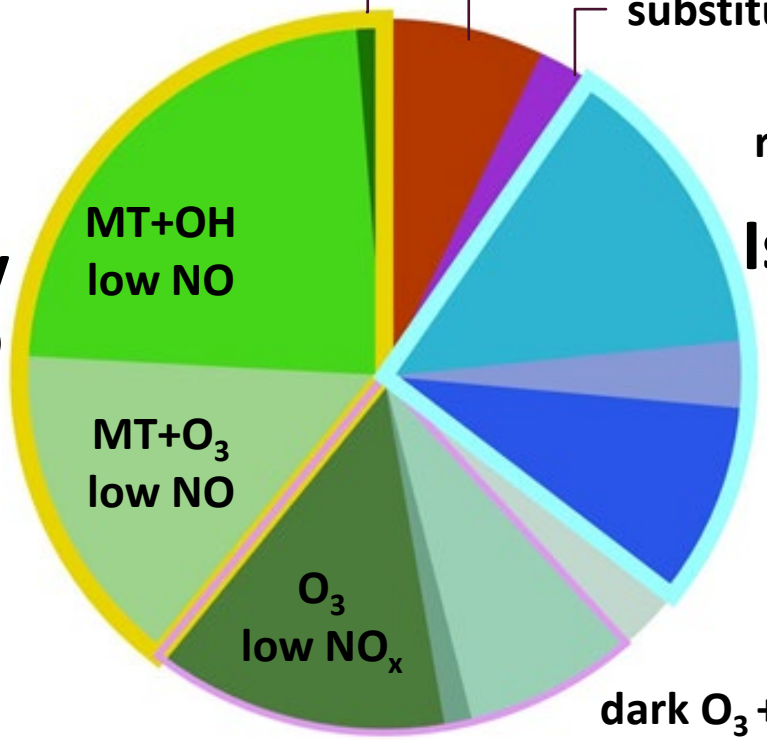
SOURCE APPORTIONMENT COMPOSITION BASIS SETS

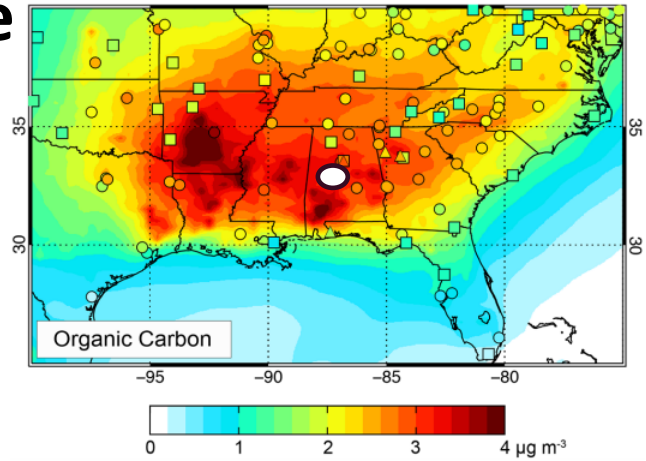
- **>18 "basis set" HR mass spectra, χ_i, from chamber expts**
  - **MT, Isop, SQT, aromatics, OH, O_3, NO_3, …**
  - **>180 unique molecular compositions**
  - **Explain ~80% of detected OA mass in SOAS**

- **Field-derived spectra, *X(t)*, fit by linear combination of basis spectra χ_i**
  - $\mathbf{X}(t) = \sum_i \alpha_i(t)\chi_i$



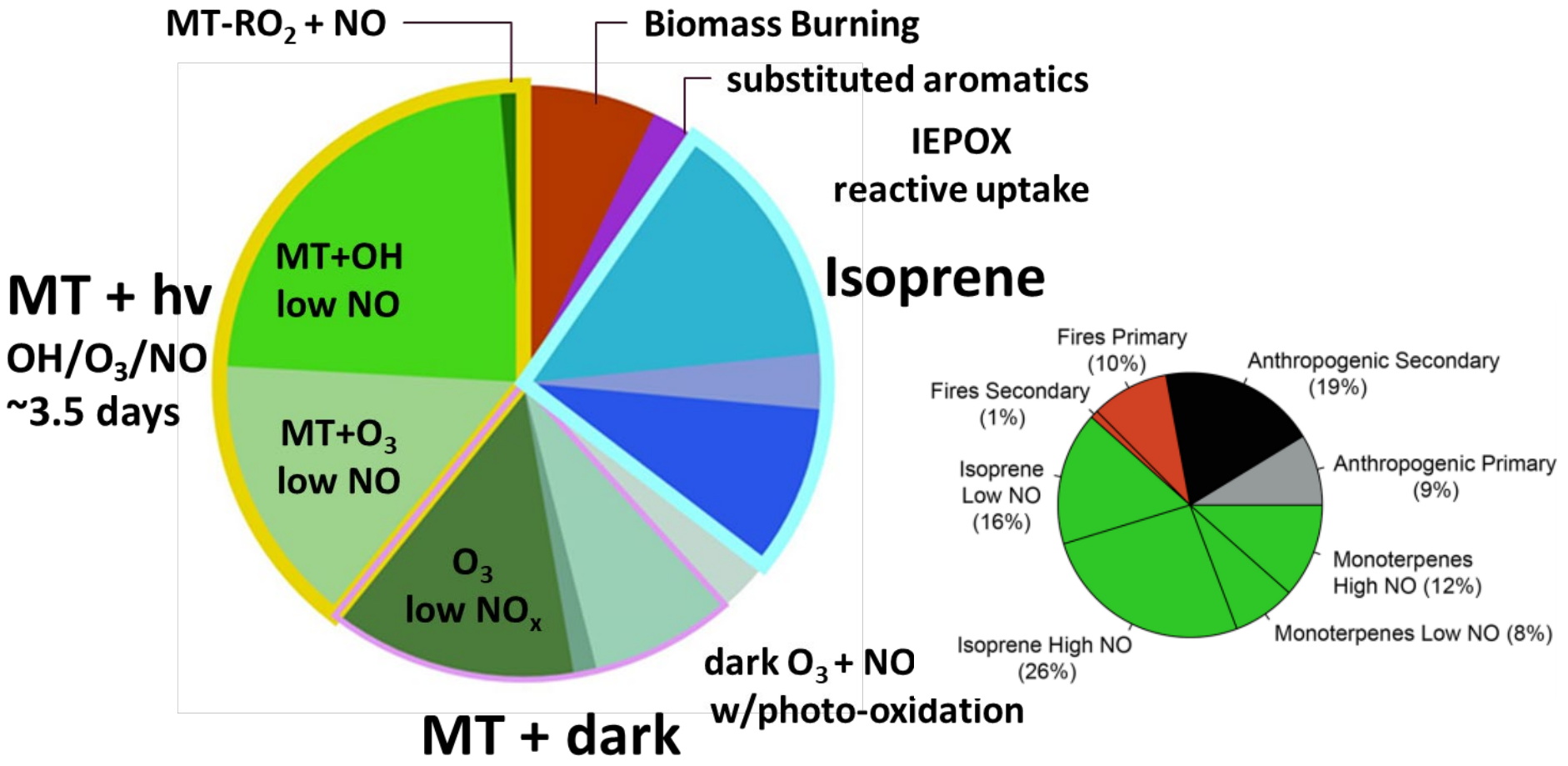
CHEMICAL PATHWAY APPORTIONMENT





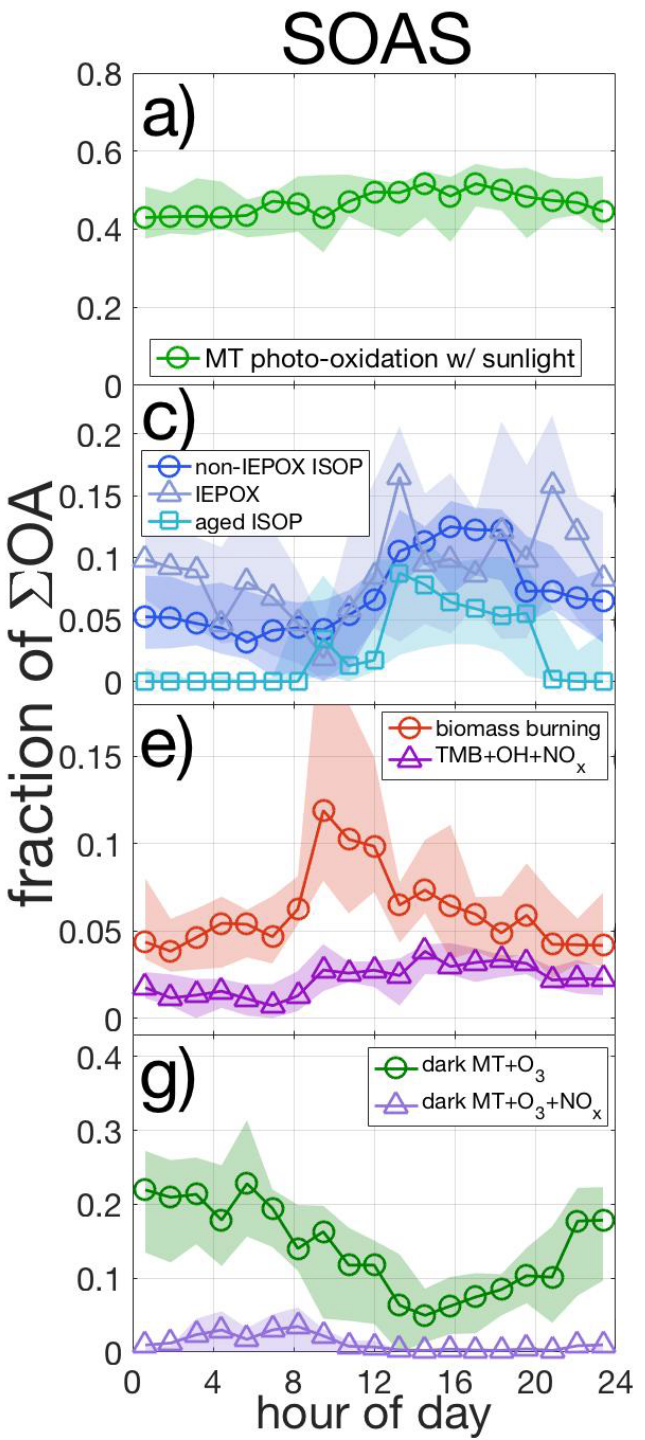
See also Haofei Zhang et al PNAS 2018

CHEMICAL PATHWAY APPORTIONMENT



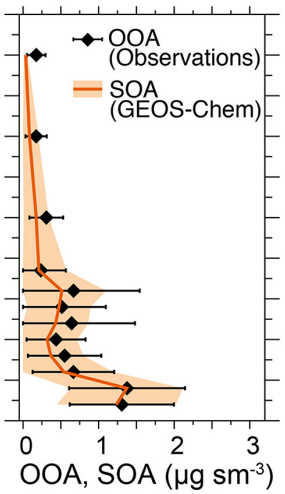
SOURCE APPORTIONMENT TAKEAWAYS

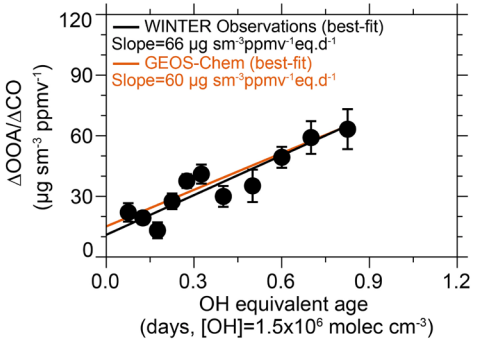
- **"Typical" chamber experiments did *not* explain observed composition *nor* volatility**
- ***…requires coupled (simultaneous) oxidation over days timescales***
- **Fresh (local) dynamic SOA mixed with aged/aging SOA**



SUMMARY

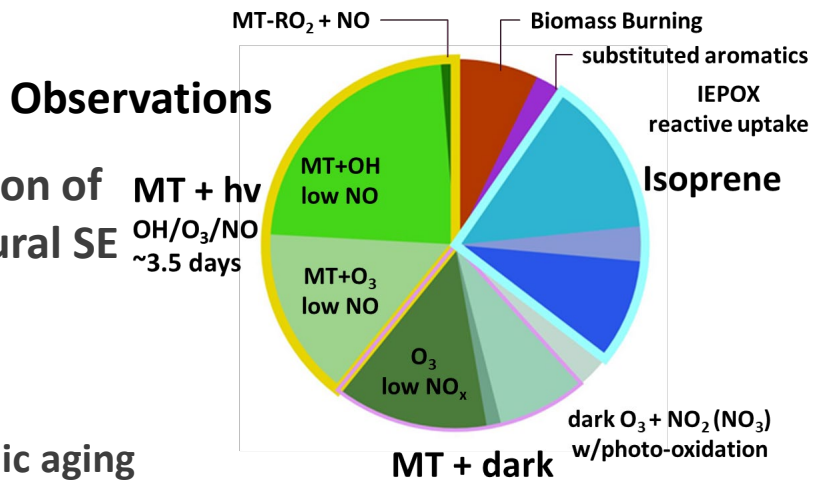
- **Simple, nearly chemistry-free SOA schemes capture wintertime OA evolution**
  - **See also S. Pai and C. Heald's work (ACPD)**
- **Problems w/simple schemes: policy relevant questions related to trends and co-emitted pollutants (NO_x, SO_2, VCP, T, …)**
- **Possible Progress: winter focused campaigns allow isolation of anthropogenic VOC → SOA (much lower BVOC)**



