Atmospheric Evolution and Chemical Aging of Organic Particulate Matter

Spyros Pandis and Neil Donahue

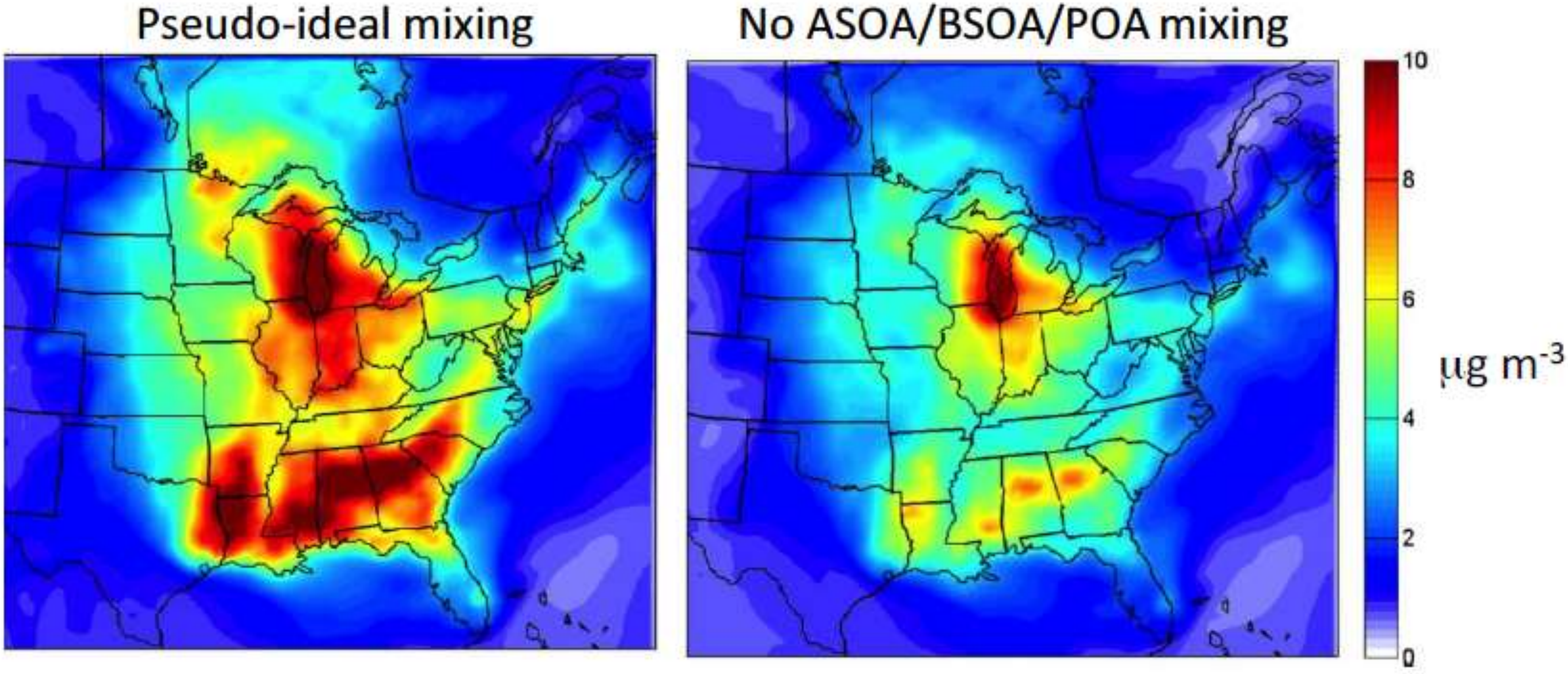
Center for Atmospheric Particle Studies (CAPS)
Carnegie Mellon University

Some Questions

- Do the biogenic and anthropogenic SOA components get along (mixing)?
- Does the biogenic SOA age gracefully (chemical aging)?
- Effects of SOA on climate relevant particle like absorption
- Can our updated models reproduce the observations of OA and particle number in areas with both biogenic and anthropogenic sources?

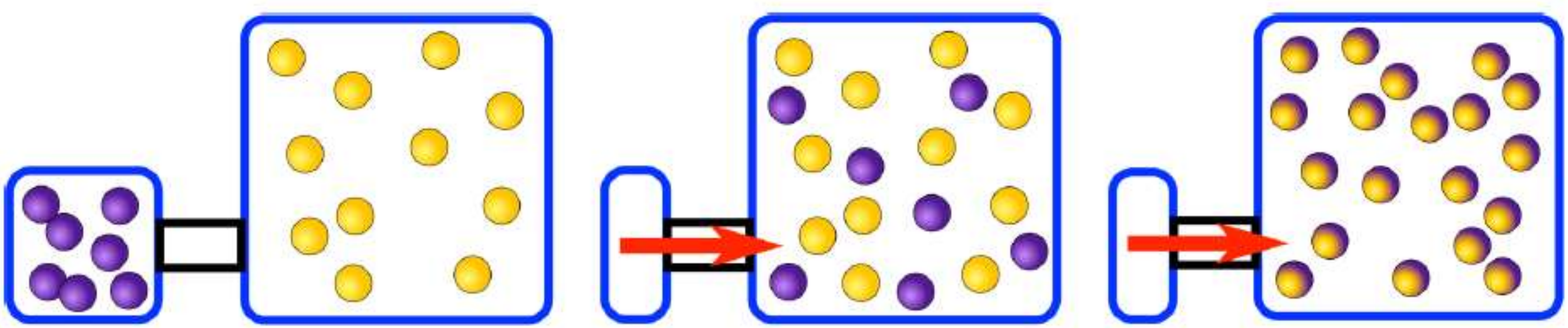
Mixing of Different OA Components

OA for Different Mixing Assumptions



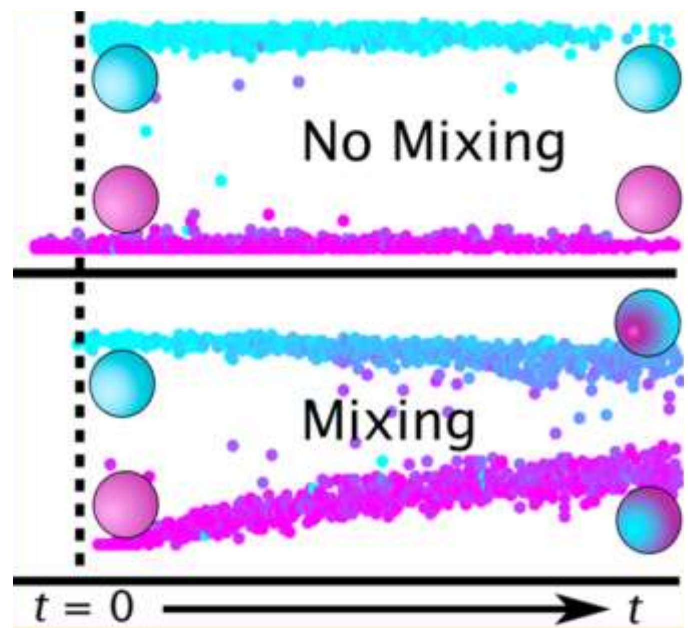
PMCAMx-Summer 2001

Mixing Experiments- Donahue



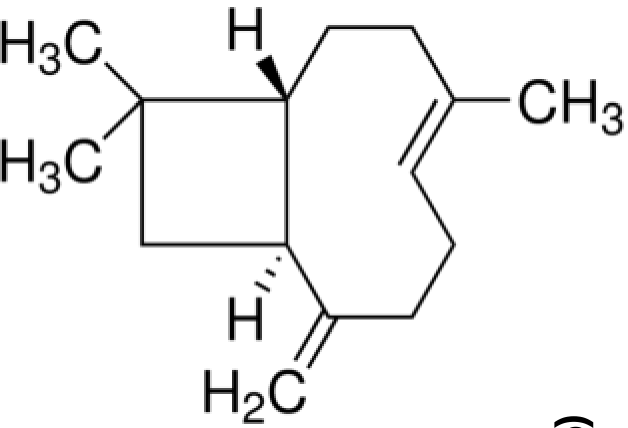
(a) (b) (c)

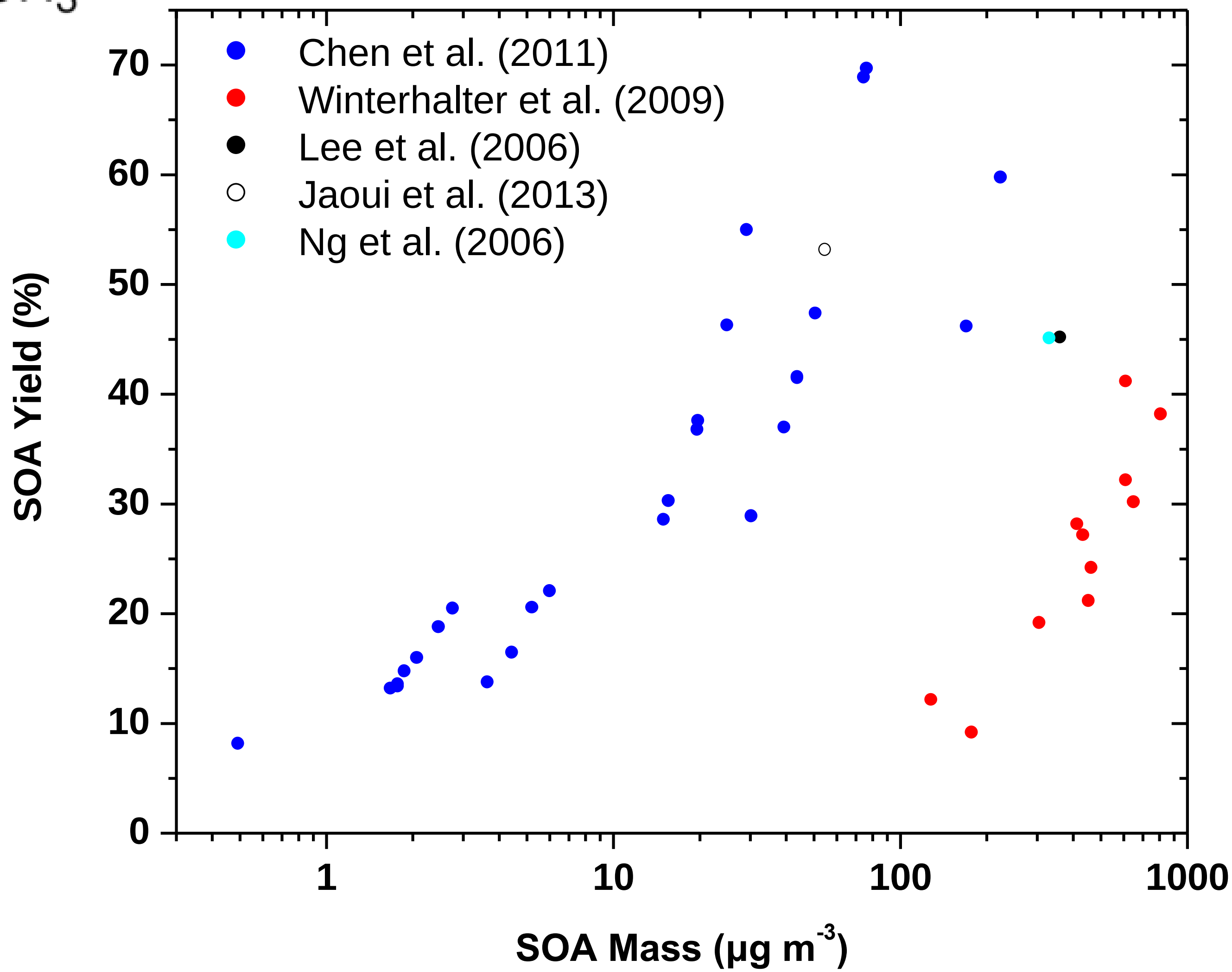
Correlation of the mass spectra of individual particles with the average initial composition of one of the two populations as a function of time.