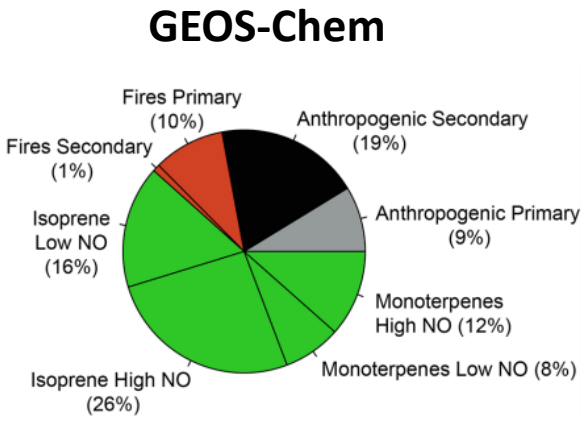


SUMMARY

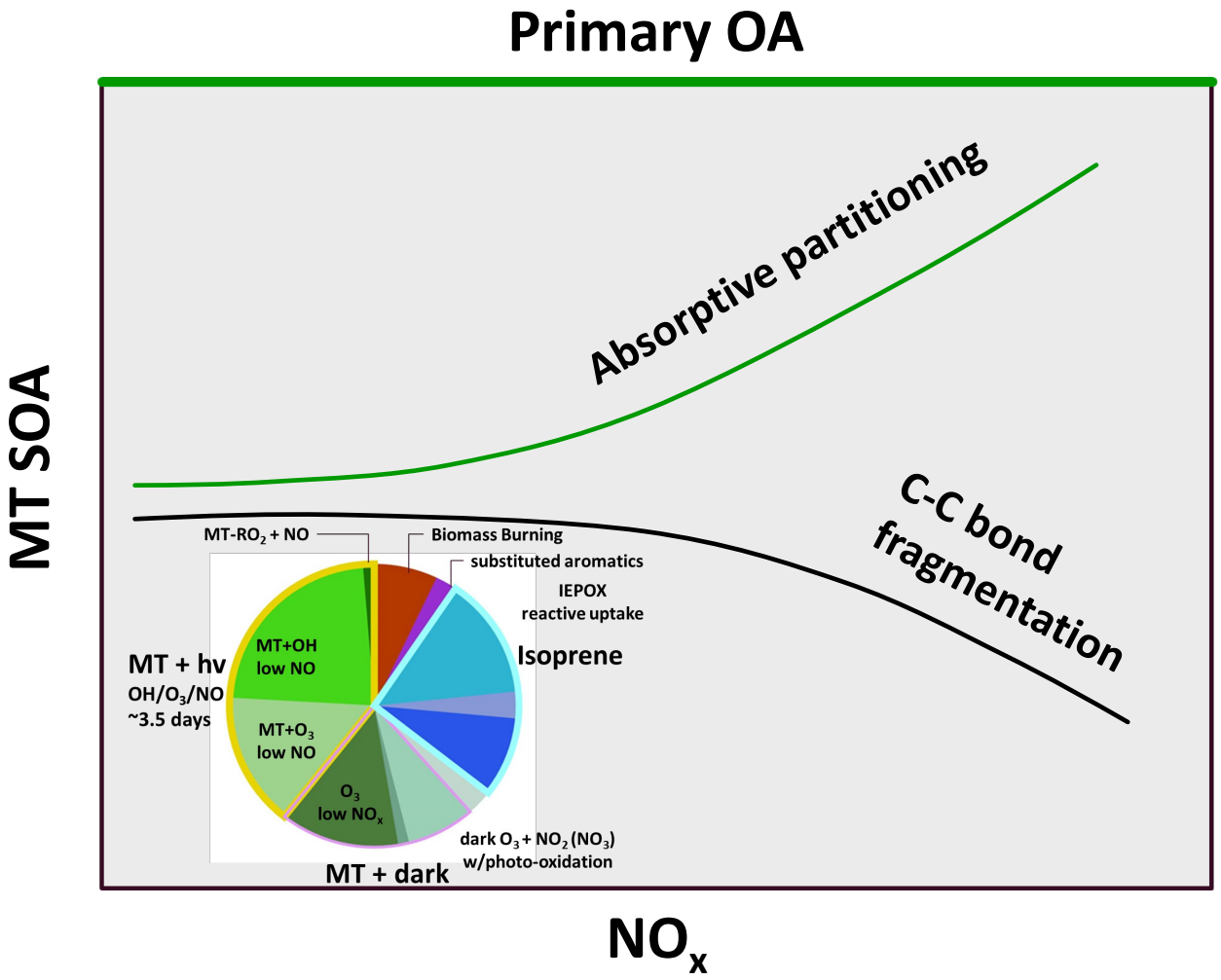
- Dominant role for "synergistic" multi-day oxidation of monoterpenes dominates summertime SOA in rural SE US location
  - Clouds? High NOx isoprene?
  - Supports use of 2-D VBS type schemes with dynamic aging of both gas and particle components



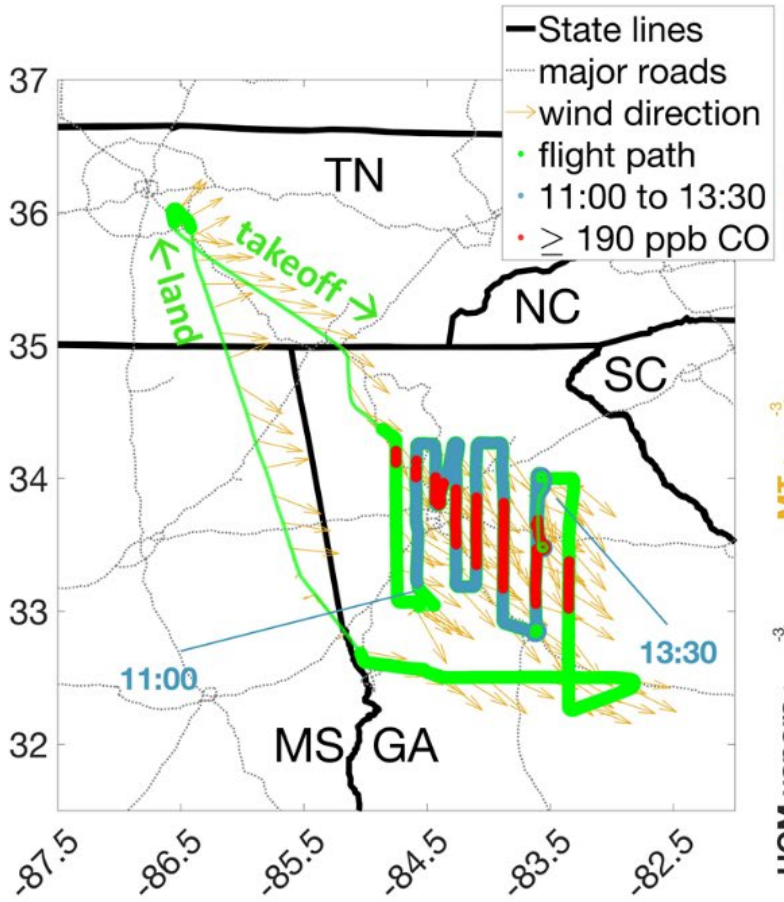
- Possible Progress:
  - Observational network of online composition
  - parameterizations for prompt/efficient MT SOA formation via autoxidation combined with aging

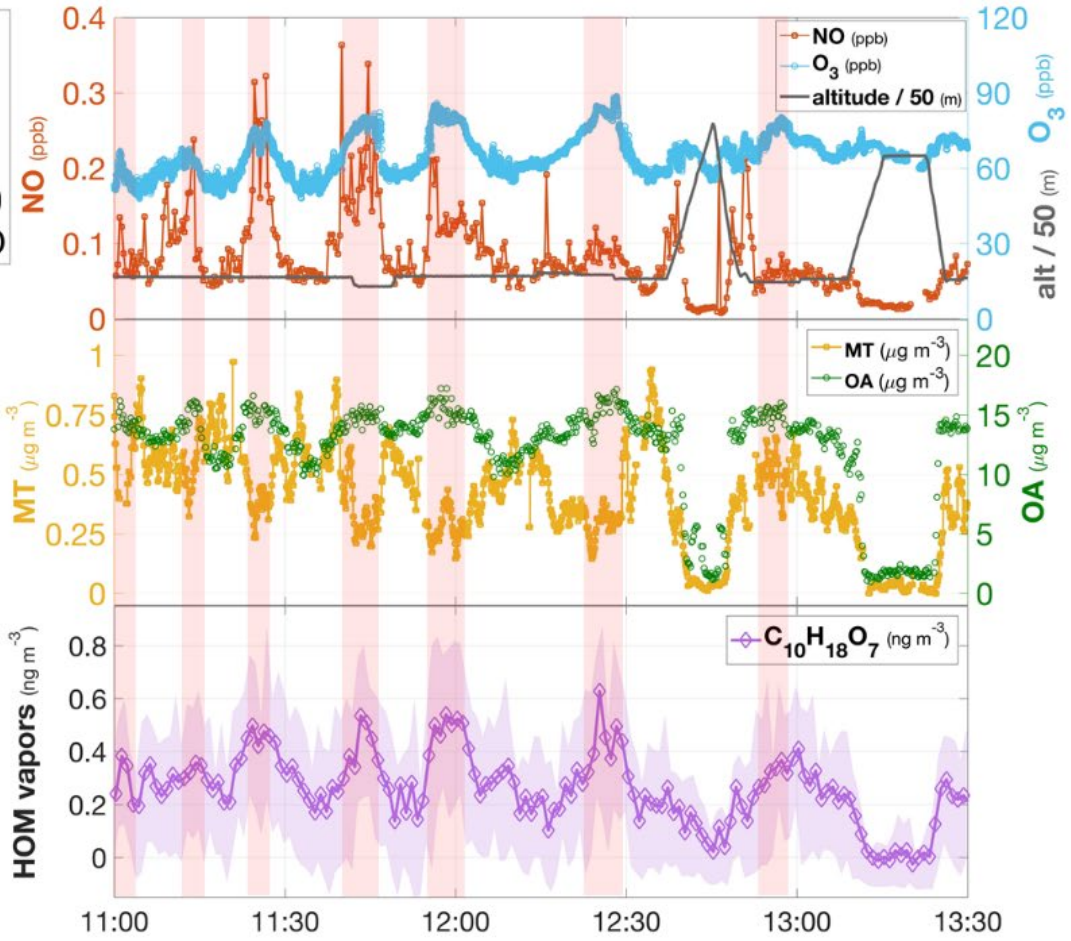


ANTHROPOGENIC PERTURBATIONS TO MT SOA



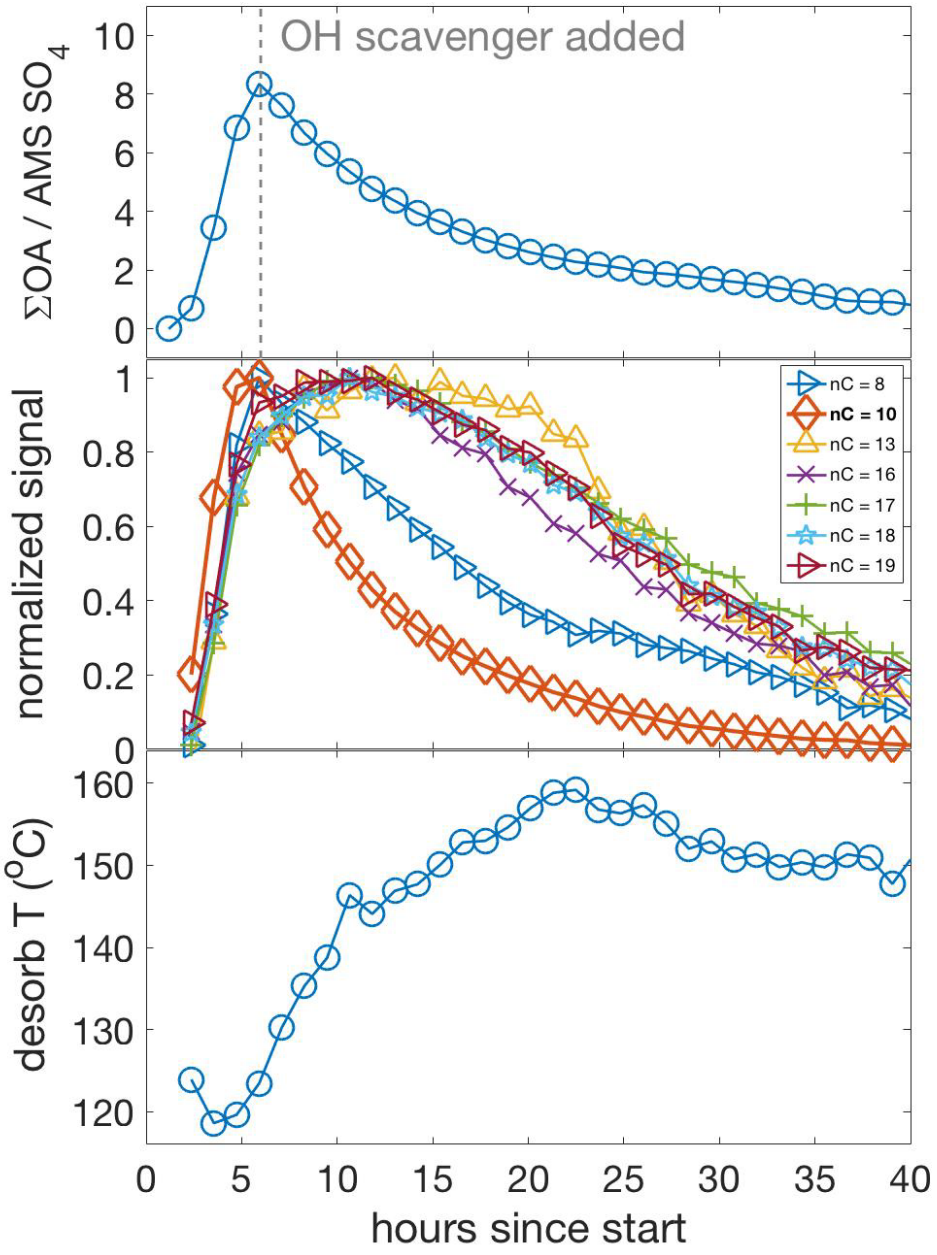
ANTHROPOGENIC EFFECTS ON BIOGENIC SOAS





Pye et al, PNAS 2019

B-PINENE SOA AGING



ANTHROPOGENIC PERTURBATIONS TO MT SOA

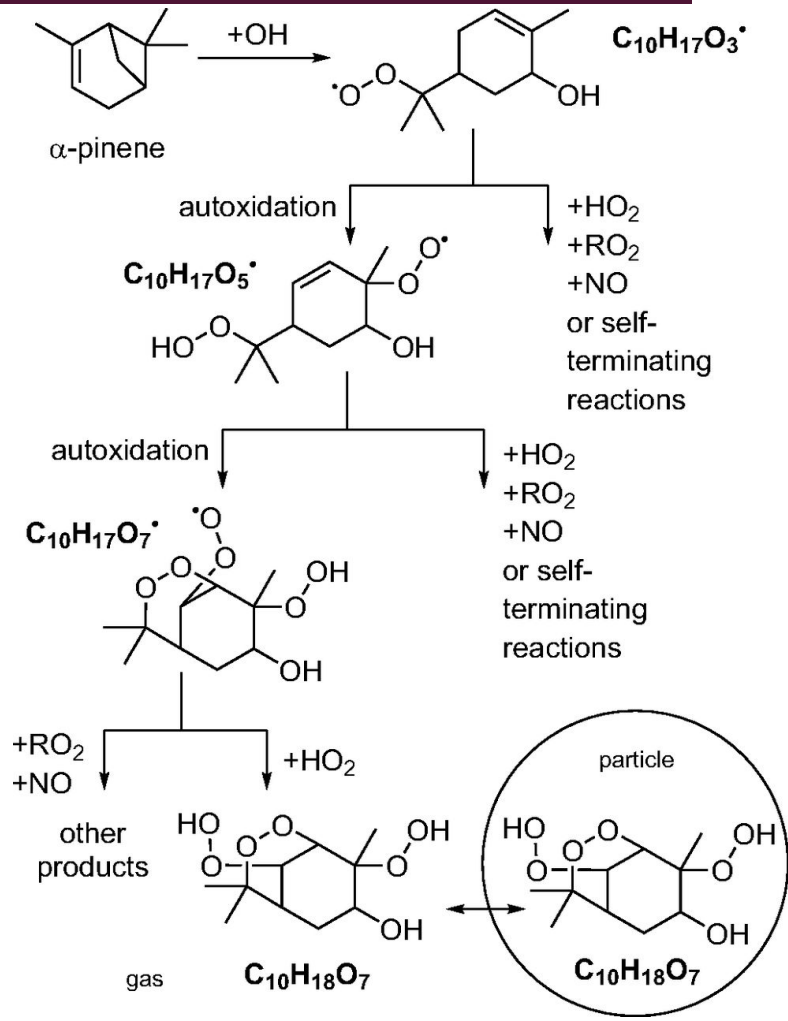
- **A fraction MT peroxy radicals undergo autoxidation**