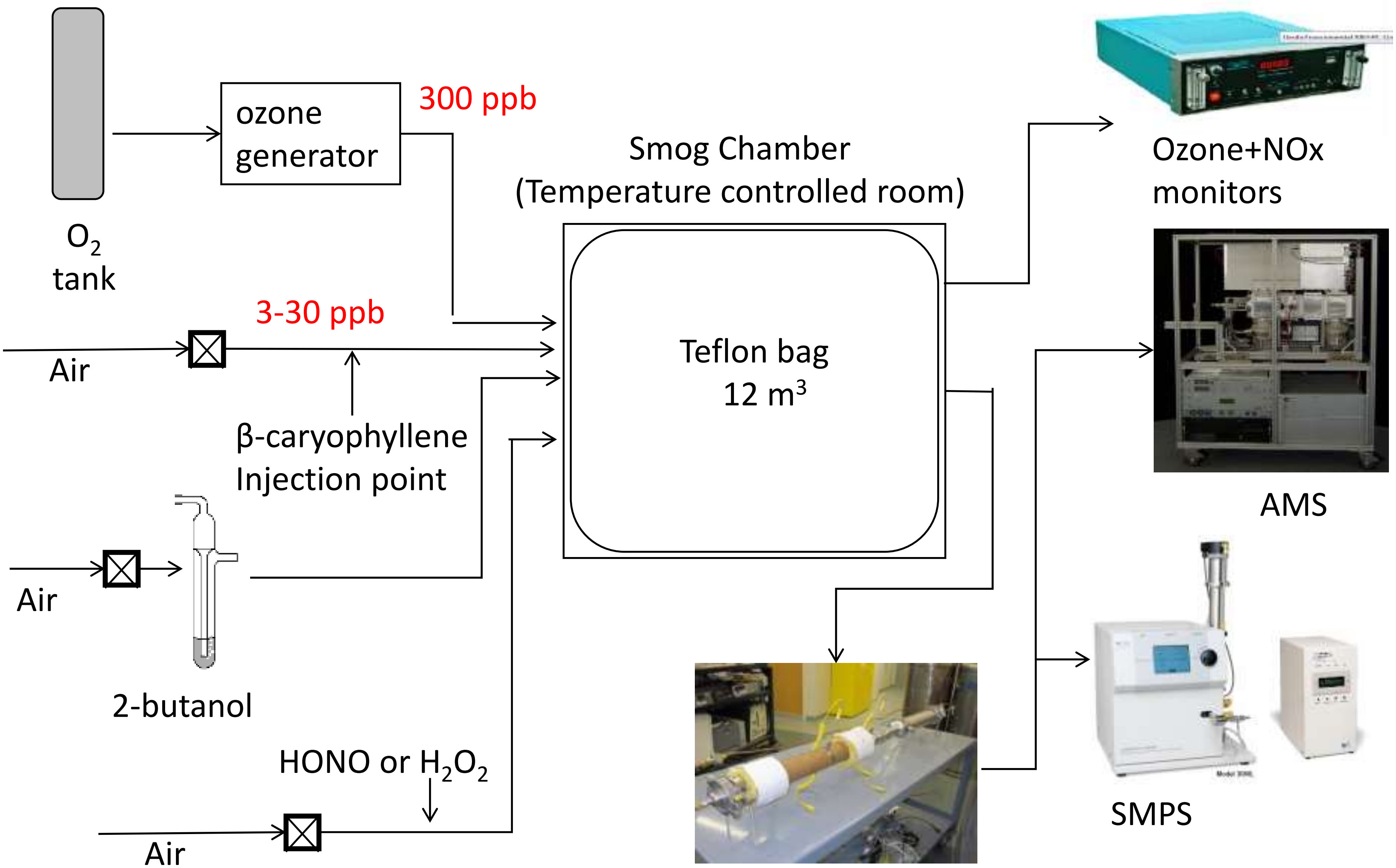
Chemical Aging of SOA

β-Caryophyllene SOA Formation

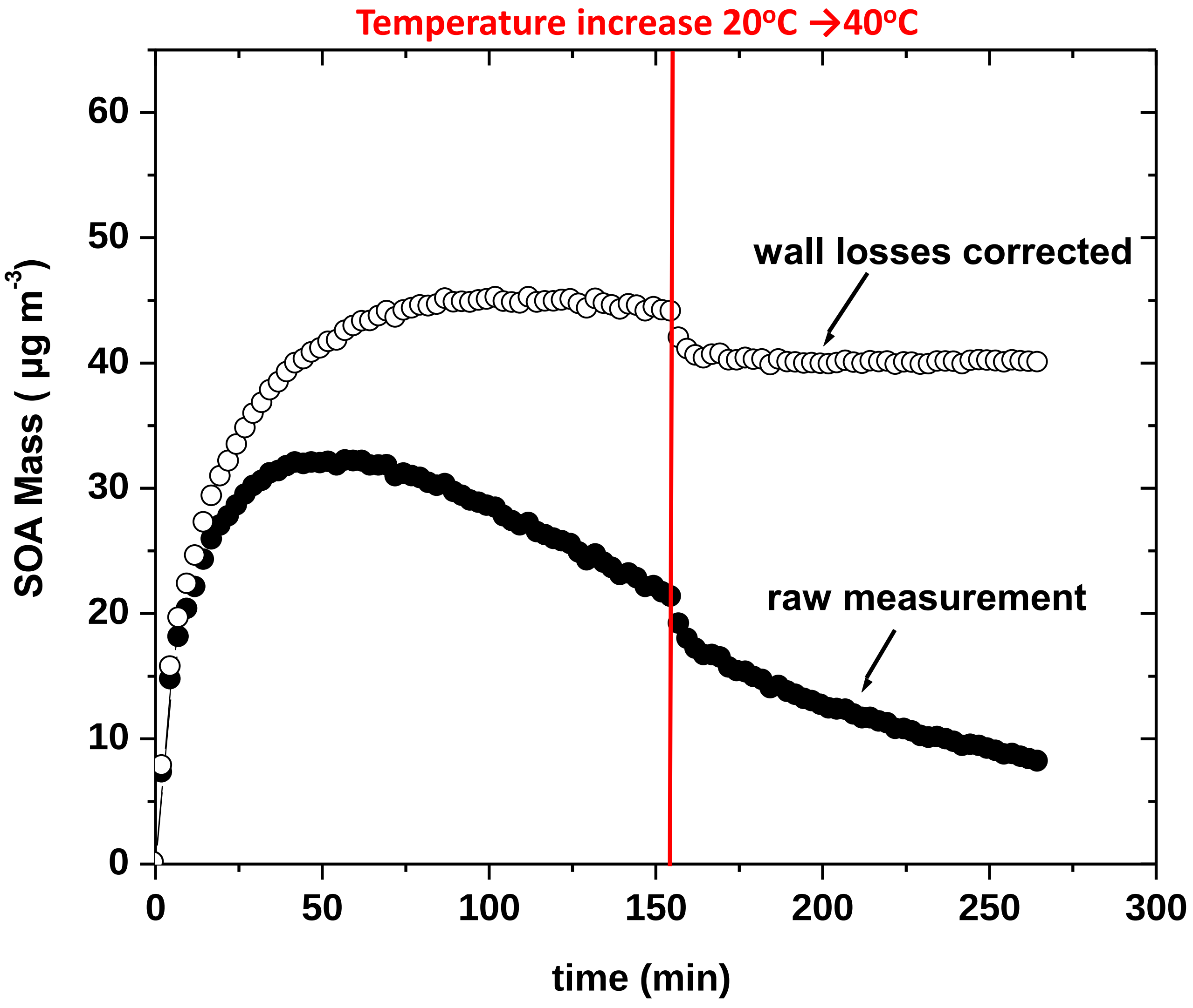




Experimental setup

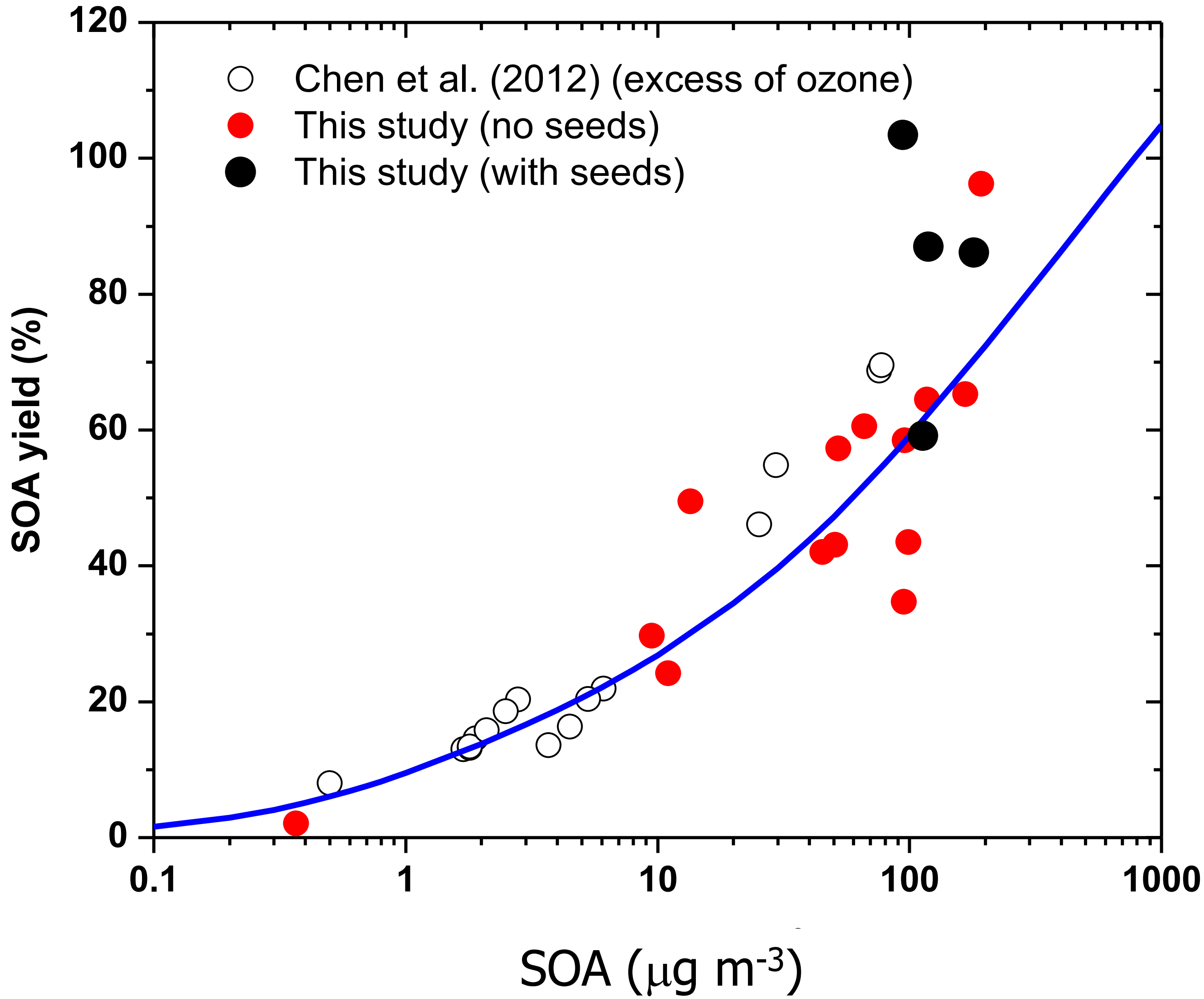


Formation-Evaporation of the SOA

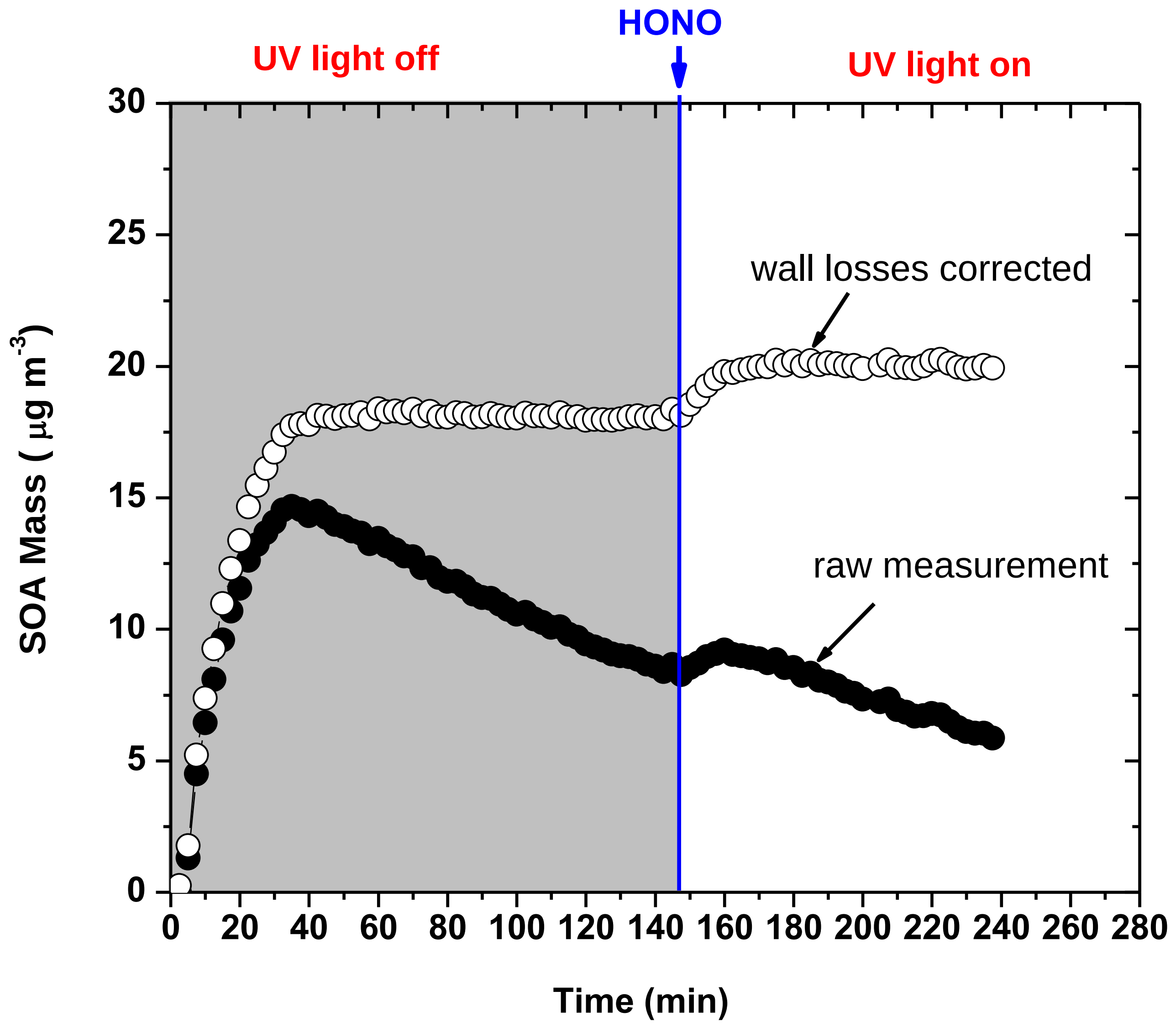


(28 ppb β-caryophyllene + 300 ppb Ozone + 2-butanol)

β-Caryophyllene ozonolysis SOA yield

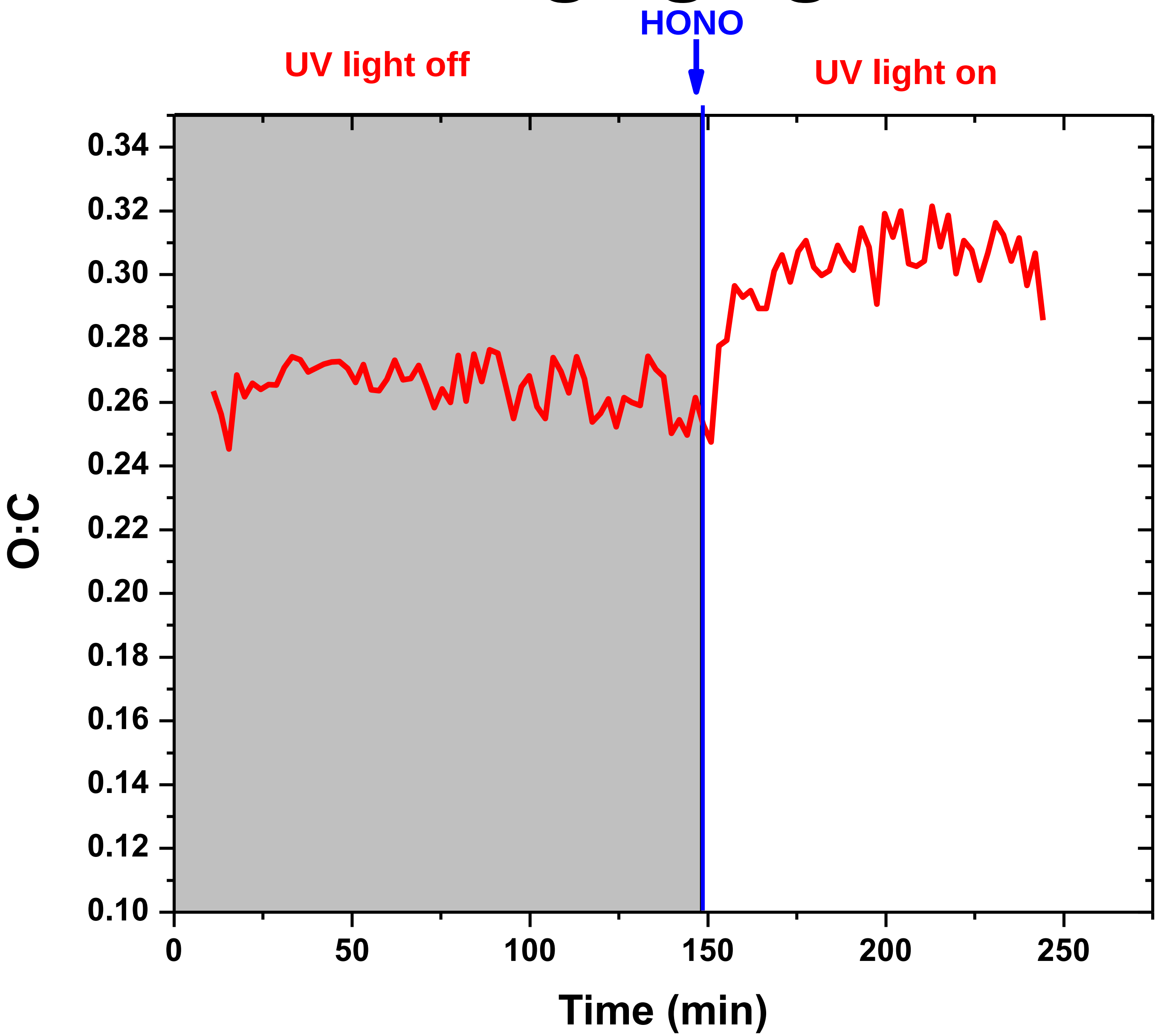


Aging of β-caryophyllene SOA by OH



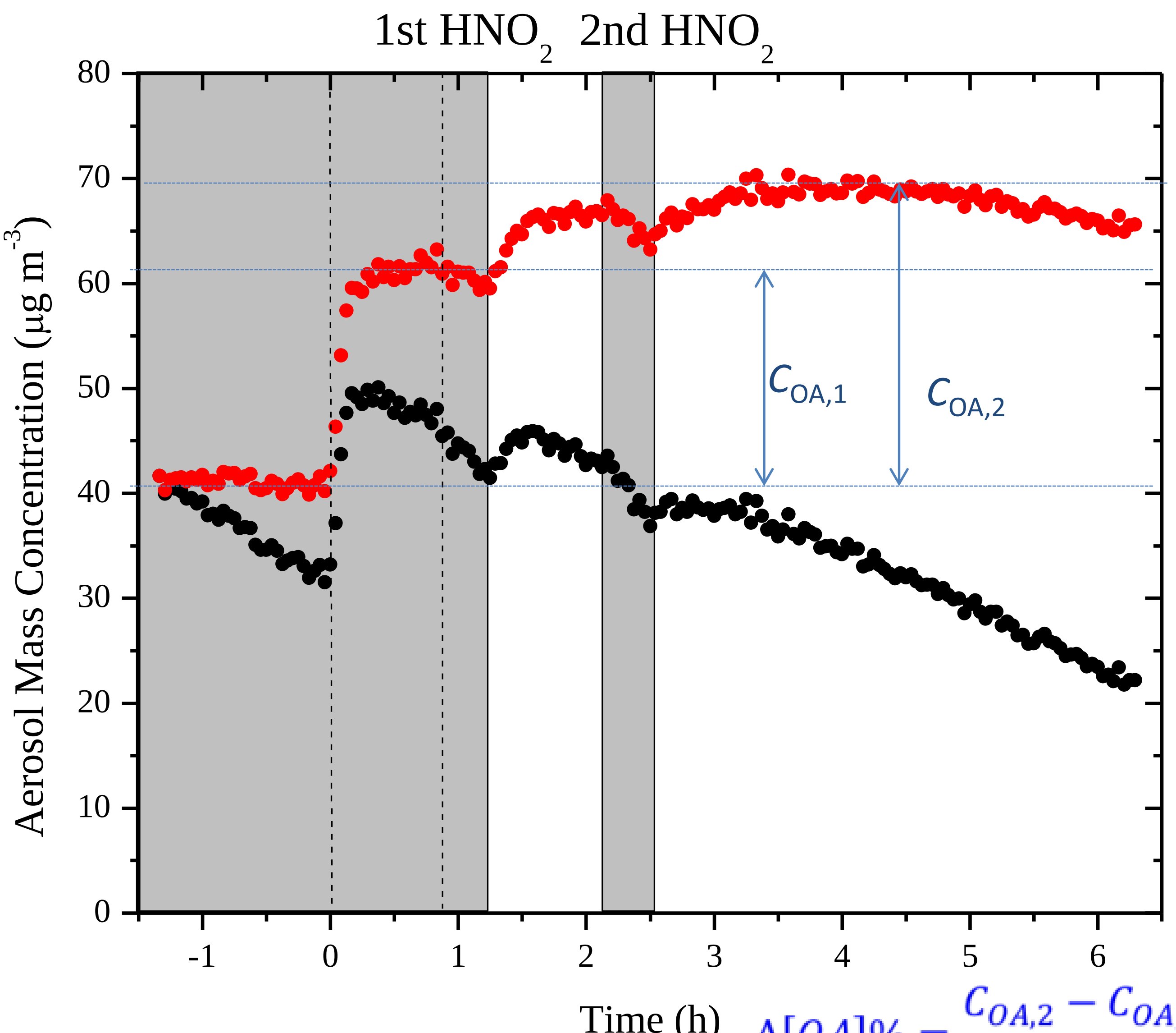
(3 ppb β-caryophyllene + 300 ppb ozone)