Ehn et al 2014, Berndt et al 2016, Zhao et al 2018

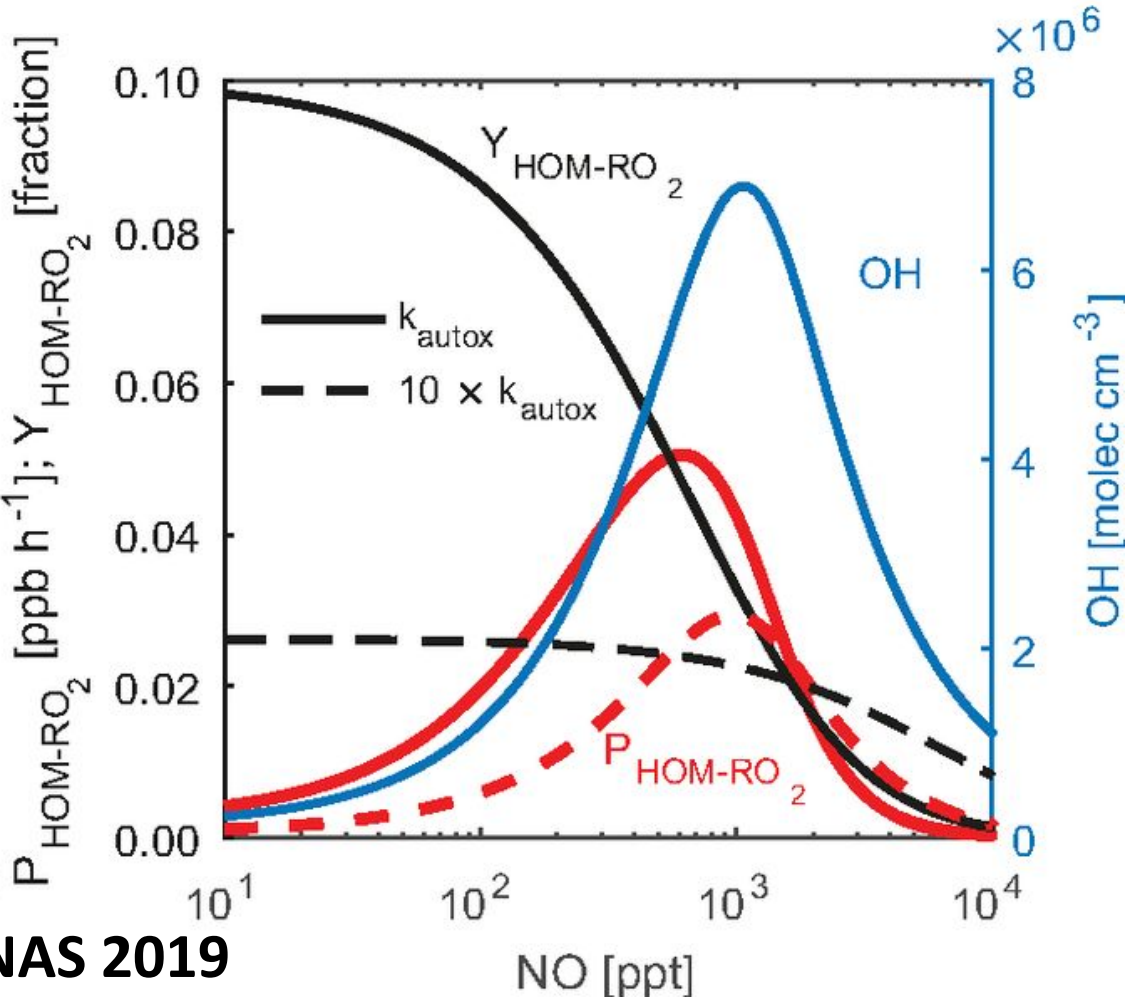
- **Autoxidation promptly forms low volatility (SOA-forming) products**

- **Autoxidation potentially suppressed by NOx**

Praske, et al 2018

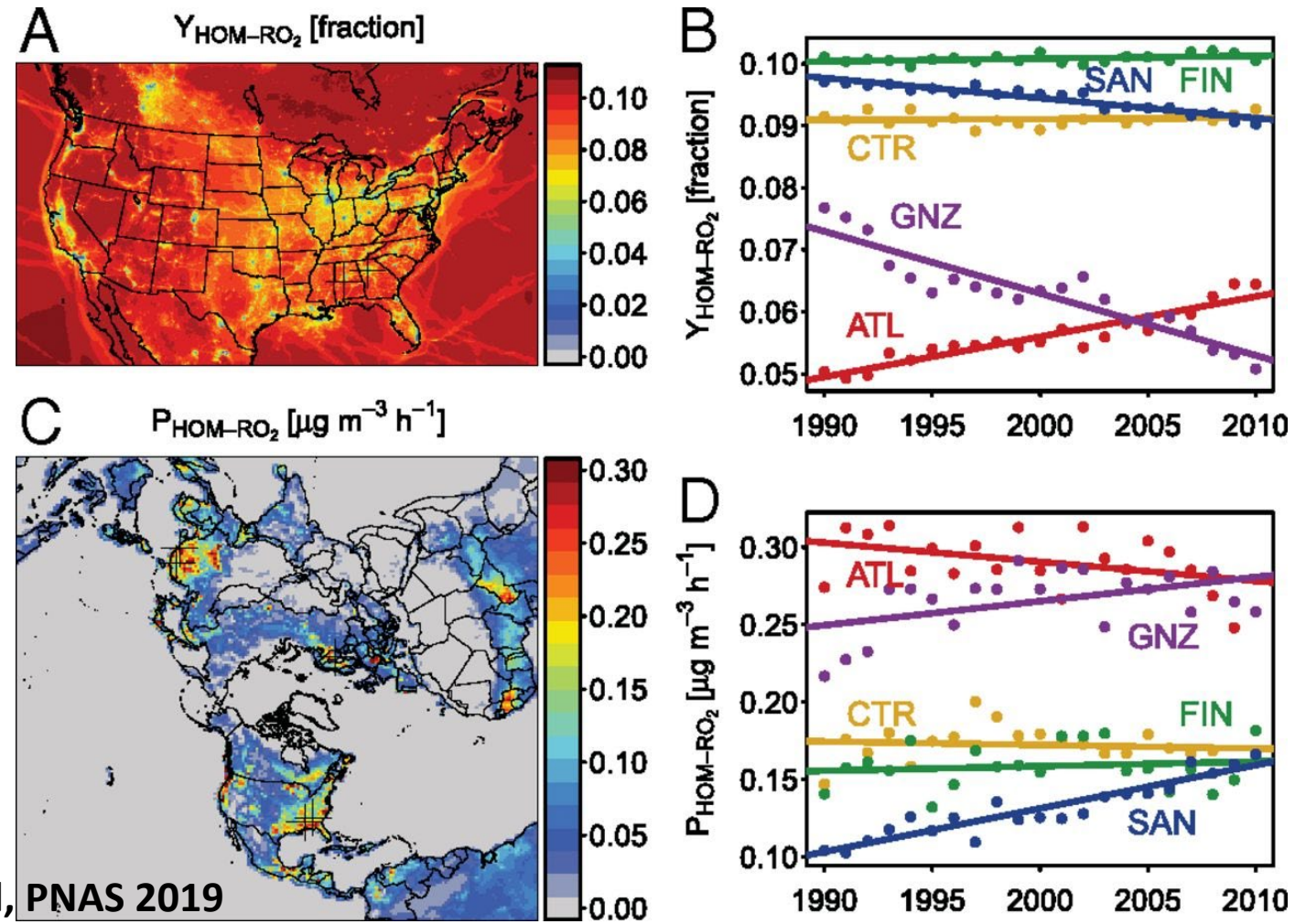


ANTHROPOGENIC PERTURBATIONS TO MT SOA



Pye et al, PNAS 2019

PREDICTED TRENDS IN MT AUTOXIDATION PRODUCTS



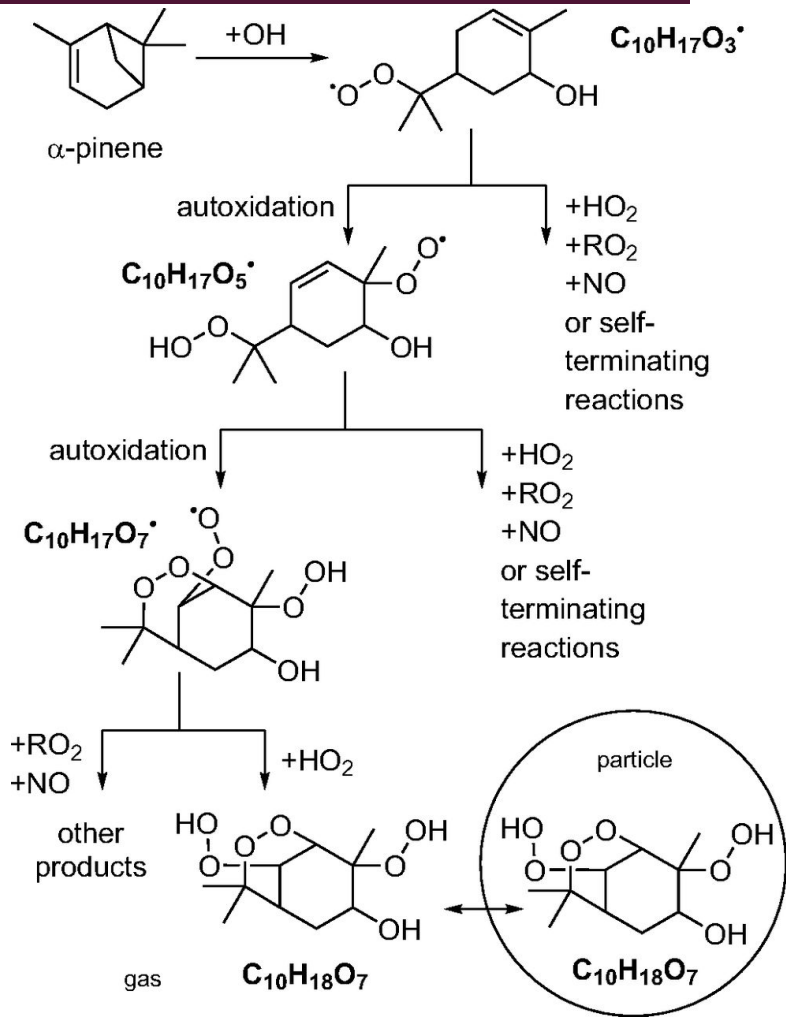
Pye et al, PNAS 2019

ANTHROPOGENIC PERTURBATIONS TO MT SOA

- **Recent work suggest ~20% of MT + OH reaction undergoes autoxidation at 0.3 to 3 s^{-1}**

  Y. Zhao et al 2018; L. Xu et al 2019

- **Equivalent to 0.3 to 1 ppb NO**

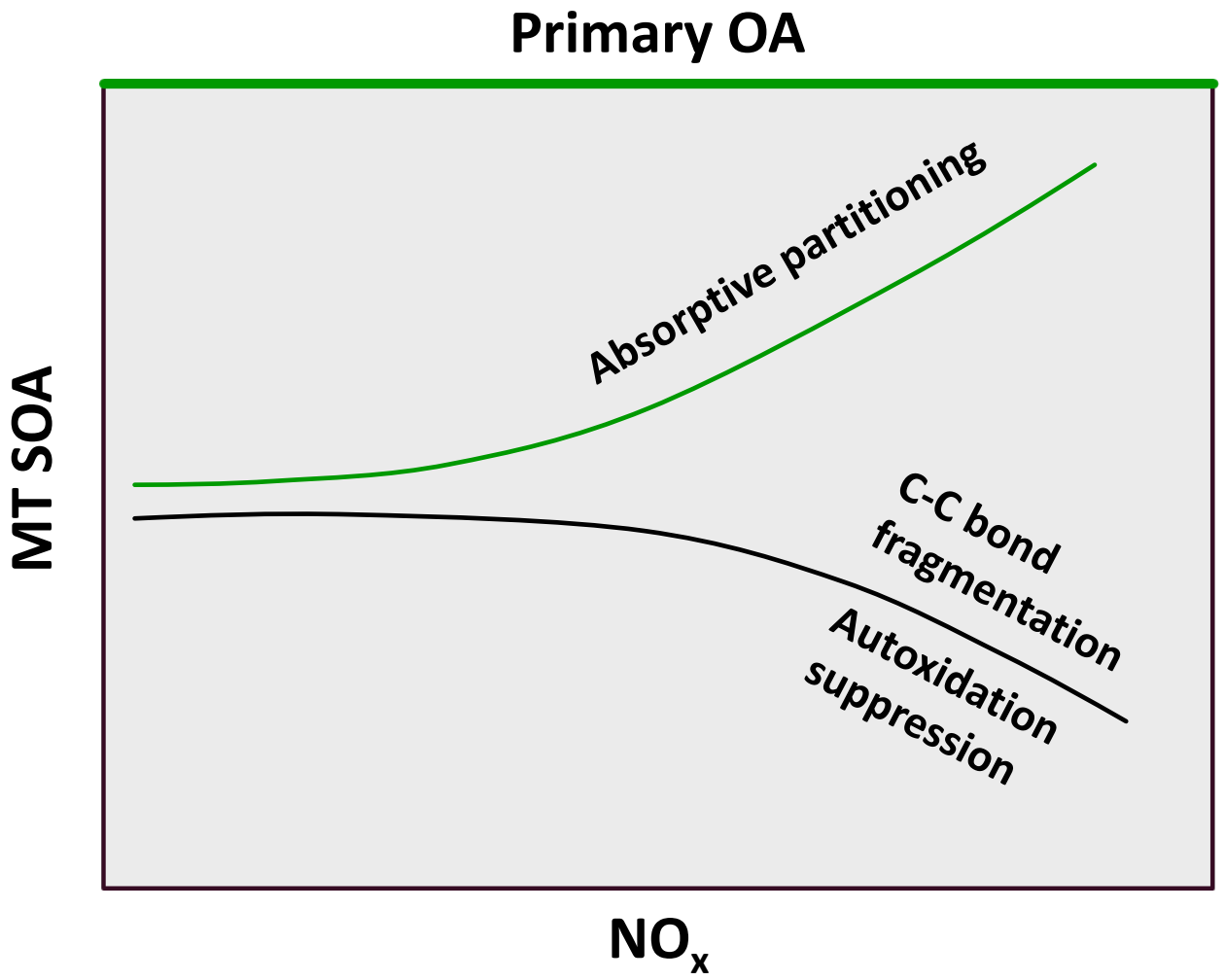


AUTOXIDATION IS A MAJOR PATH TO MT SOA

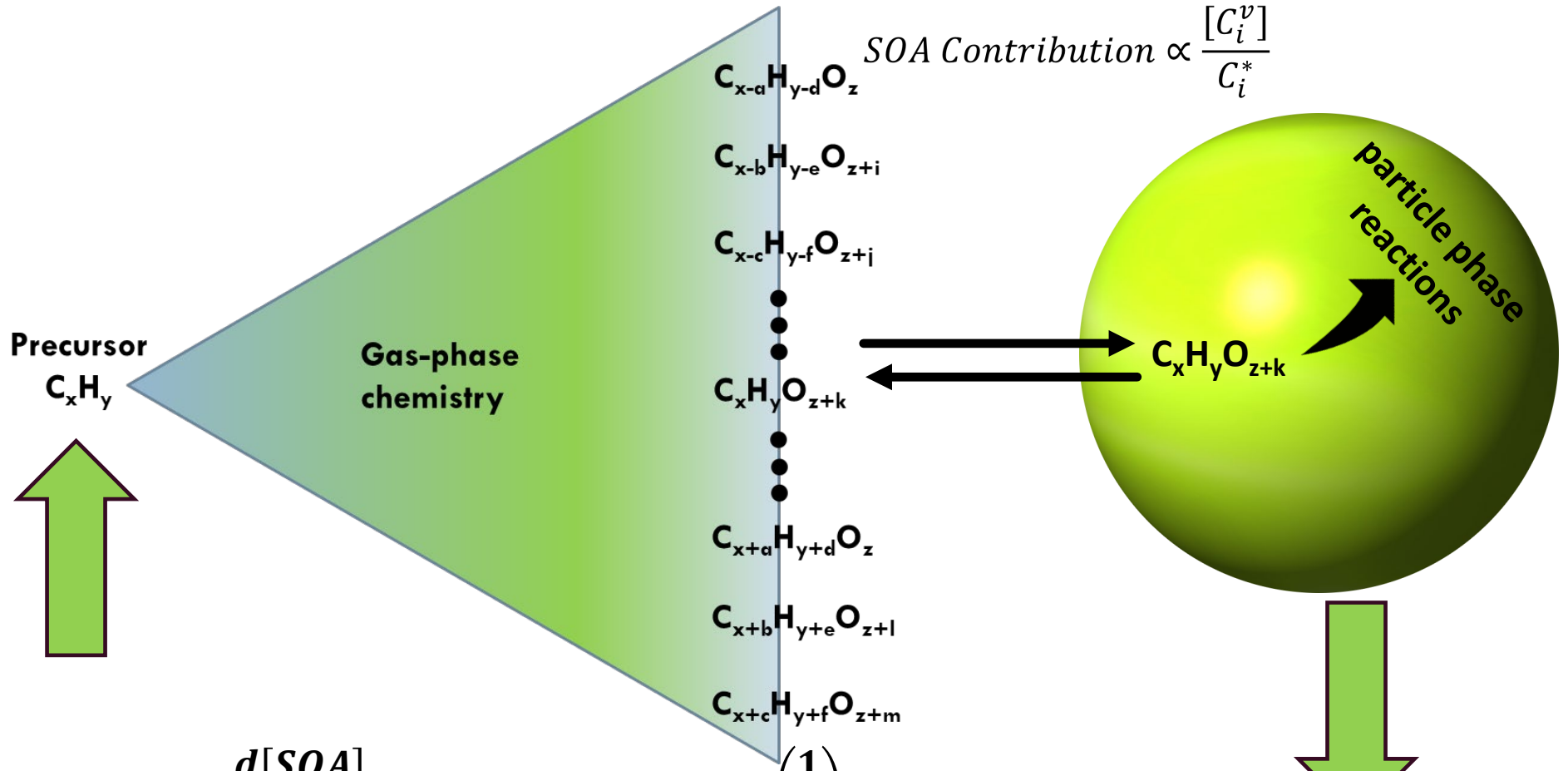
- **CMAQ and common explicit schemes do not reproduce SOA magnitude, volatility, nor oxidation extent without autoxidation**

	f_{autox}	**$Yield_{SOA}$**	**O:C**	**nC**	**C***
	% by mole	% by mass	mol mol^{-1}	-	µg m^{-3}
MCM v3.3.1	0	<1	0.59	8	104
Regional CTM	0	7	0.52	8	55
HOM mechanism	3.3	17	0.64	10	1.3
Observed	**≥2.4**	**12 ± 4.6**	**0.68**	**9**	**0.08**

ANTHROPOGENIC PERTURBATIONS TO MT SOA

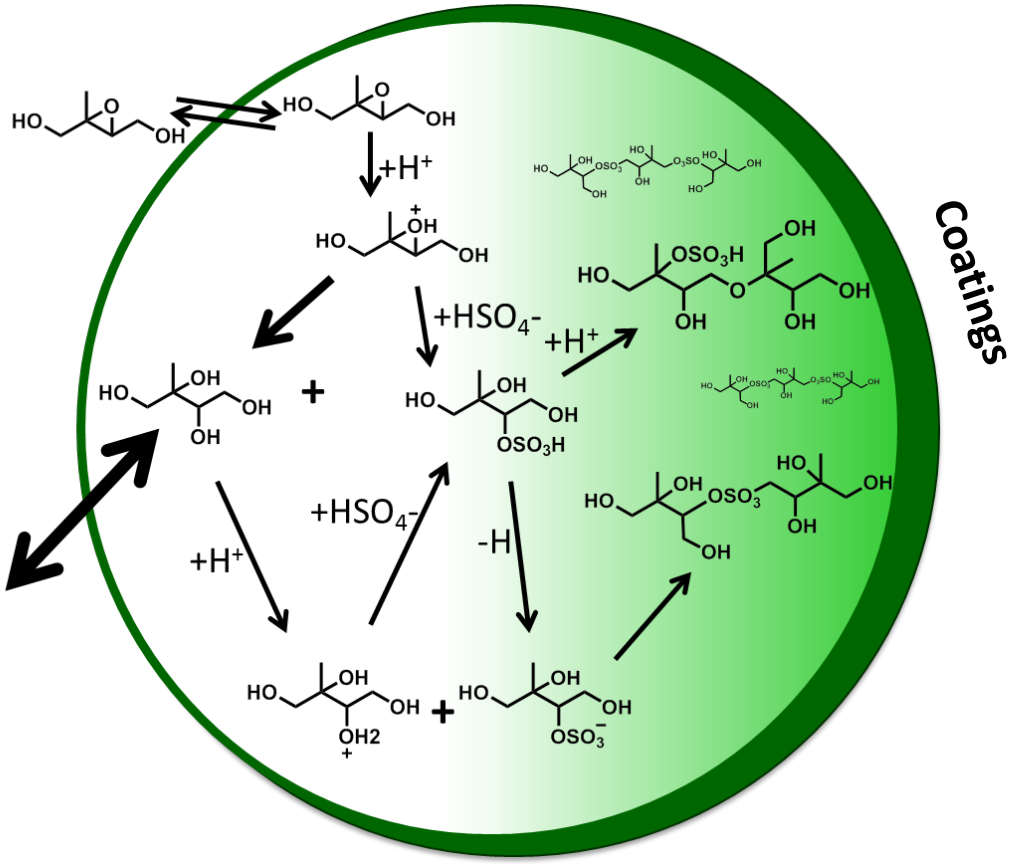


THE CHALLENGE: PRECURSORS-PATHWAYS-VOLATILITY

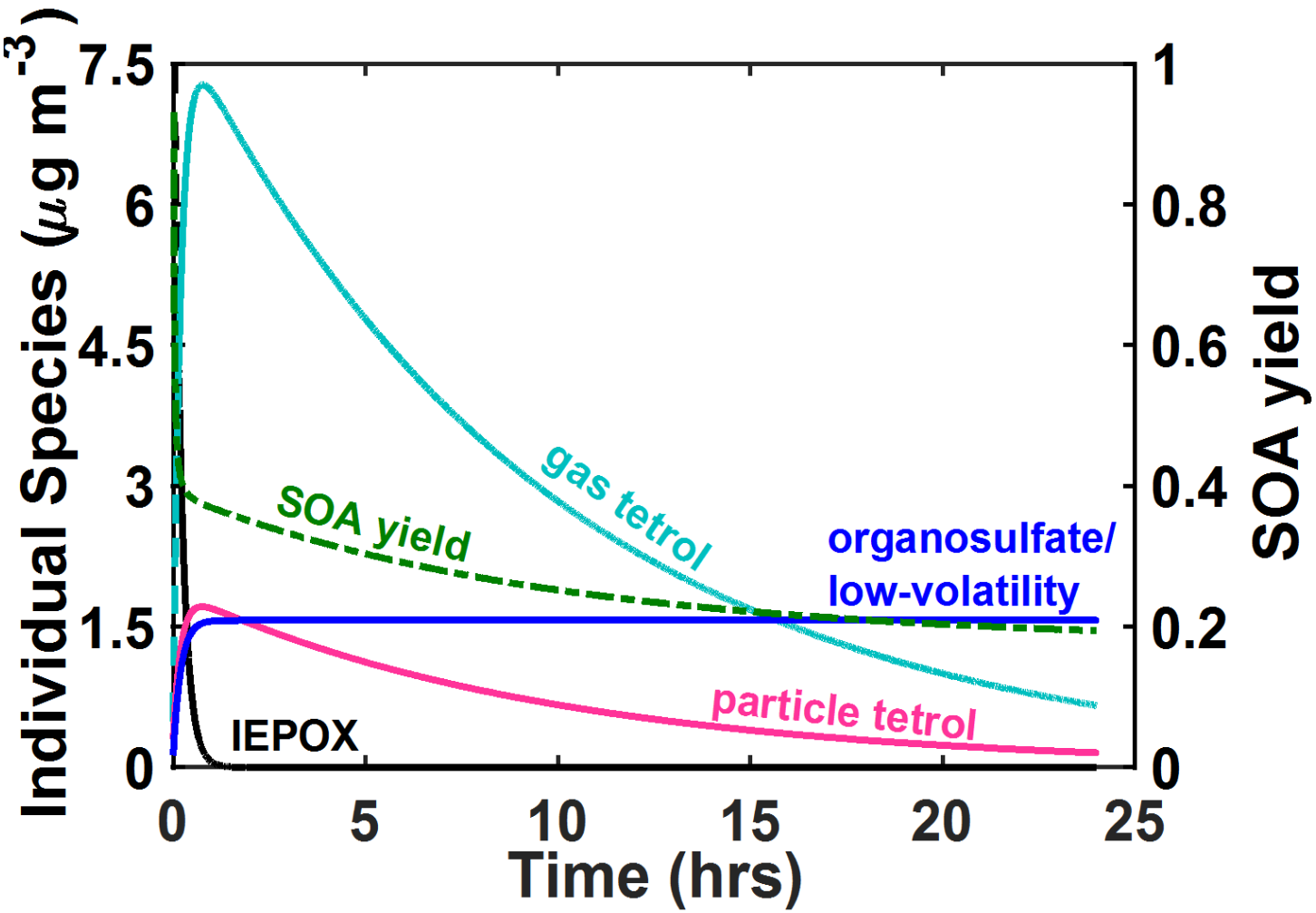


$$\frac{d[SOA]_{ox}}{dt} = Y_{ox}k[VOC][Ox] - \left(\frac{1}{\tau}\right)[SOA_{ox}] - U \cdot \nabla[SOA_{ox}]$$