O:C during aging of SOA



Aging of a-pinene SOA

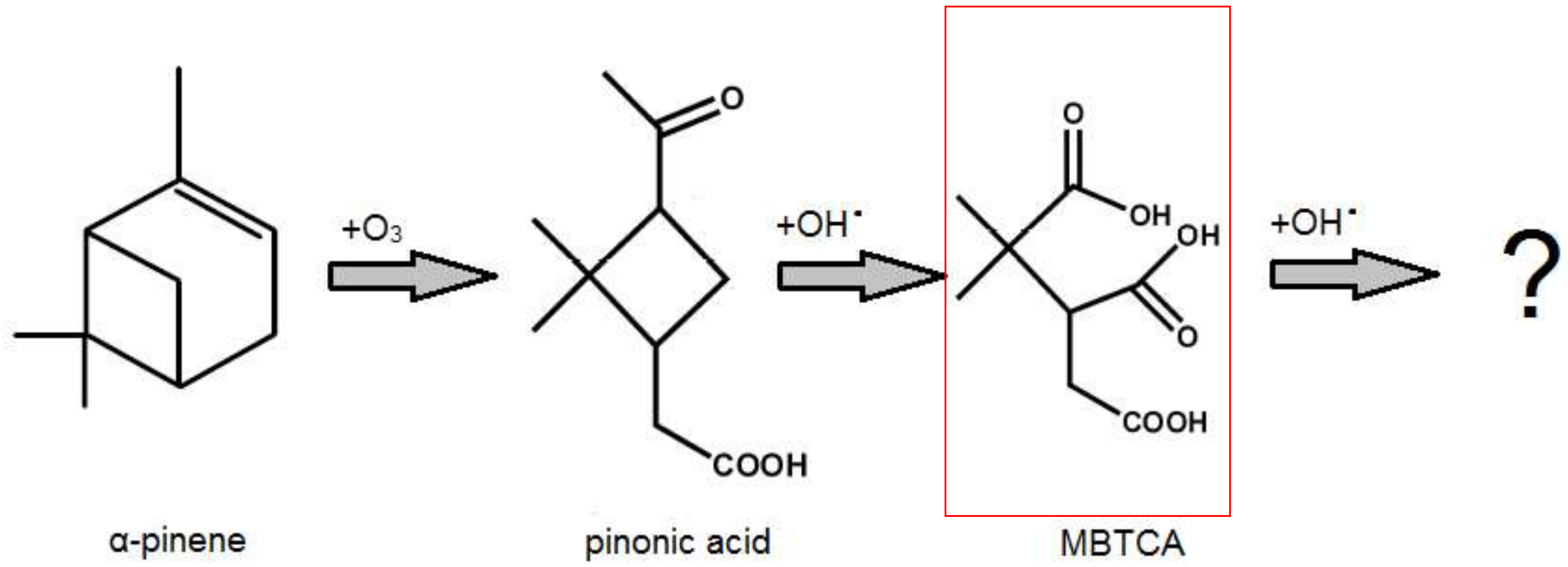
PM Mass Concentration



$$\Delta[OA]\% = \frac{C_{OA,2} - C_{OA,1}}{C_{OA,1}} \times 100\%$$

MBTCA Production and Aging

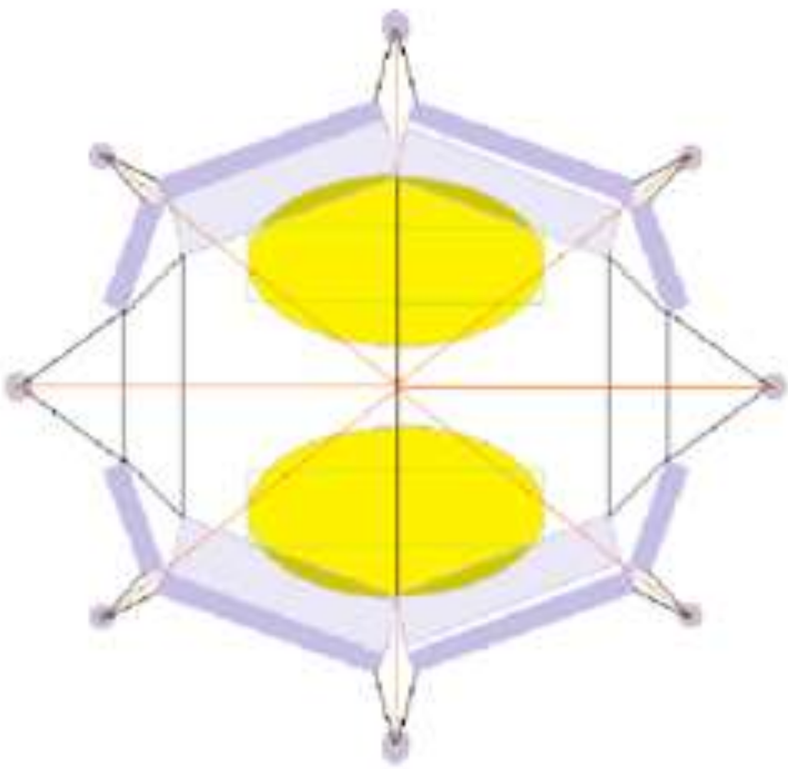
(3-methyl-1,2,3-butanetricarboxylic acid)