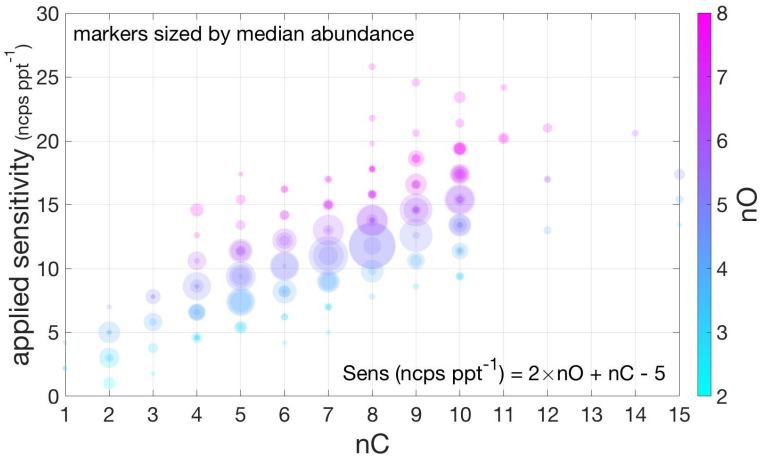
IEPOX SOA PATHWAYS AND FEEDBACKS

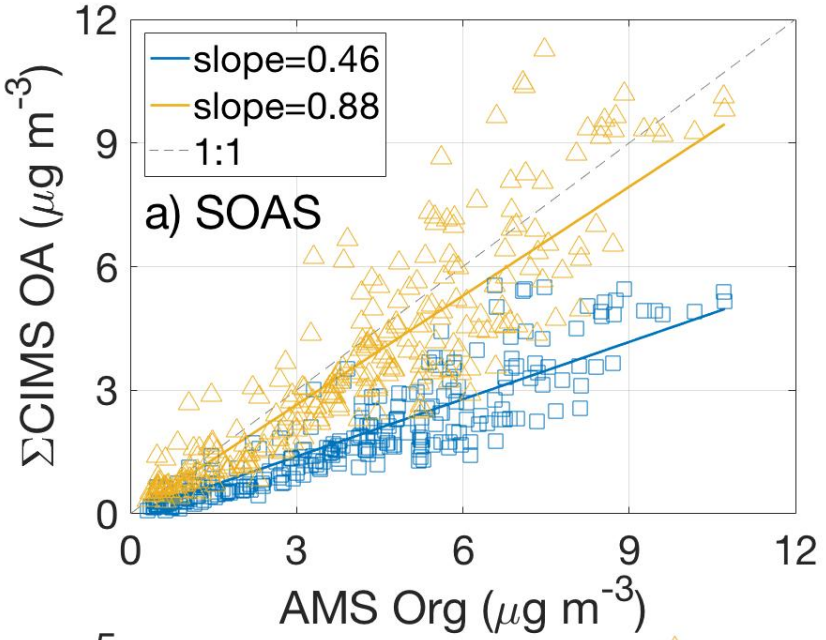


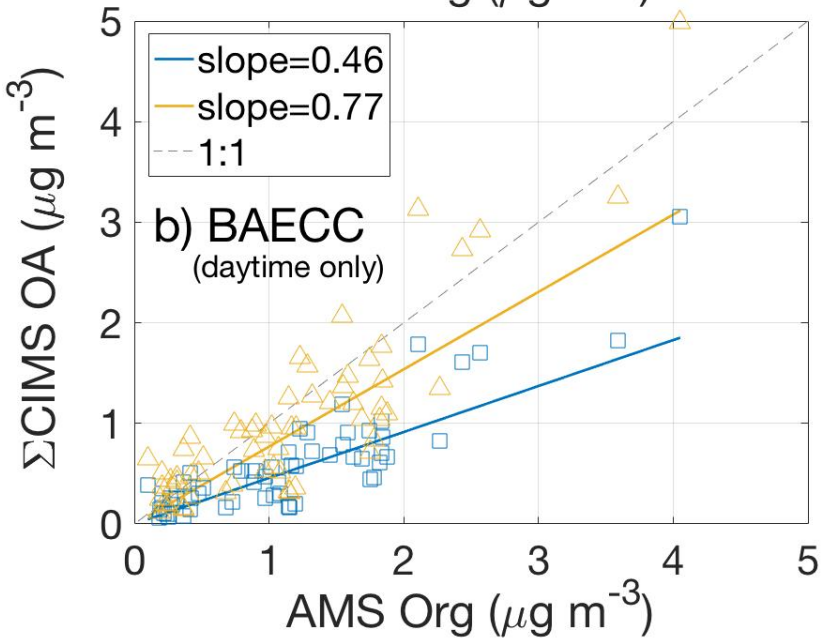
EVOLUTION OF IEPOX-SOA

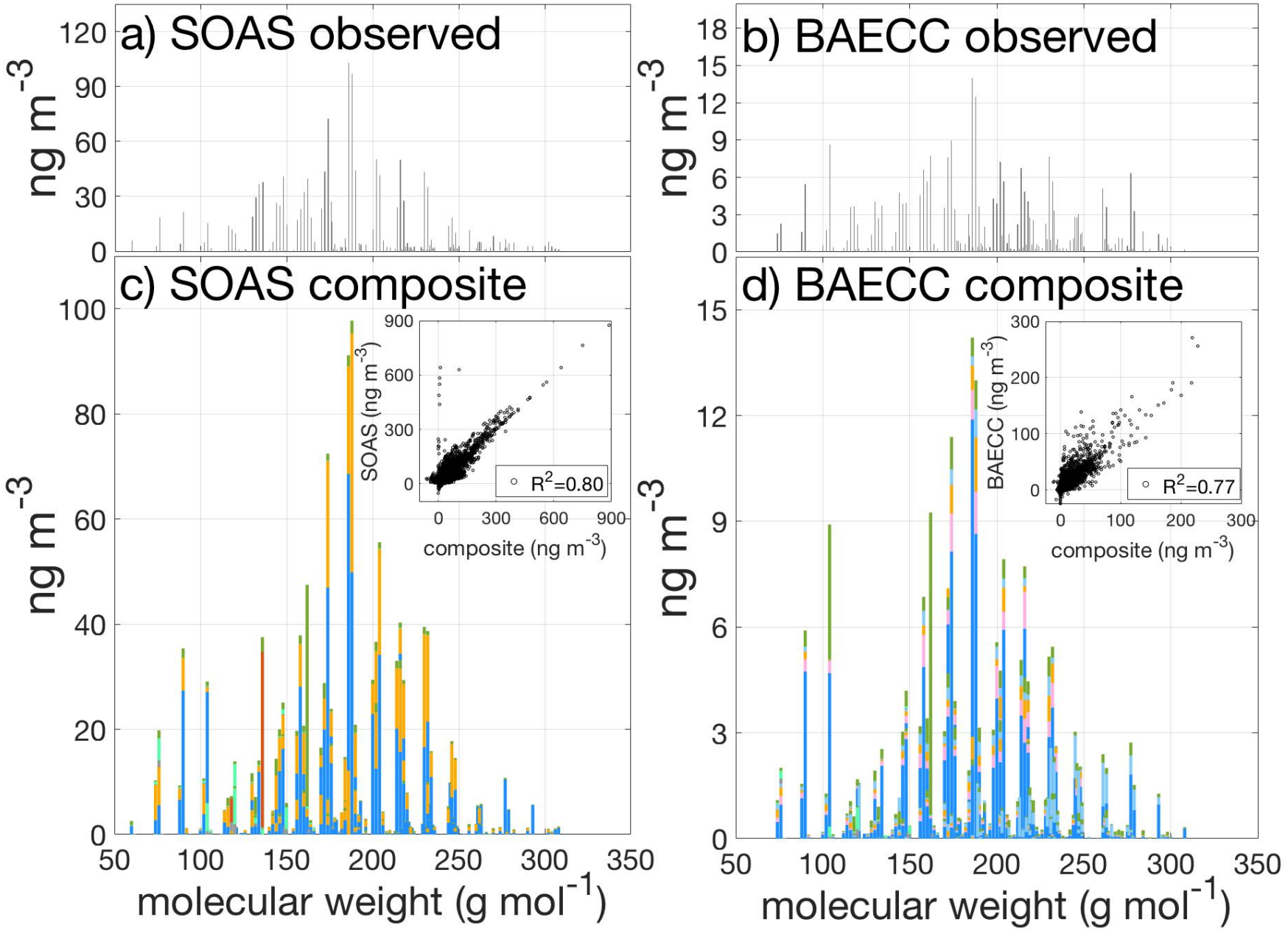


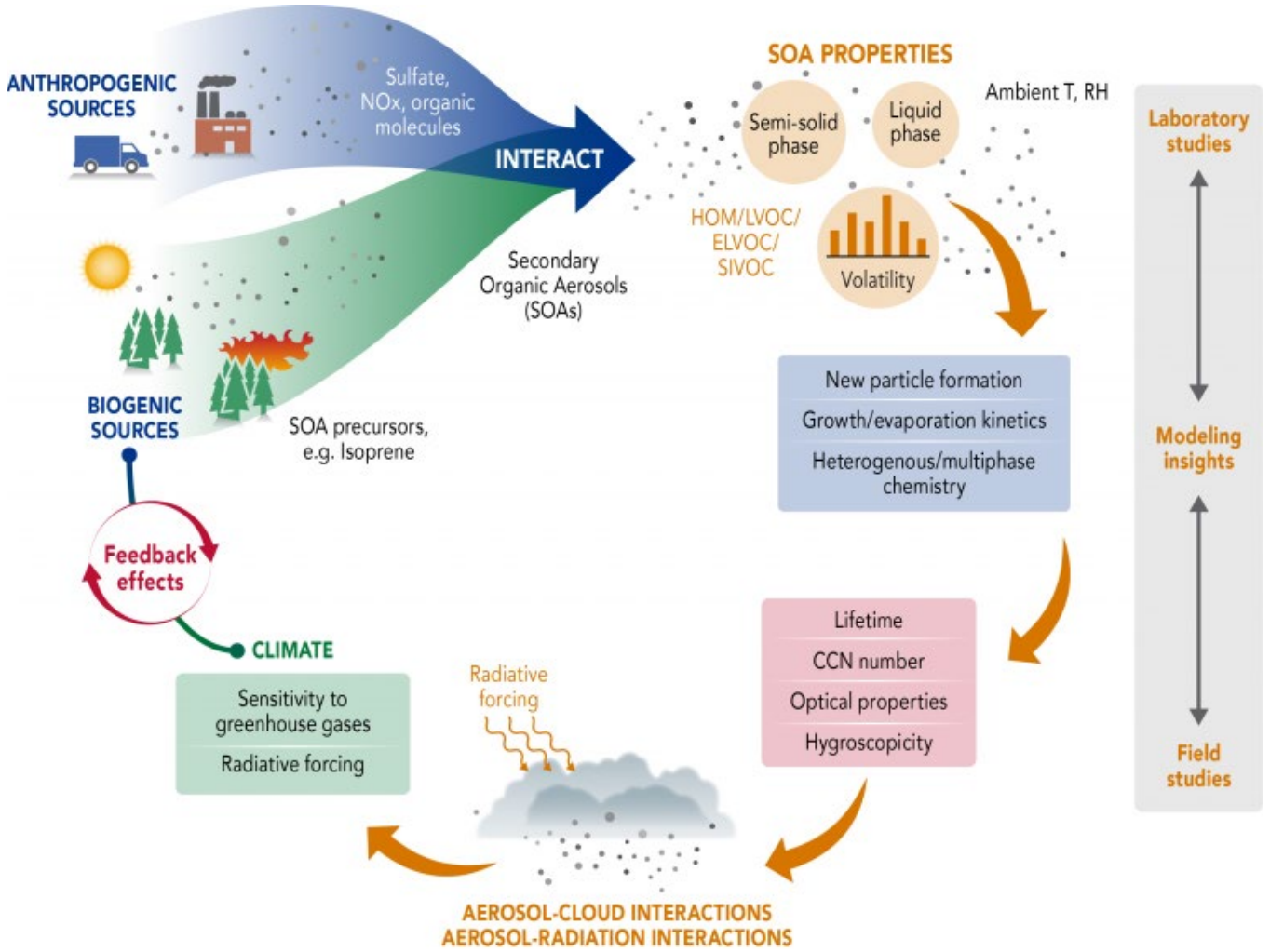
AMS VS FIGAERO-CIMS



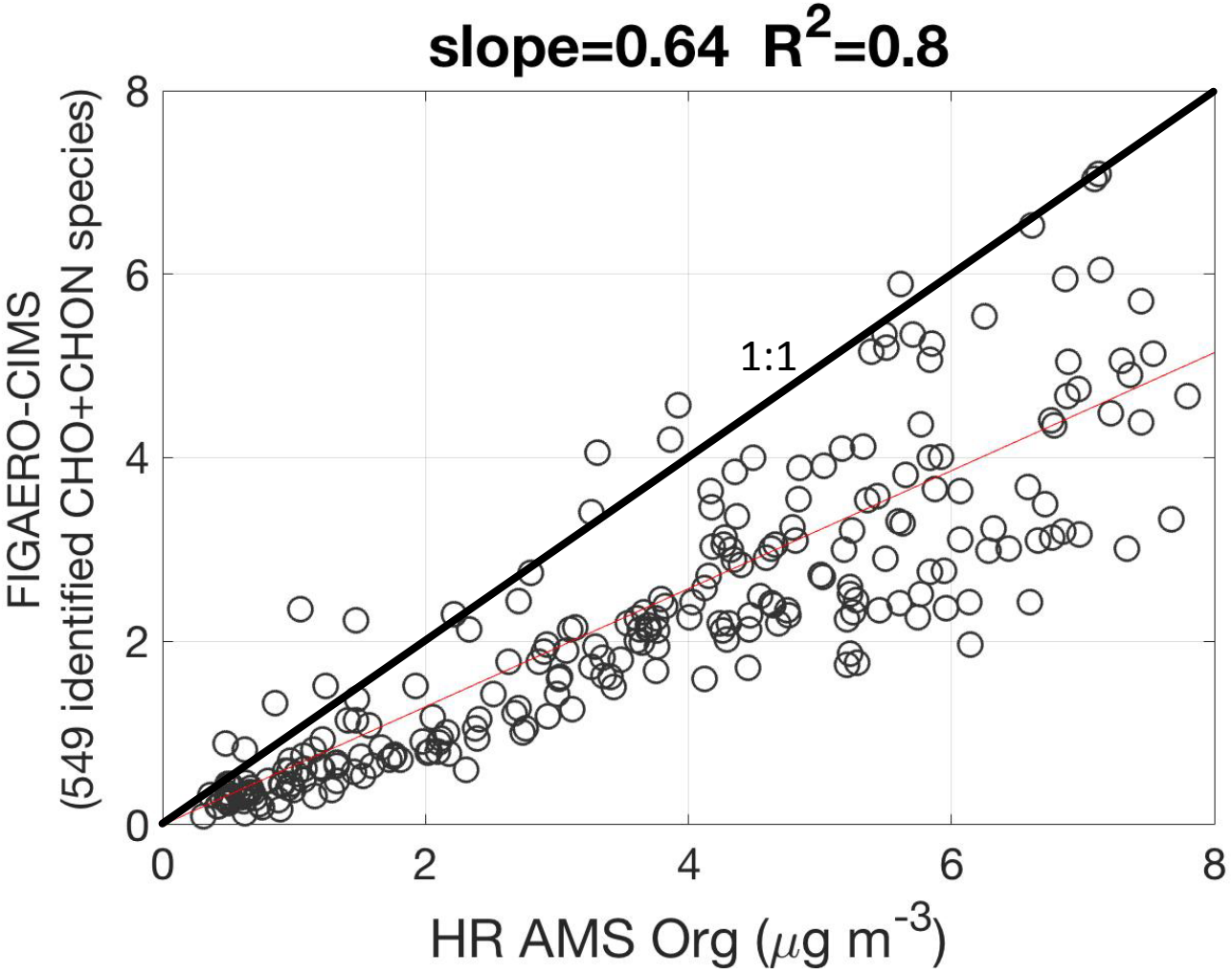





a) SOAS observed
b) BAECC observed
c) SOAS composite
d) BAECC composite
ng m-3
molecular weight (g mol-1)
SOAS (ng m-3)
BAECC (ng m-3)
composite (ng m-3)
R2=0.80
R2=0.77


ANTHROPOGENIC SOURCES
Sulfate, NOx, organic molecules
INTERACT
SOA PROPERTIES
Ambient T, RH
Semi-solid phase
Liquid phase
HOM/LVOC/ ELVOC/ SIVOC
Volatility
Secondary Organic Aerosols (SOAs)
BIOGENIC SOURCES
SOA precursors, e.g. Isoprene
New particle formation
Growth/evaporation kinetics
Heterogenous/multiphase chemistry
Laboratory studies
Modeling insights
Field studies
Feedback effects
CLIMATE
Sensitivity to greenhouse gases
Radiative forcing
Radiative forcing
Lifetime
CCN number
Optical properties
Hygroscopicity
AEROSOL-CLOUD INTERACTIONS
AEROSOL-RADIATION INTERACTIONS

FIGAERO-IODIDE CIMS COMPARED TO AMS



See, e.g., Lopez-Hilfiker et al AMT 2016

DATA SETS OF SIMULTANEOUS COMPOSITION & VOLATILITY

Felipe Lopez-Hilfiker

Ben Lee

SOAFFEE Chamber Expts

John Shilling (PNNL)

Emma D'Ambro

Claudia Mohr

Biogenic Aerosols-Effects on Clouds and Climate (BAECC)

Hyytiälä, Finland spring/summer 2014

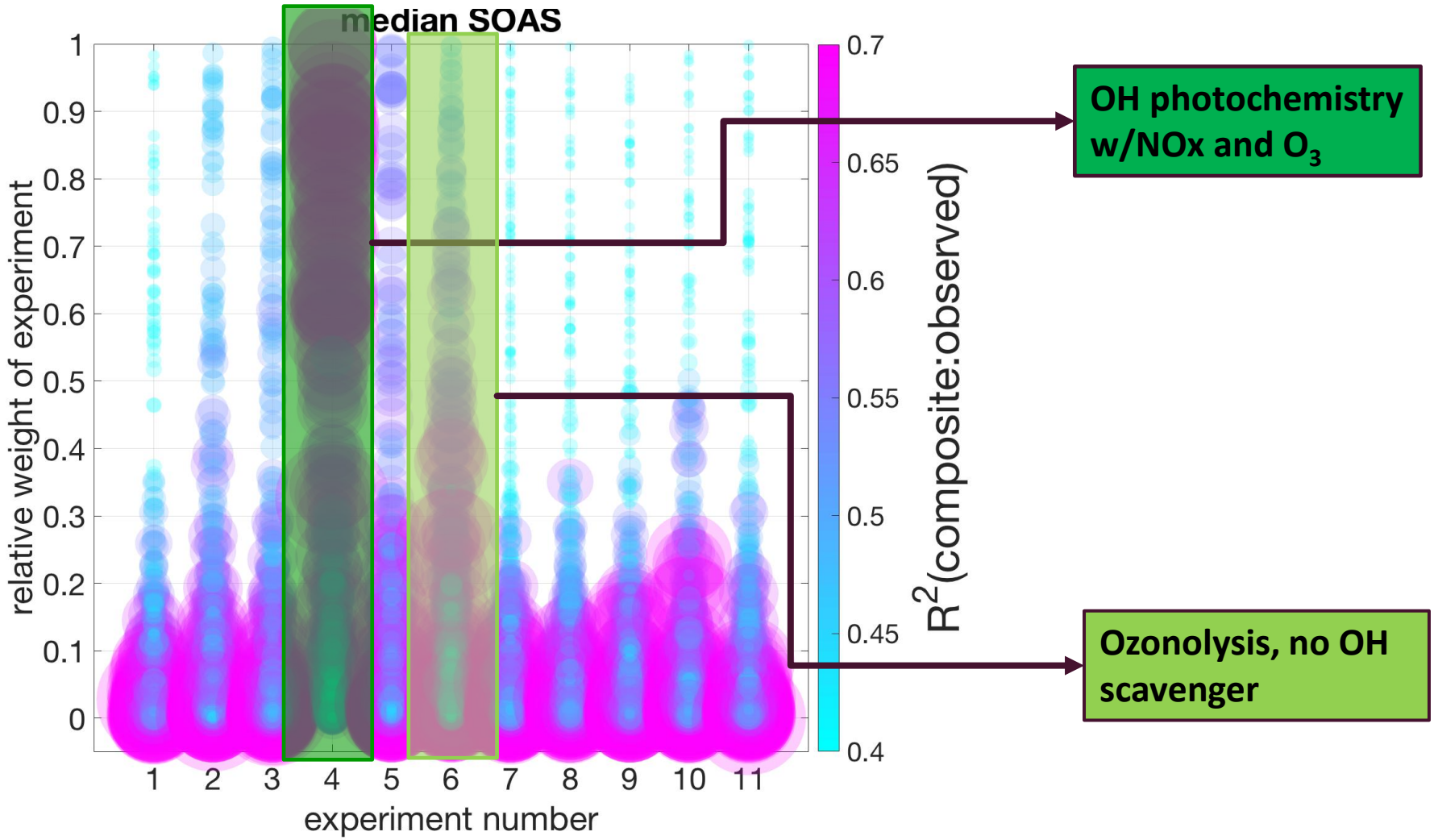
Boreal forest, mostly conifers

Southern Oxidant Aerosol Study (SOAS)

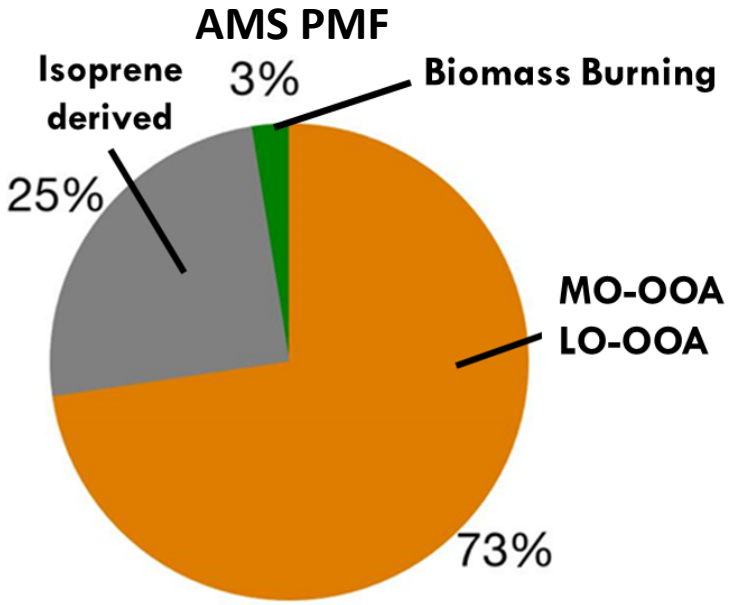
Centreville, AL in Summer 2013

Mixed broadleaf & conifers

MONTE CARLO METHOD WEIGHT ASSIGNMENTS

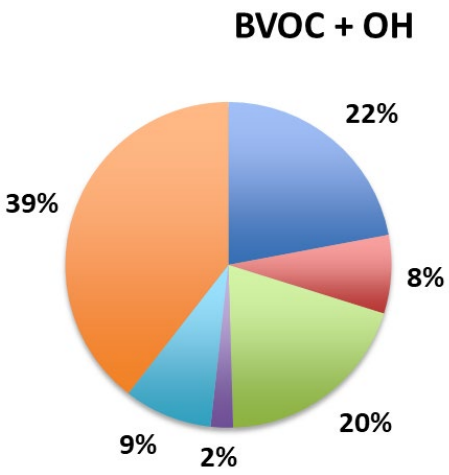


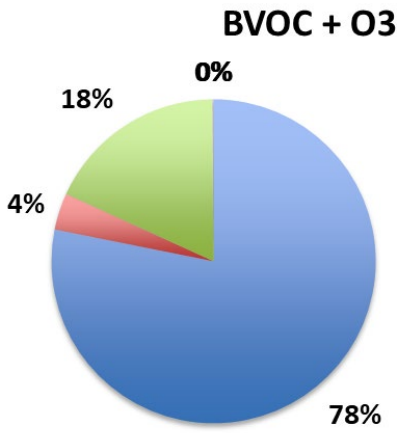
CHEMICAL PATHWAY APPORTIONMENT

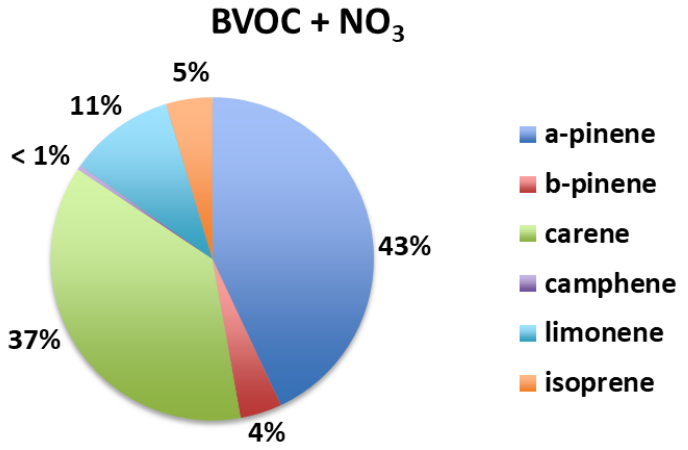


Hu et al, ACP 2016
Xu et al, PNAS 2014

BAECC (HYYTIÄLÄ) REACTIVITY







DISCUSSION: UNIQUENESS OF PATHWAY

α-pinene + OH

α-pinene + OH + L_O_3 + L_NO_x

α-pinene + OH + M_O_3 + M_NO_x

α-pinene + OH + H_O_3 + H_NO_x

α-pinene + OH + M_O_3

α-pinene + O_3 (dark)

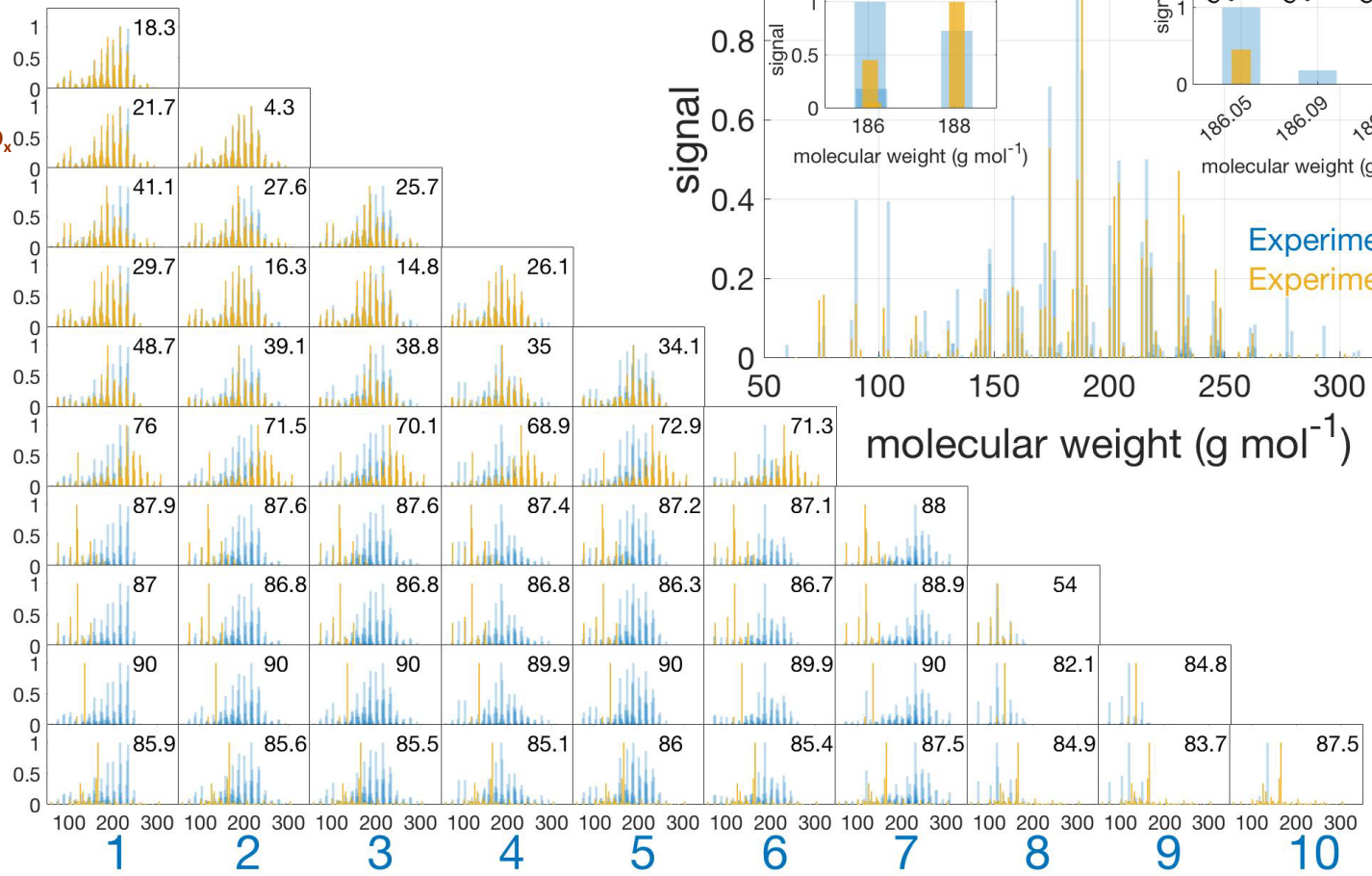
α-pinene + O_3 + NO_x (dark)

Isoprene + OH + H_NO_x

Isoprene + OH + L_NO_x

IEPOX + aqueous acidic seed

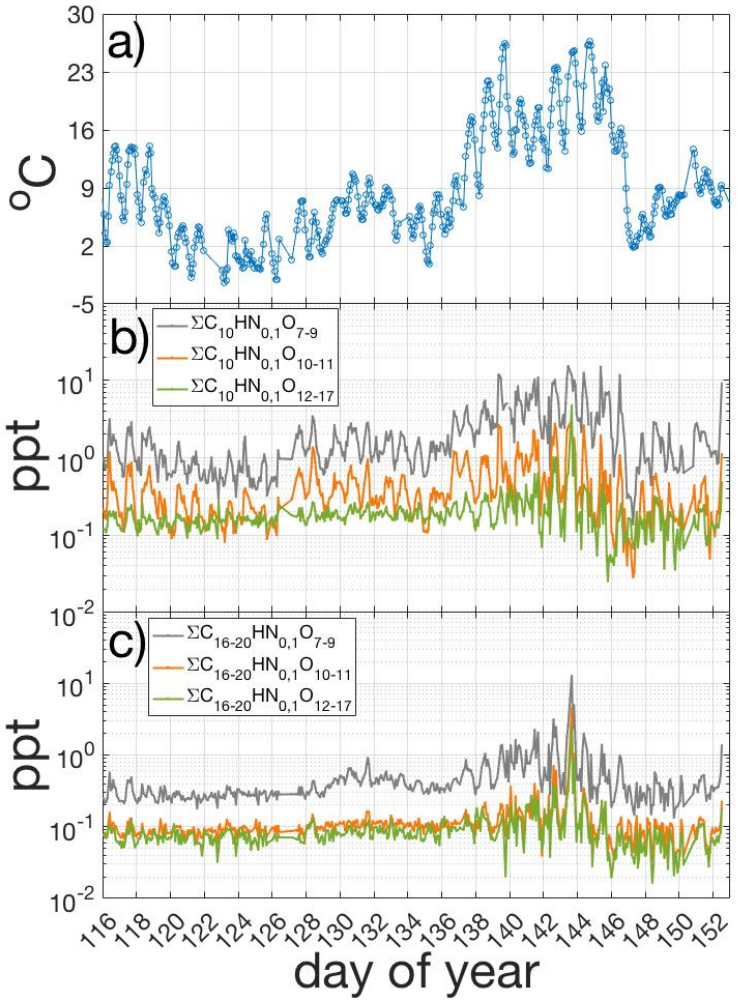
"BB" derived from residuals

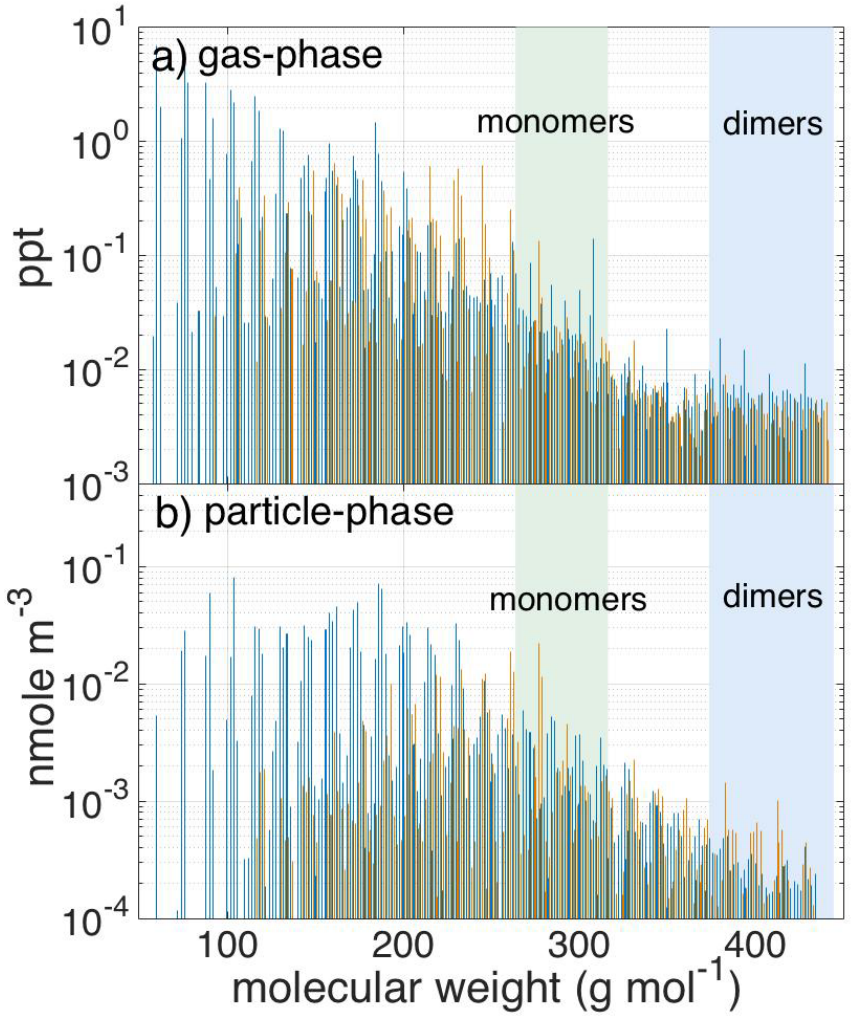


DISCUSSION: UNIQUENESS OF "α-PINENE"

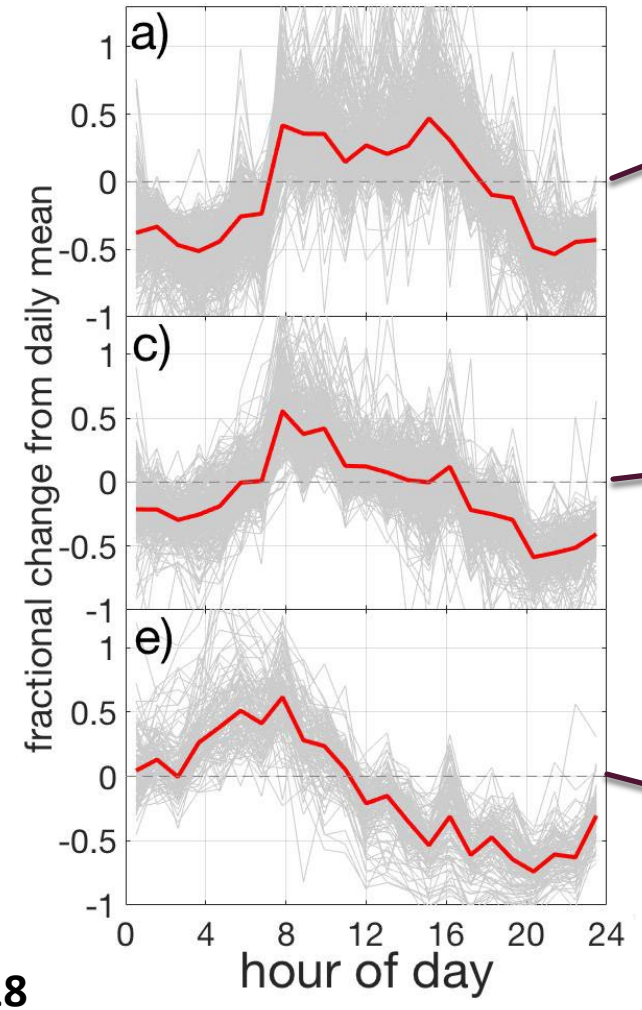
Monoterpene:	a-pinene	b-pinene	carene	limonene	camphene
Chemical Formula:	$C_{10}H_{16}$	$C_{10}H_{16}$	$C_{10}H_{16}$	$C_{10}H_{16}$	$C_{10}H_{16}$

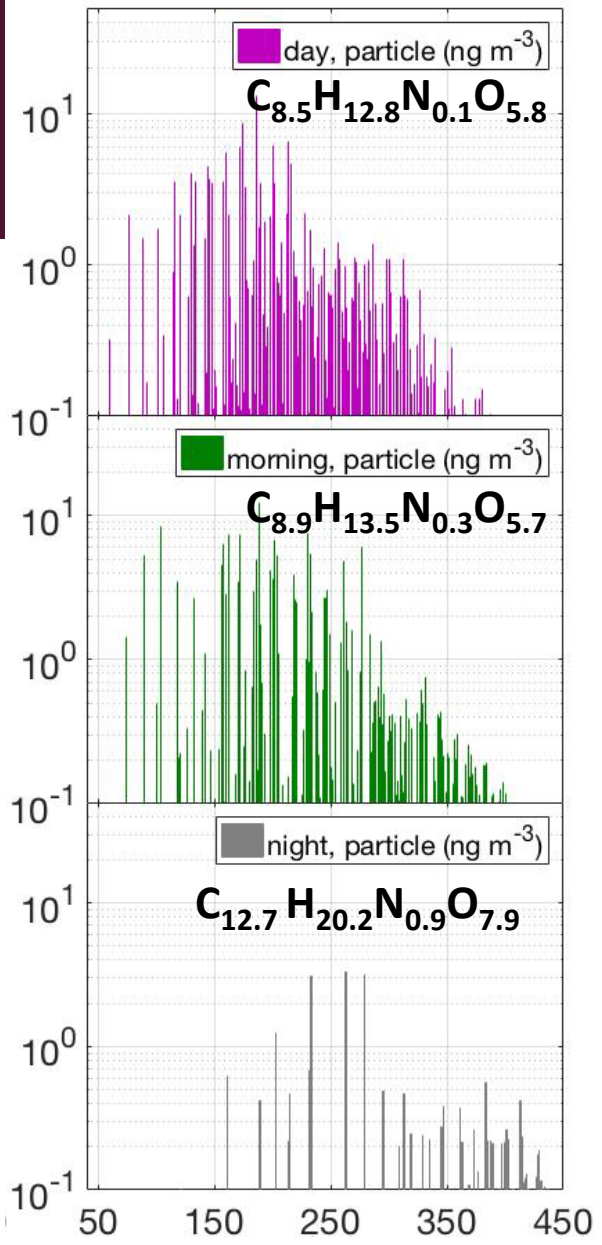
BAECC @ HYYTIÄLÄ (LEE ET AL ACP 2018)