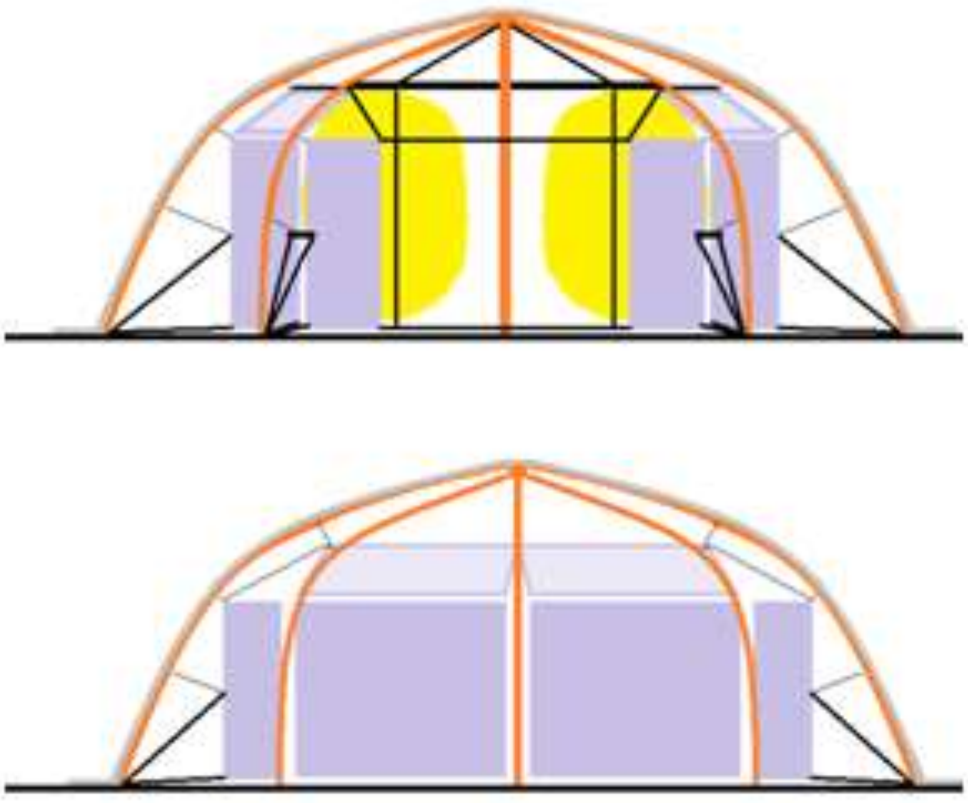


Ambient Perturbation Experiments

Dual Mobile Chamber System

Dual Mobile Smog Chamber System

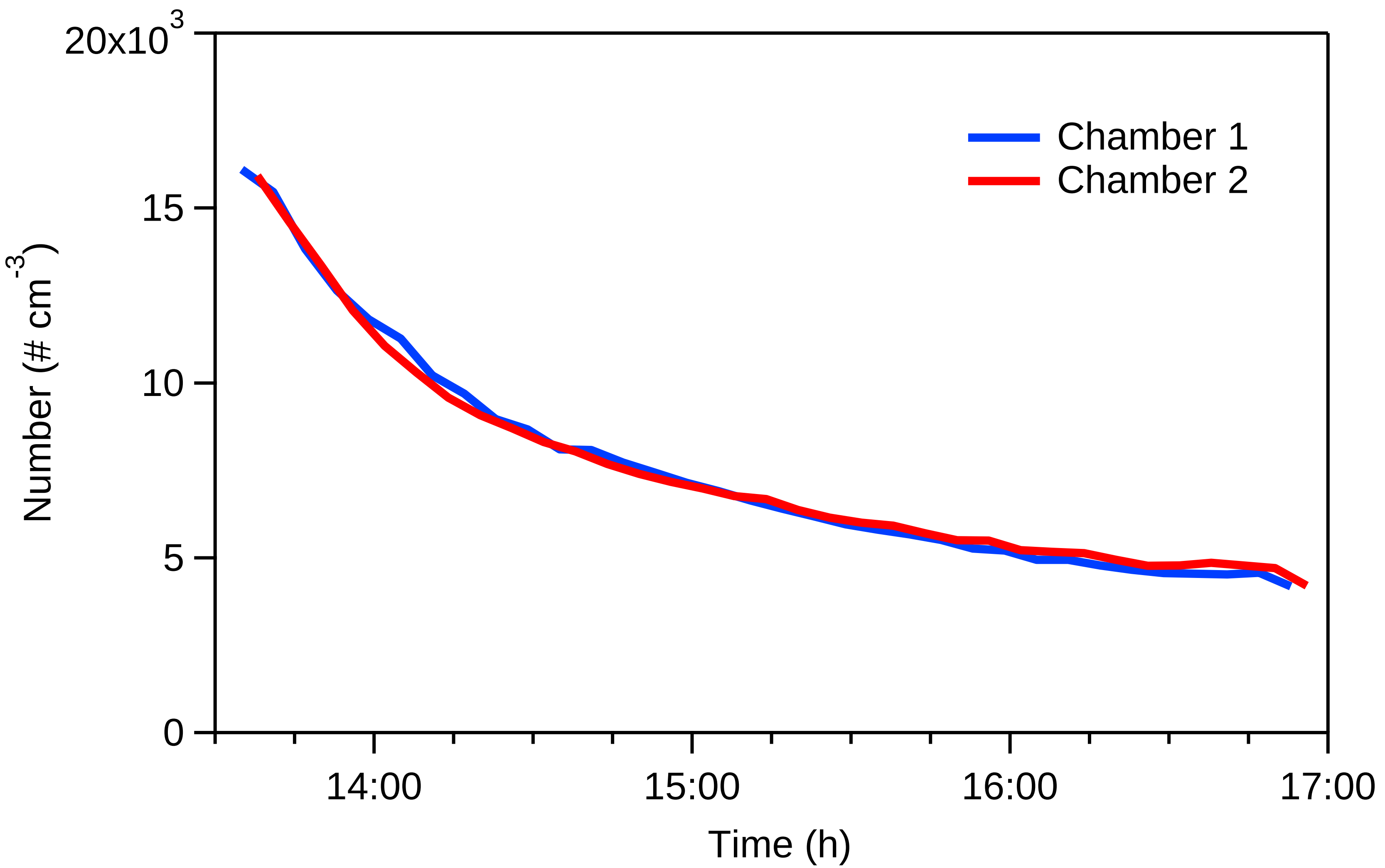




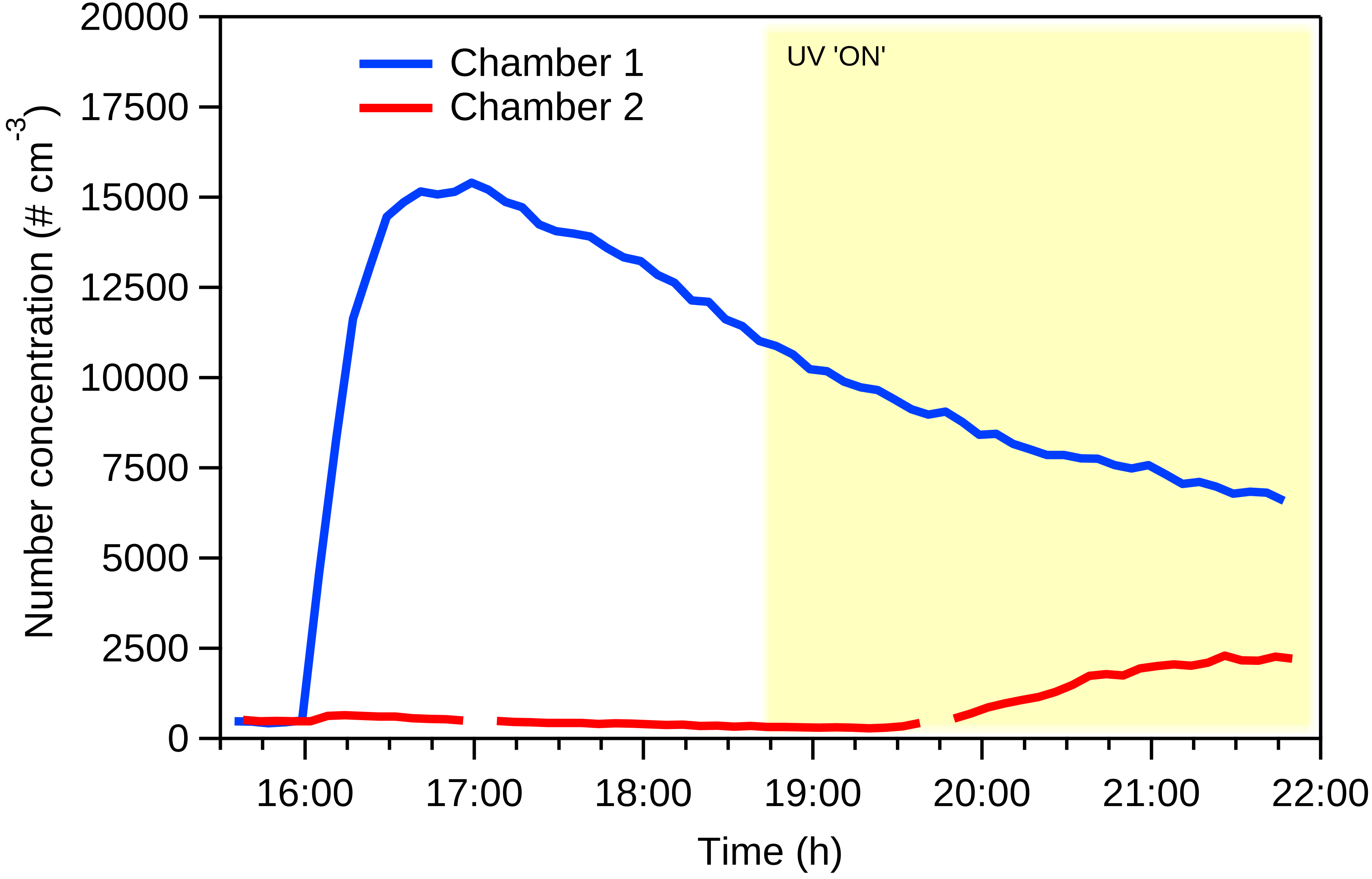
Instrumentation in Mobile Laboratory

Mobile Smog Chambers

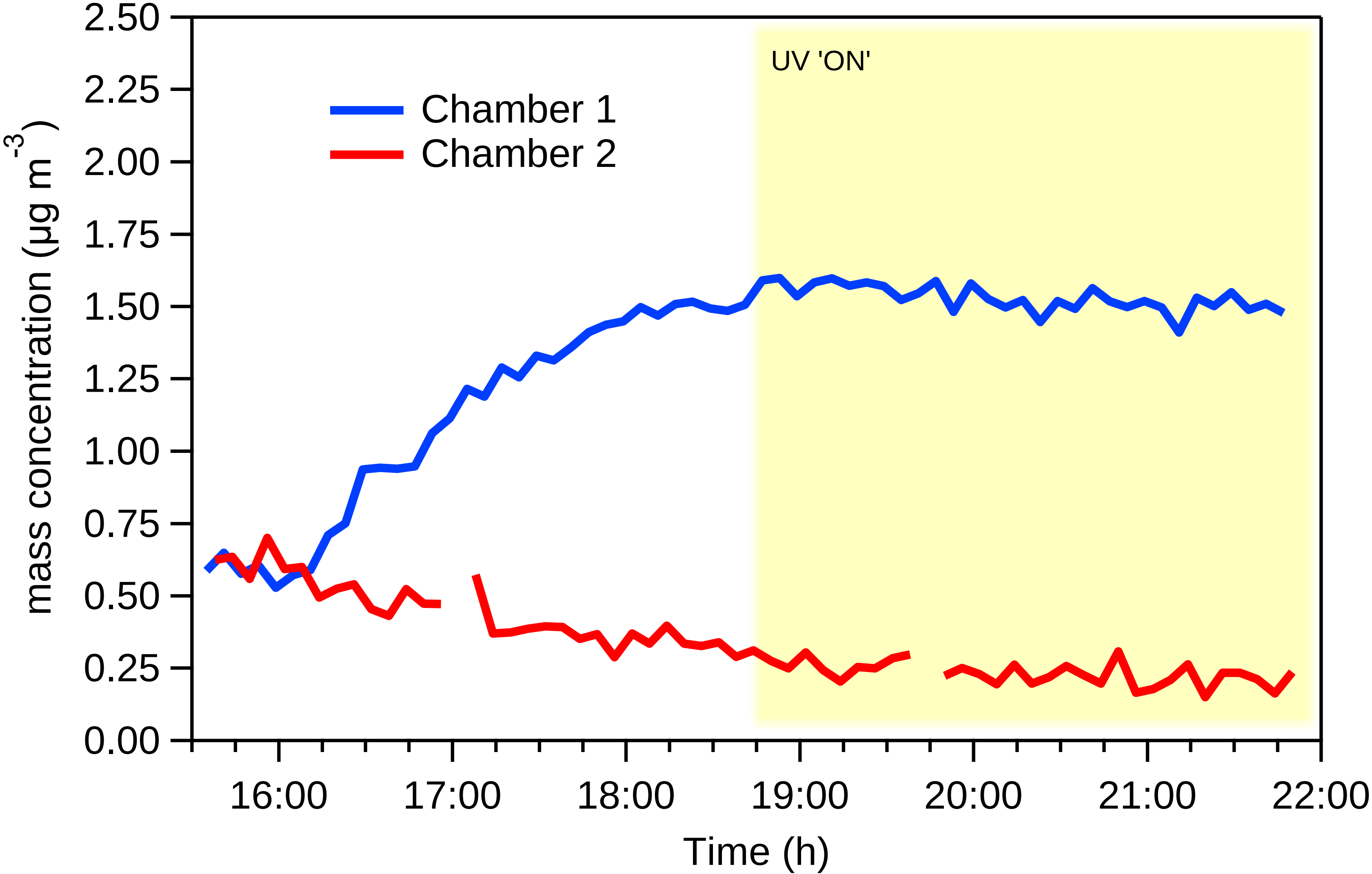
Baseline Characterization



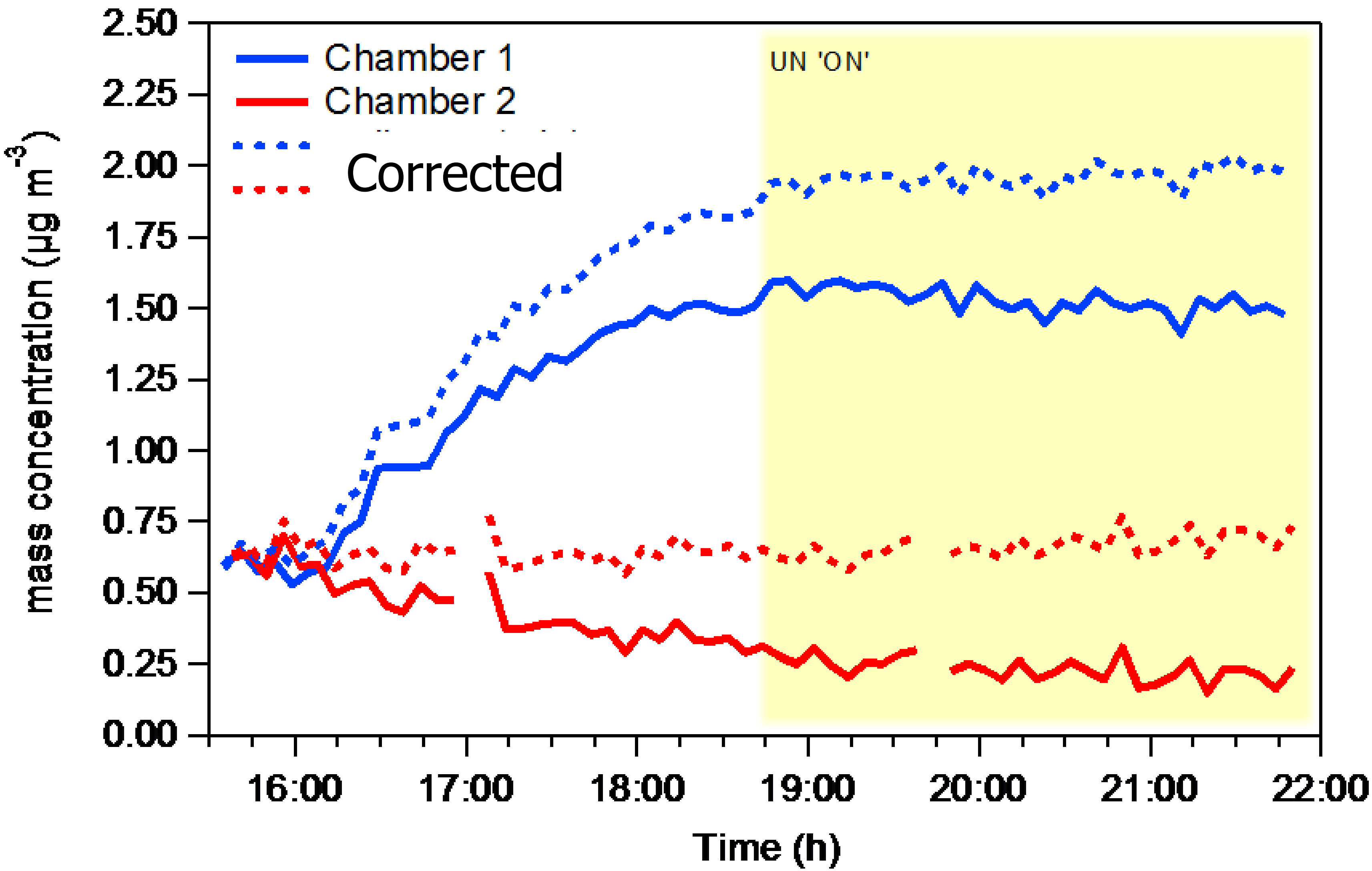
α-Pinene Addition to Chamber 1



OA Mass Concentration
(a-pinene addition)

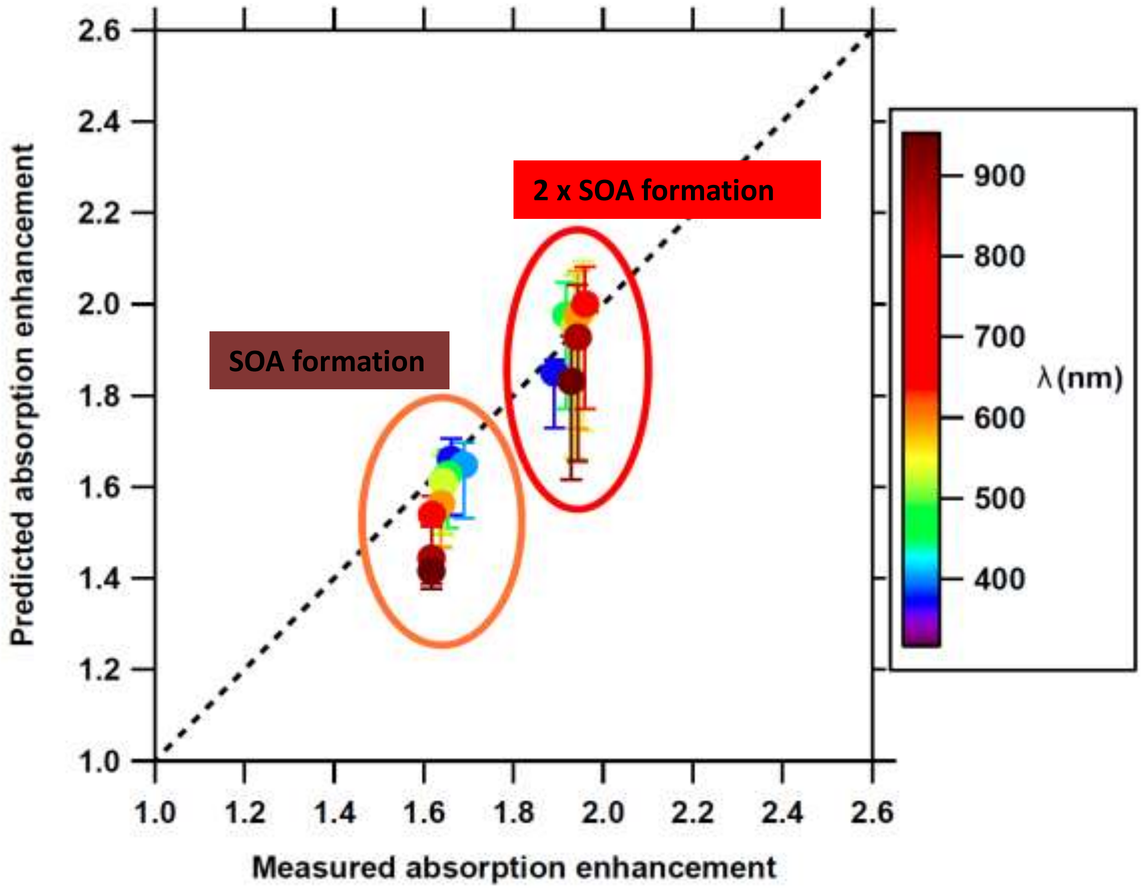


Wall-Loss Corrected OA Concentrations



Absorption by SOA+BC

Comparison of Mie theory with measurements



The D-toluene SOA - soot particles have core shell morphology and their absorption is consistent with Mie theory predictions.