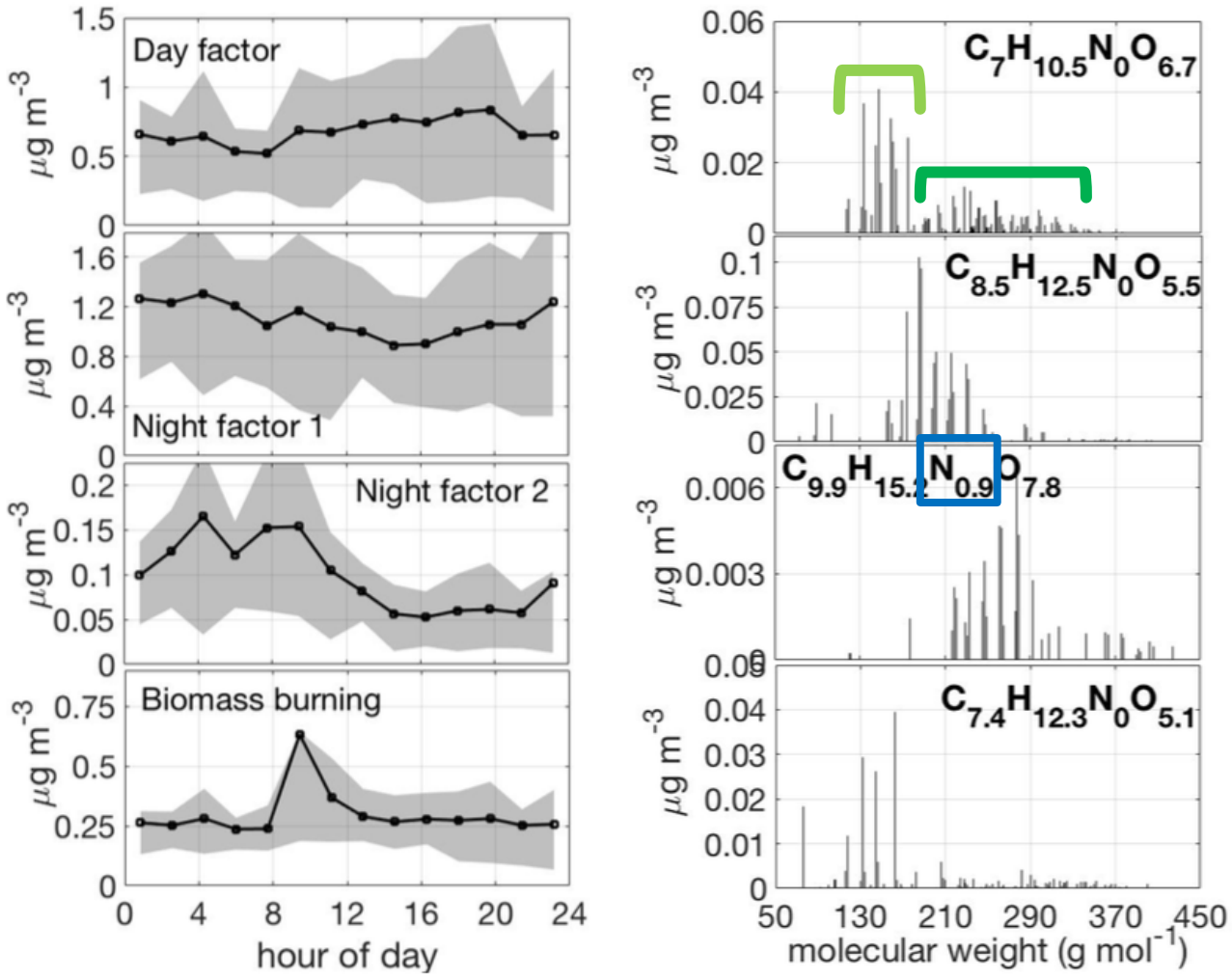
FACTORIZATION OF FIGAERO SPECTRA



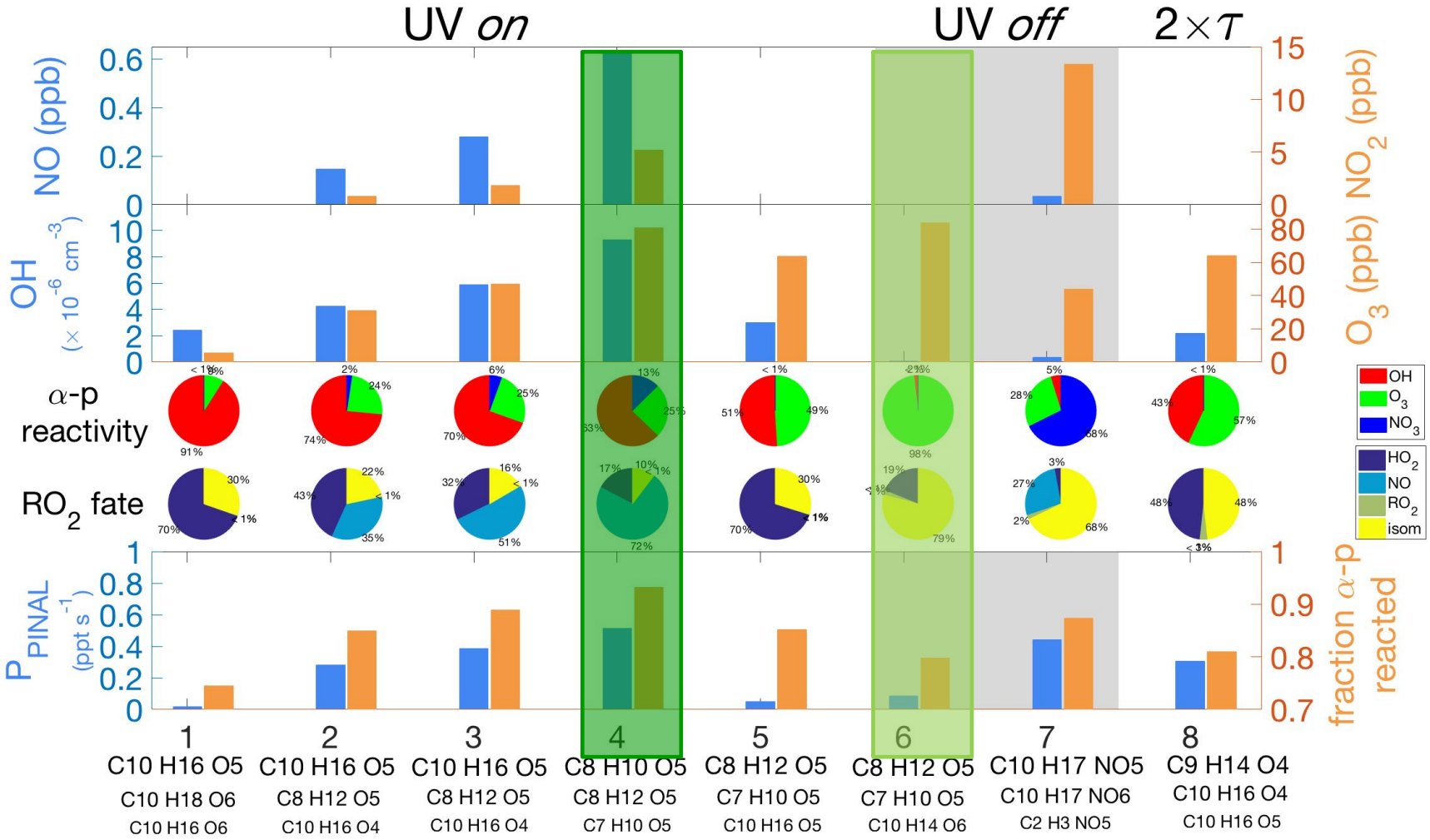


Lee et al ACP 2018

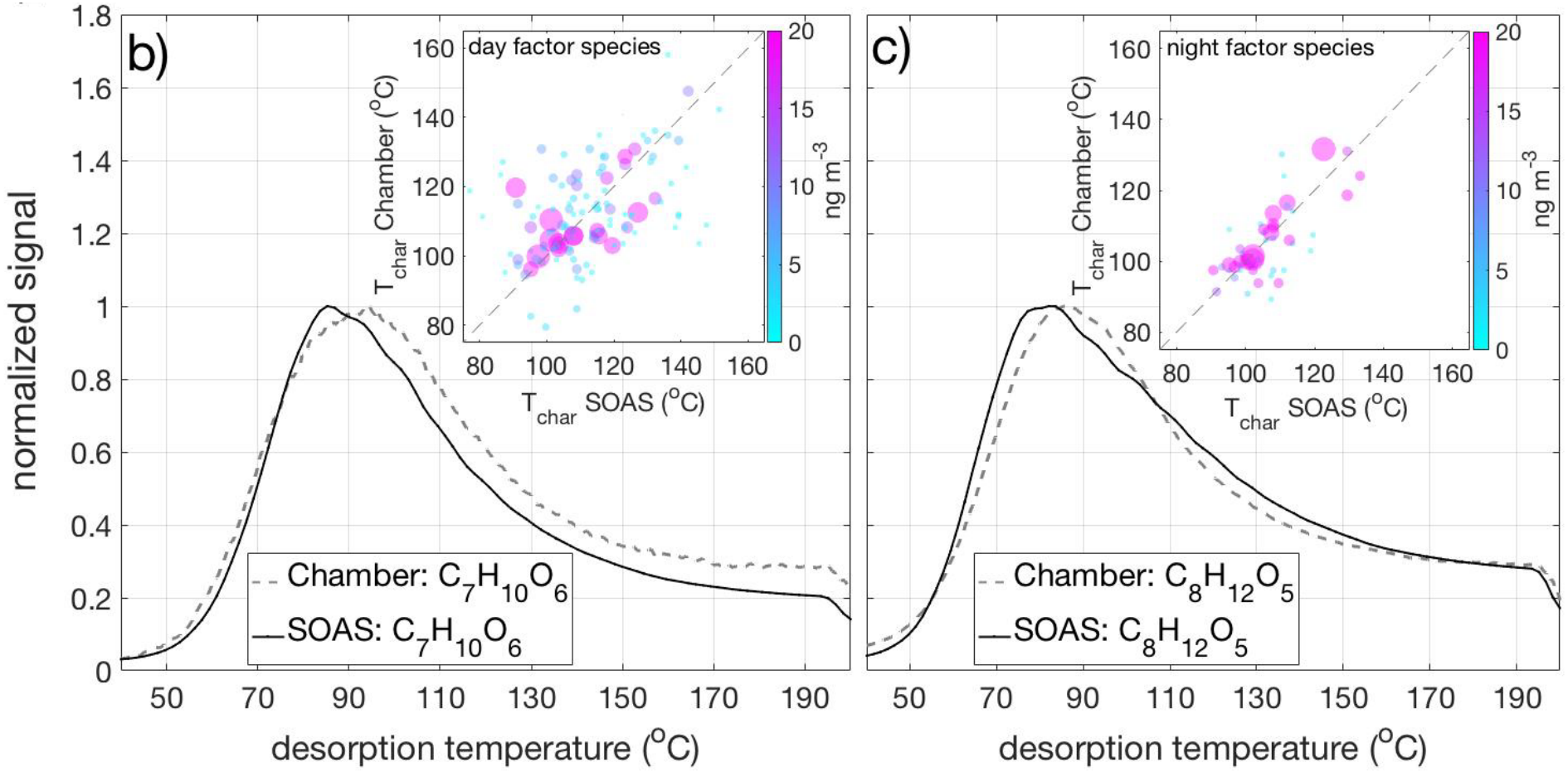
SOAS FIGAERO-CIMS FACTORIZATION



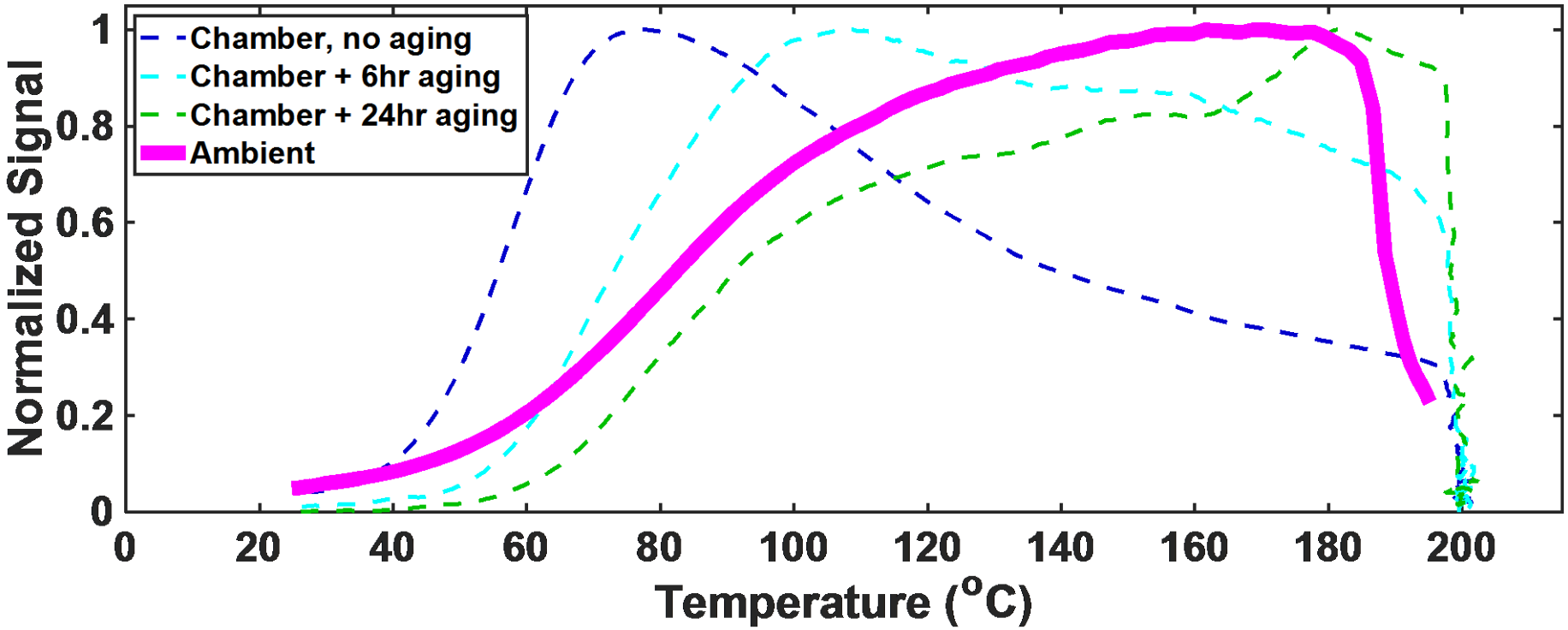
OXIDANTS/AGING/PEROXY RADICAL FATE



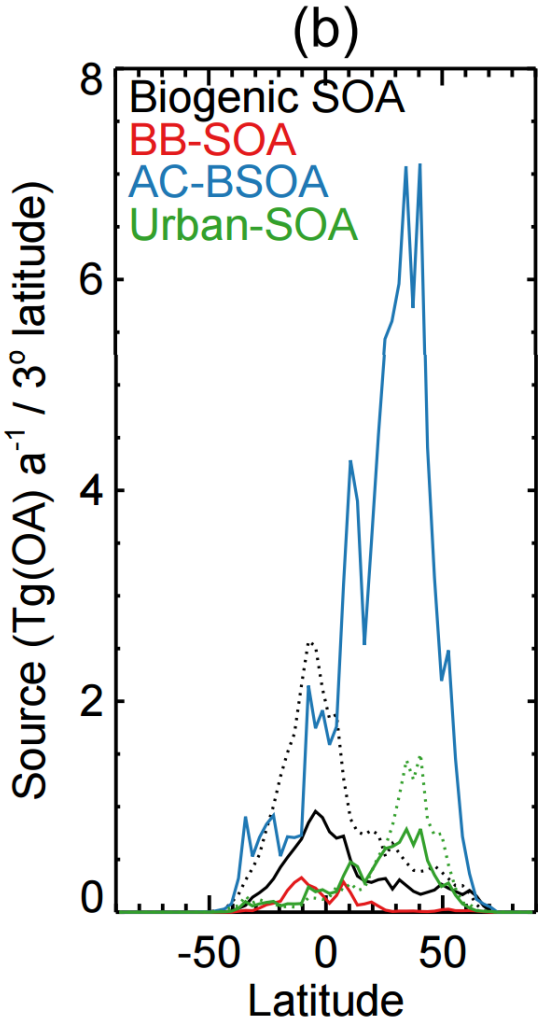
DISCUSSION: AGING/VOLATILITY (SOAS)



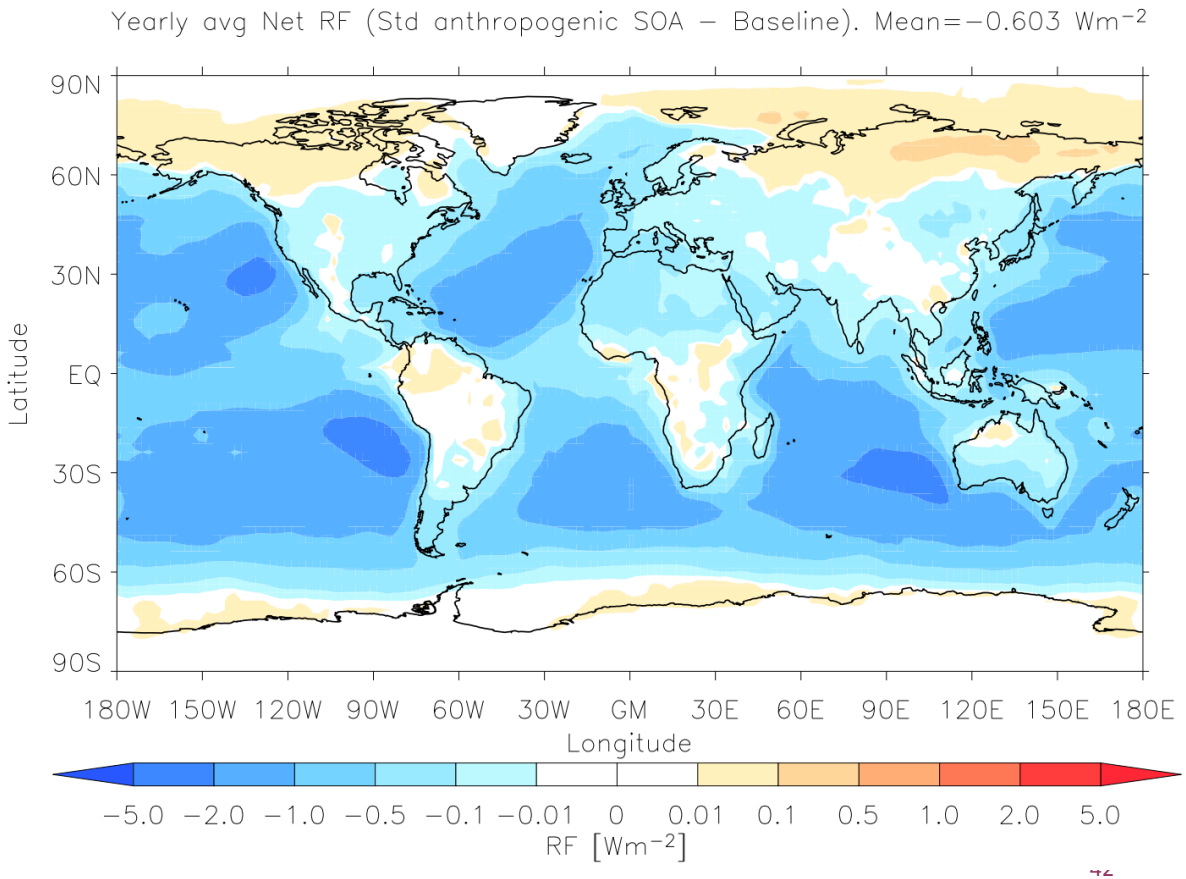
DISCUSSION: AGING/VOLATILITY (HYYTIÄLÄ)



SECONDARY ORGANIC AEROSOL (SOA) - IMPORTANCE

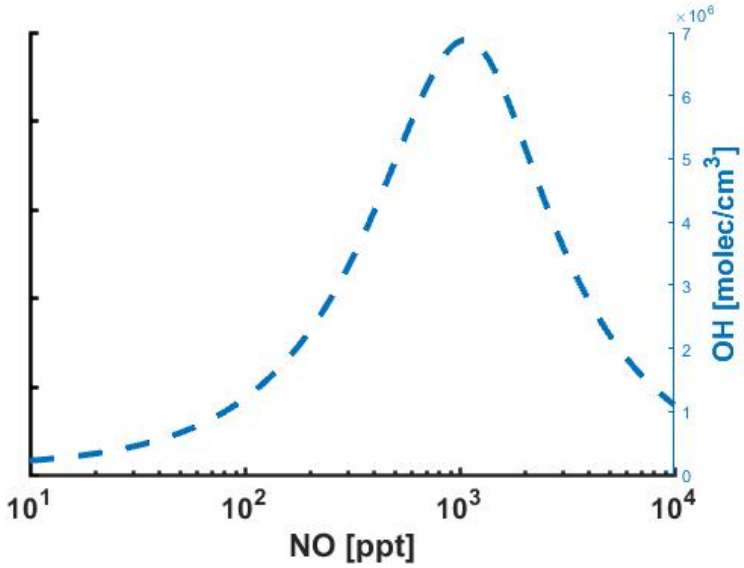


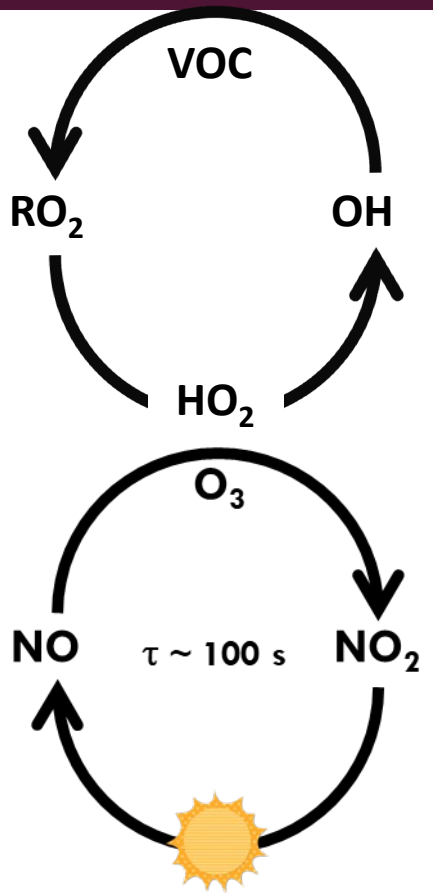
Spracklen et al ACP 2011



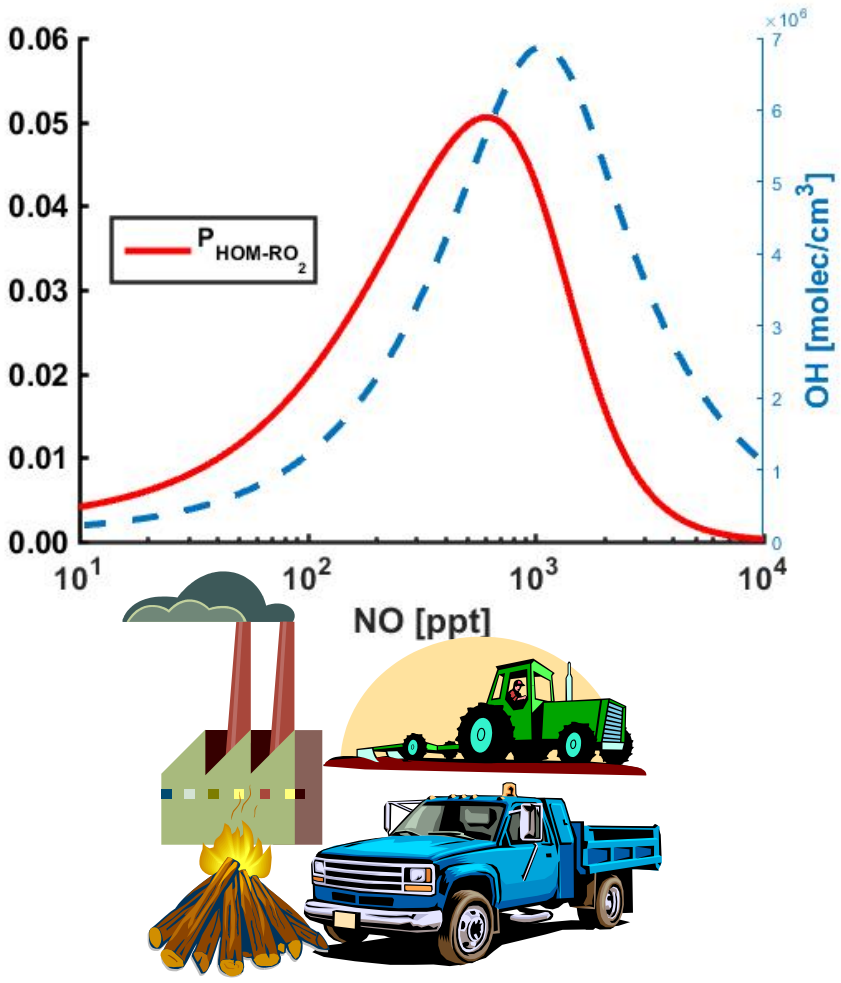
ACRF ~ - 0.6 W/m²

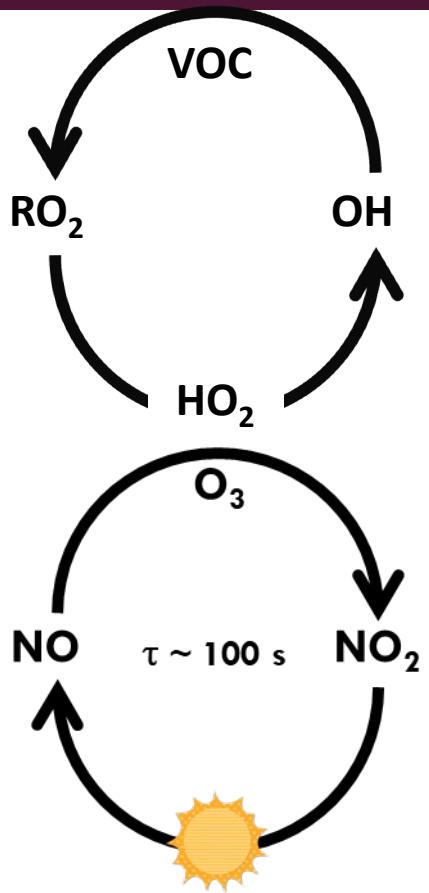
NITROGEN OXIDES AFFECT OH AND O_3



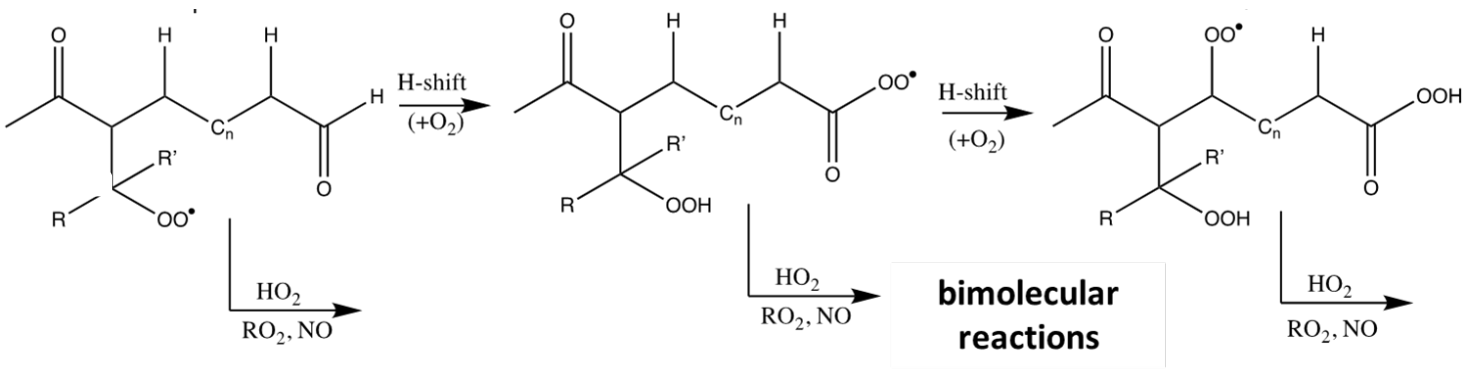


NITROGEN OXIDES AFFECT OH AND AUTOXIDATION

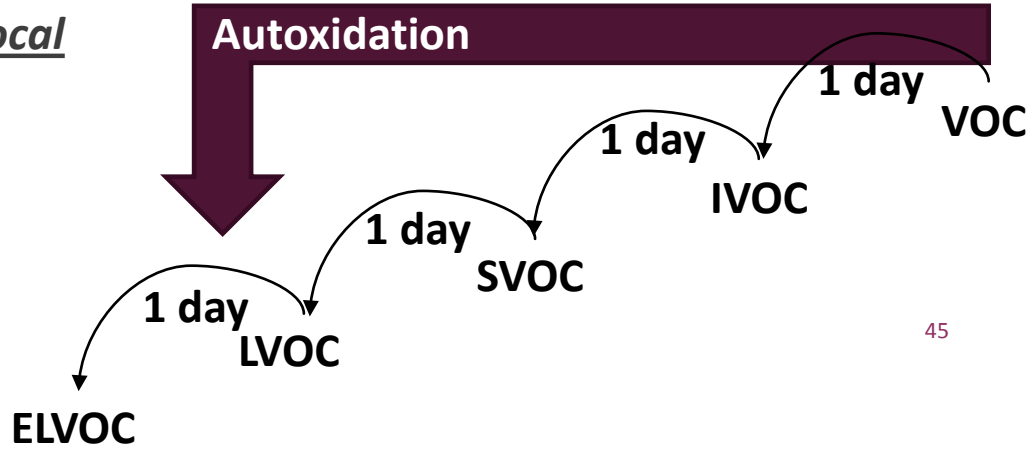




ORGANIC PEROXY RADICAL ($RO_2^{\cdot}$) AUTOXIDATION



- If autoxidation is important, SOA formation rates should ***sensitive to local perturbations*** in oxidants



Crounse et al JPC 2011
Ehn et al Nature 2014
Rissanen, et al J. Phys Chem 2015