PMCAMx Evaluation
Summer 2012, Italy

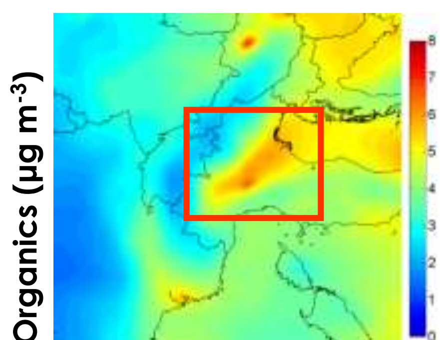
OA in a Polluted Area (Po Valley, Italy)

Extensive AMS measurements from 6 June until 8 July 2012

➢ **Ground measurements**

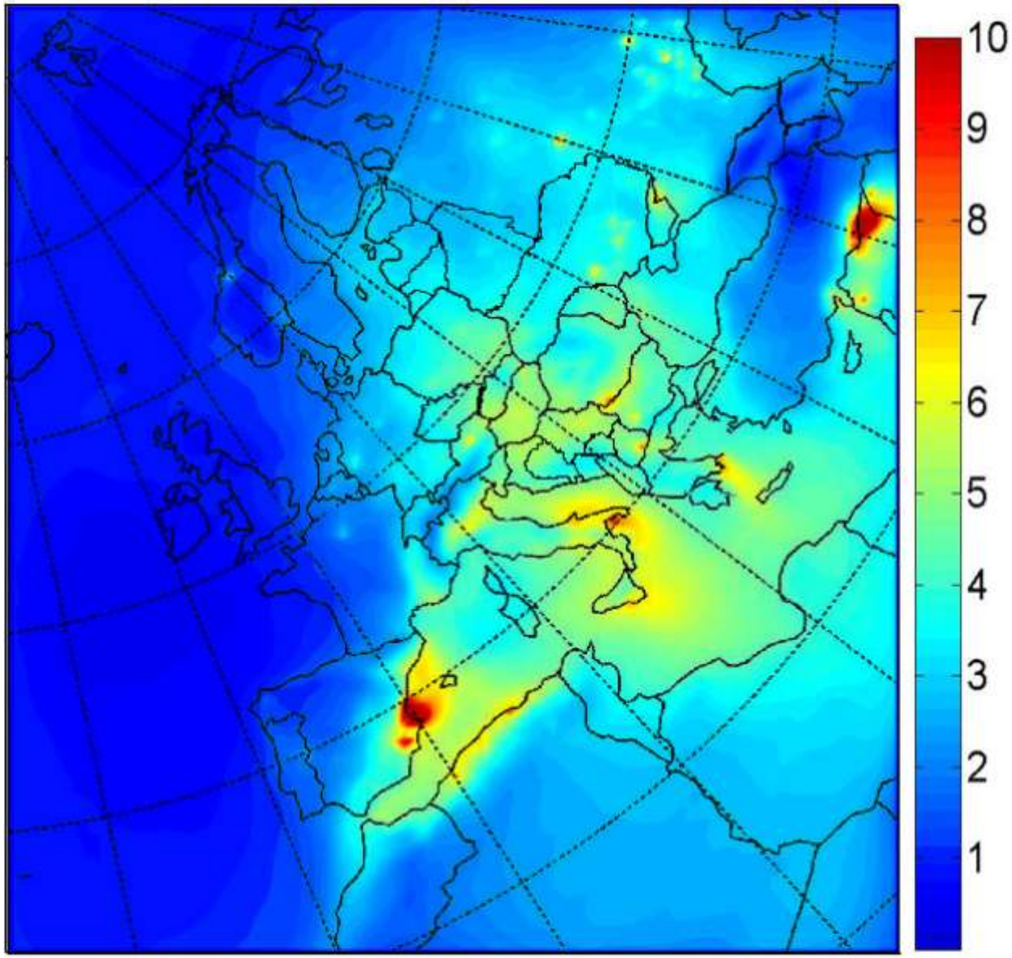
➢ **Zeppelin measurements**

- Central site of the PEGASOS 2012 campaign
- Rural area in Po Valley
- **Agricultural** sources
- **Industrial** sources



PMCAMx

Application of PMCAMx over Europe



OA (μg m^{-3}), June – July 2012

Europe

5400 × 5832 km^2 region

36 × 36 km^2 grid resolution

14 vertical layers (up to 6 km)

Meteorology

WRF

Emissions

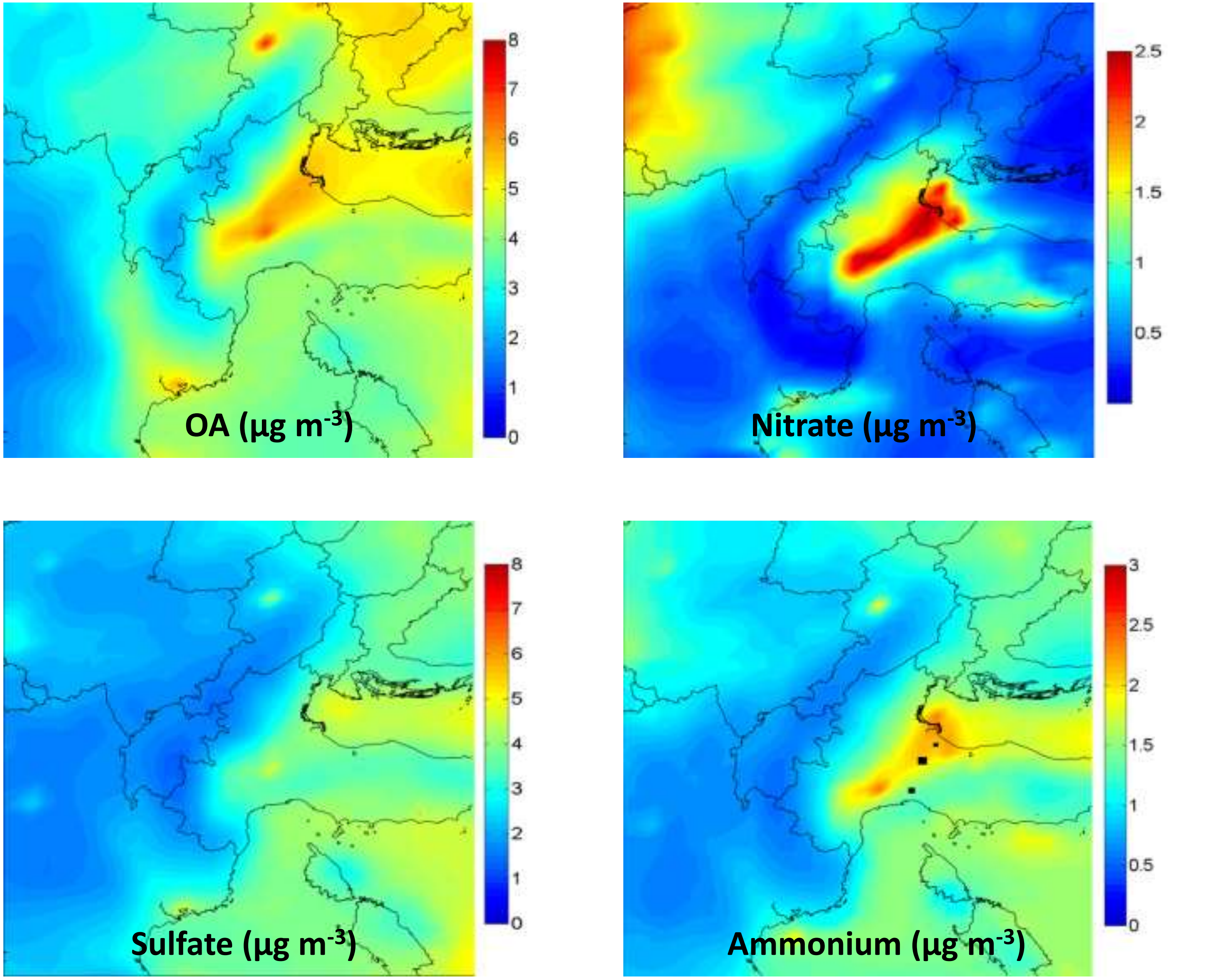
Anthropogenic (TNO – GEMS)

Biogenic (MEGAN)

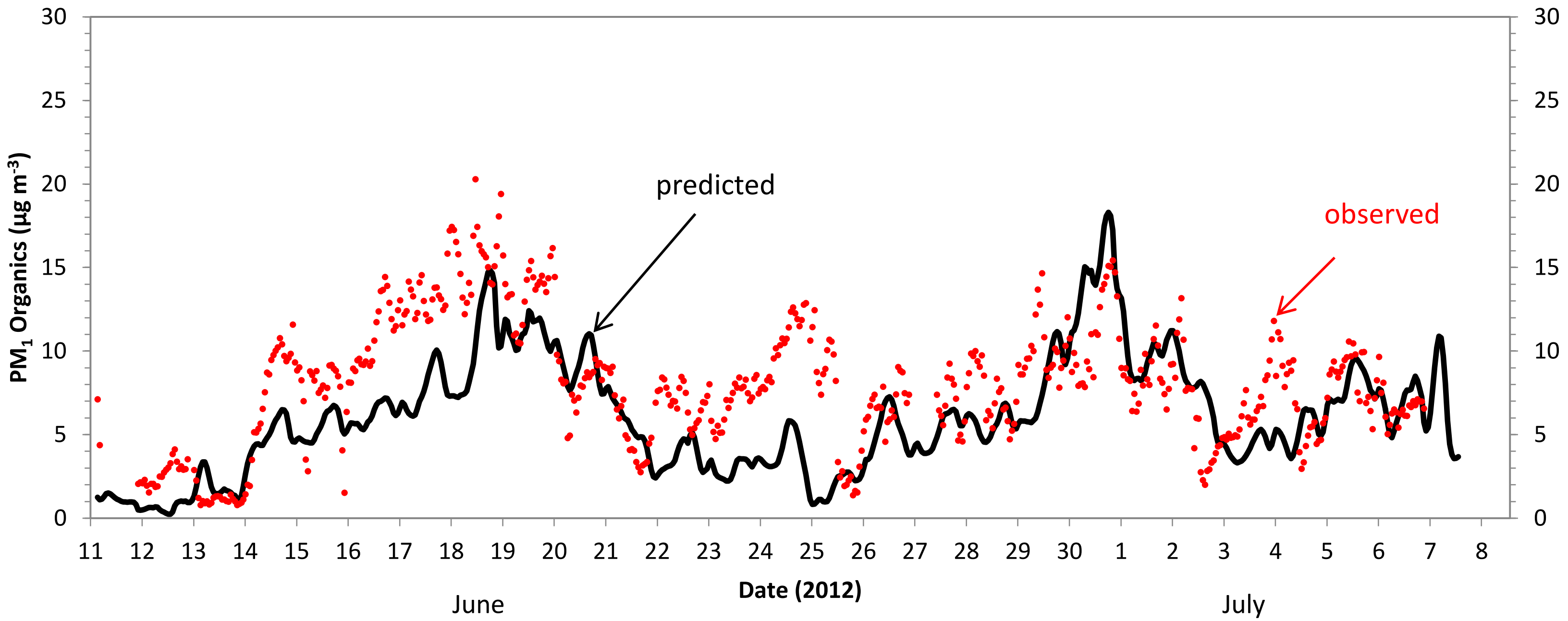
SAPRC-99

Volatility basis-set

Predicted $PM_{2.5}$ concentrations – Summer 2012



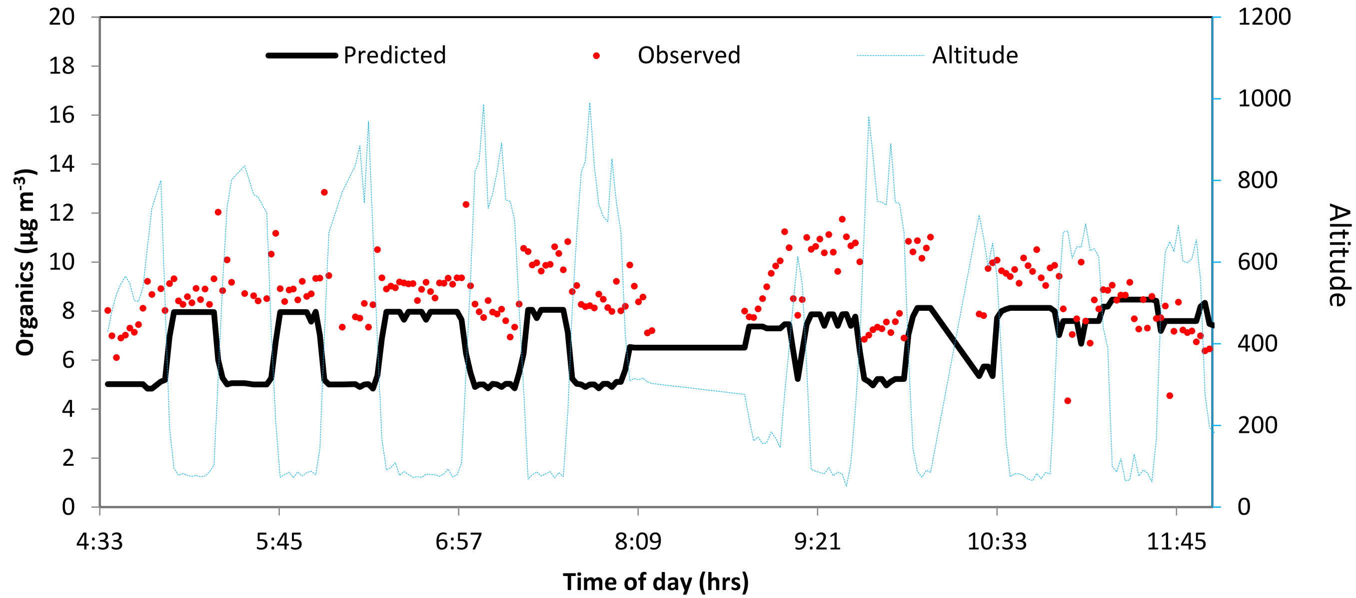
PM$_1$ Organics (µg m^{-3}) – Bosco Fontana



Mean predicted: 6.07 µg m^{-3}
Mean observed(AMS): 8.10 µg m^{-3}

Comparisons with zeppelin observations - OA

20/6



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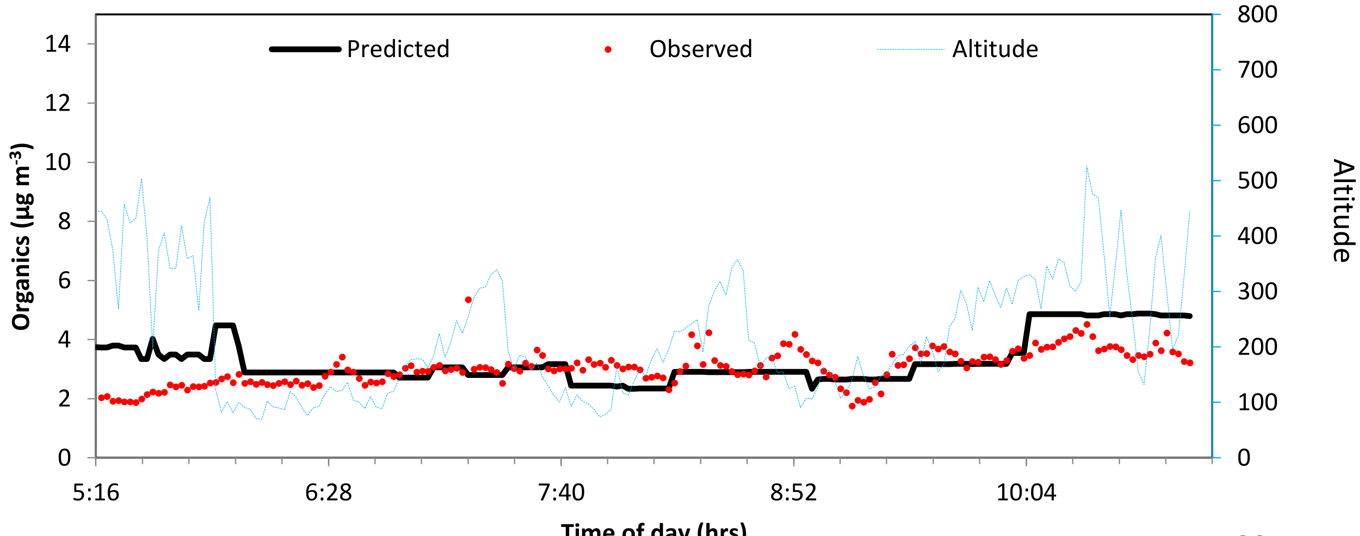
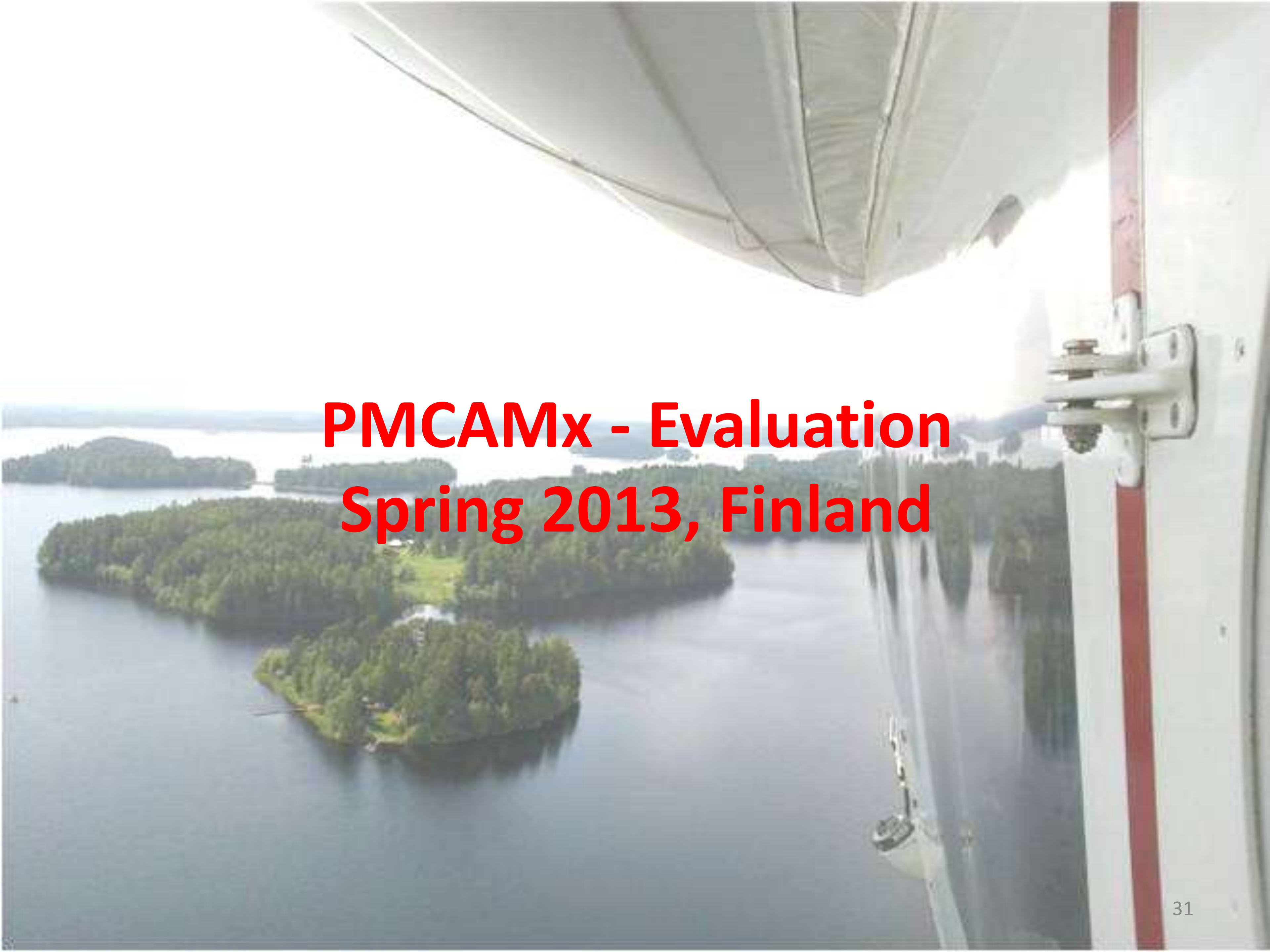
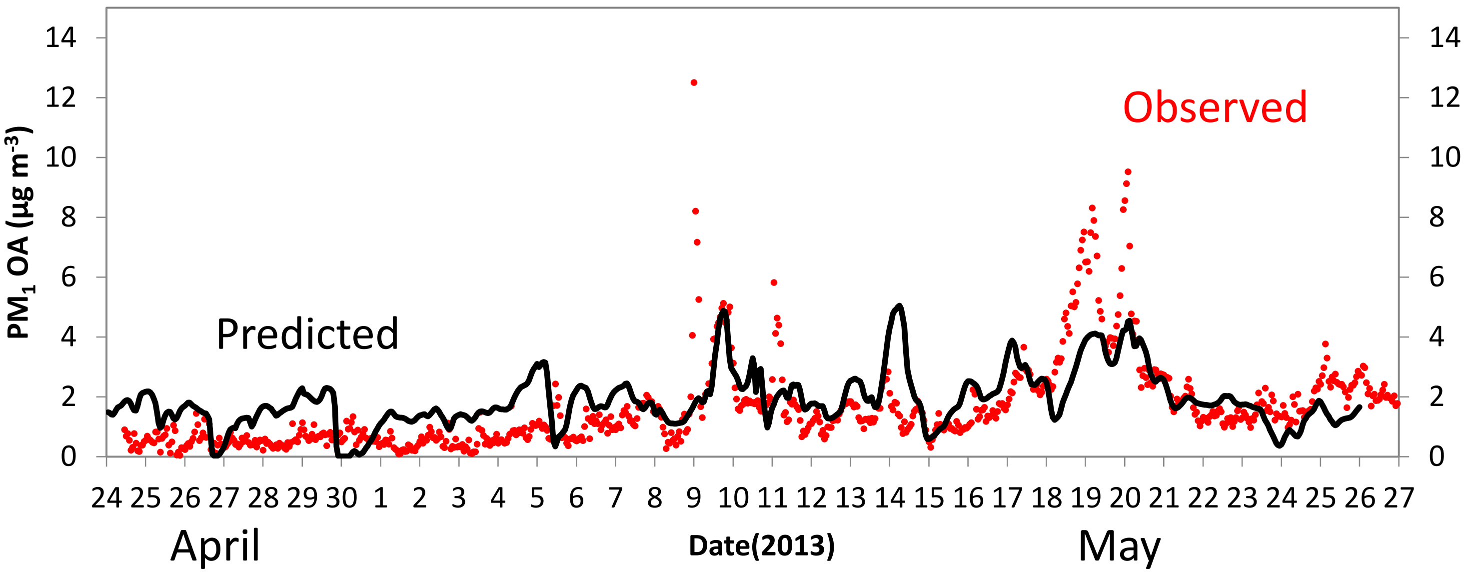
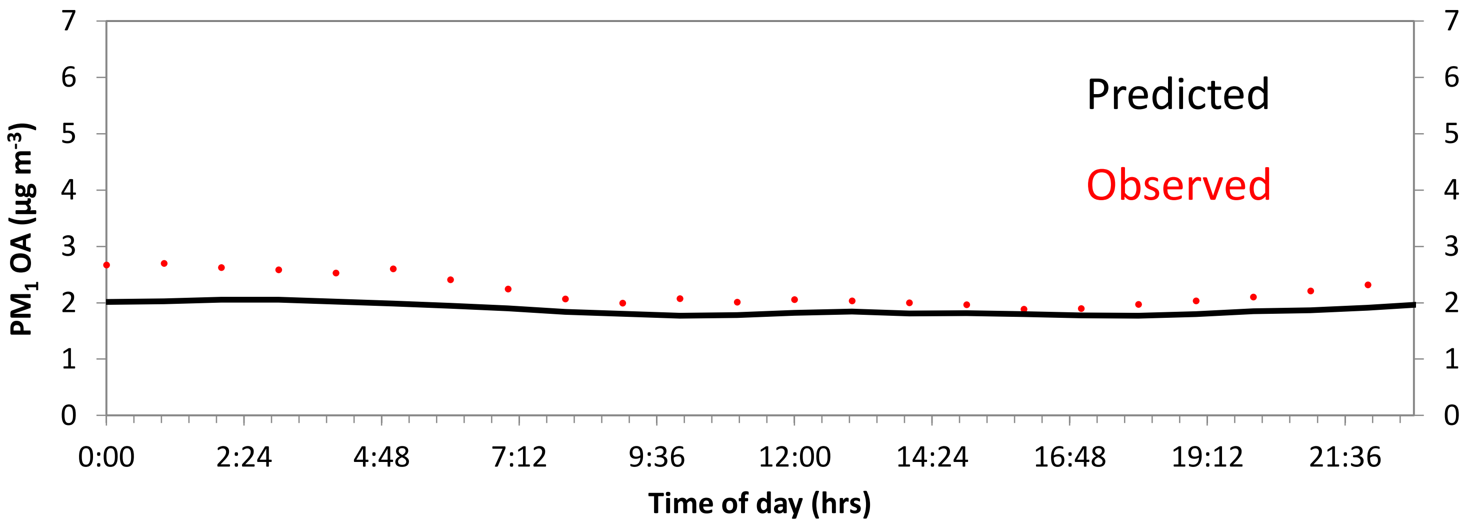




PMCAMx - Evaluation
Spring 2013, Finland

PM$_1$ Organics (μg m^{-3}) - Finland

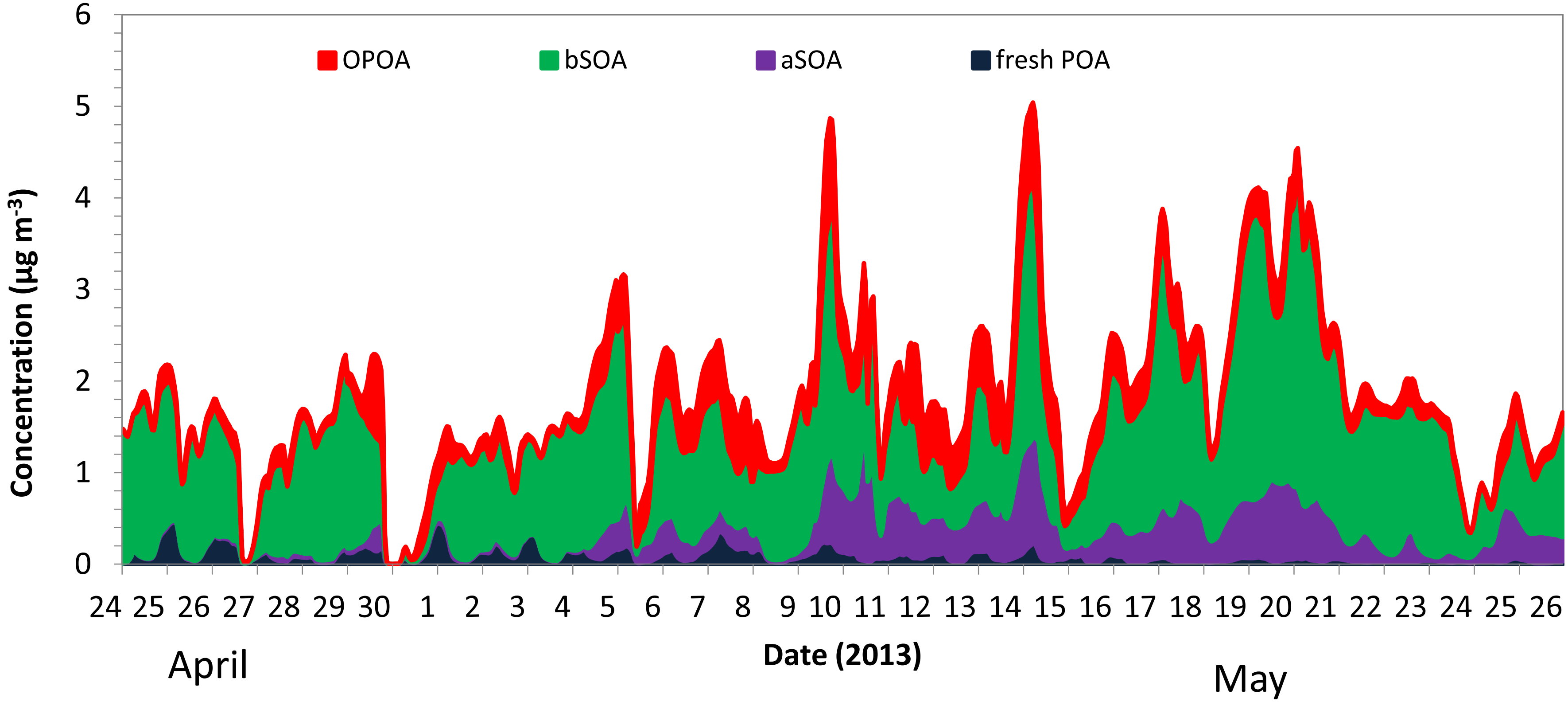




Predicted : 1.9 μg m^{-3}

Observed : 2.1 μg m^{-3}

Diurnal OA Sources - Finland



aSOA mean predicted = 0.3 µg m^{-3}

bSOA mean predicted =1.2 µg m^{-3}

Fresh POA mean predicted = 0.1 µg m^{-3}

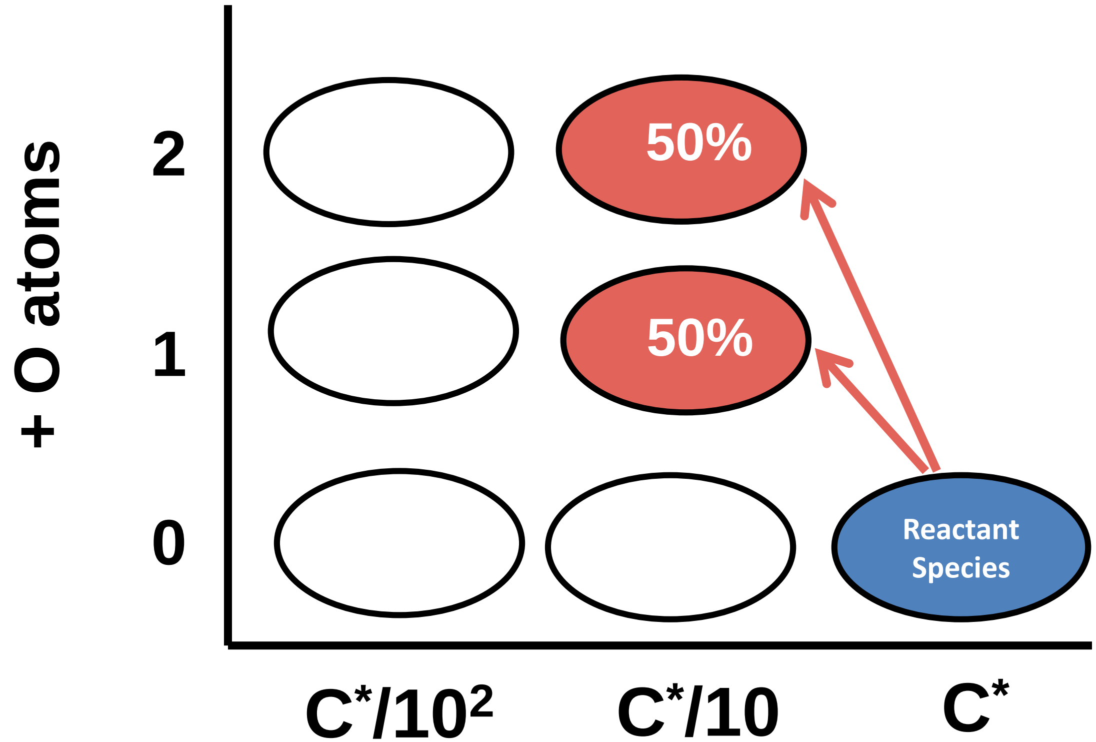
Oxygenated POA mean predicted = 0.3 µg m^{-3}

PMCAMx-Evaluation

1-D Trajectory 2-D VBS Version

Homogeneous chemical aging (with OH) Simple Functionalization- Base case

(Murphy et al., ACP, 2011)

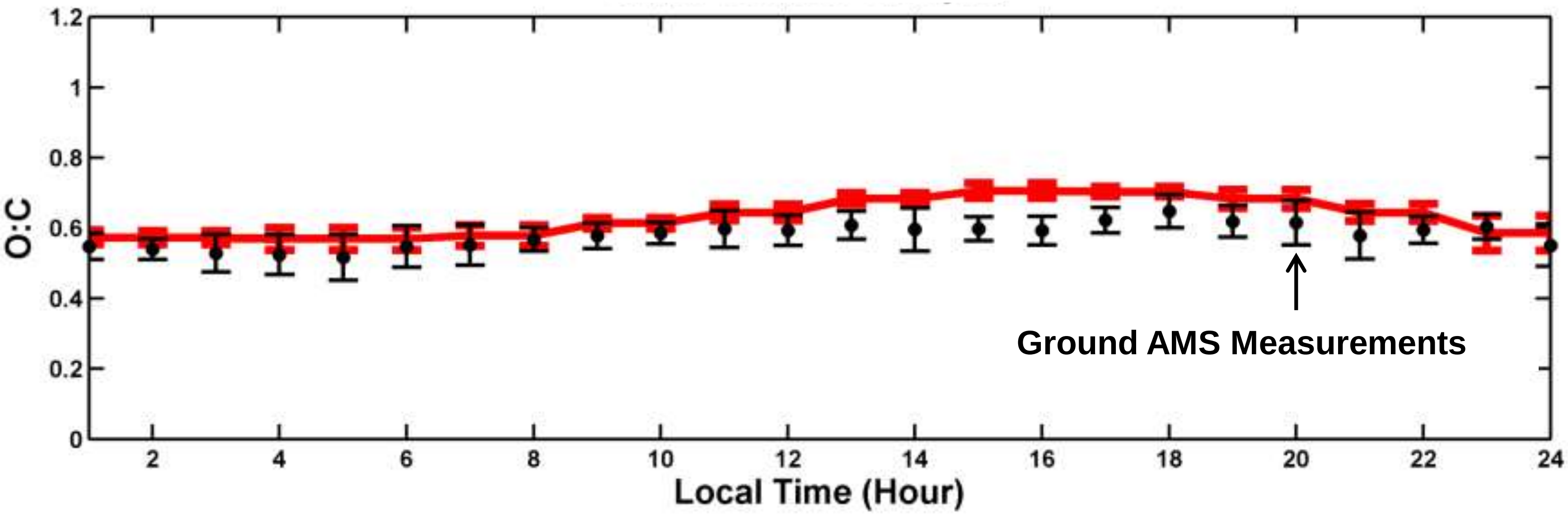


Reaction constants:

- **$k_{OH} = 1 \cdot 10^{-11}$ cm³ molec⁻¹s⁻¹** for aSOA and bSOA
- **$k_{OH} = 4 \cdot 10^{-11}$ cm³ molec⁻¹s⁻¹** for SOA-sv, SOA-iv

negligible bSOA aging

Average Diurnal O:C
(San Pietro Capofiume, Italy)

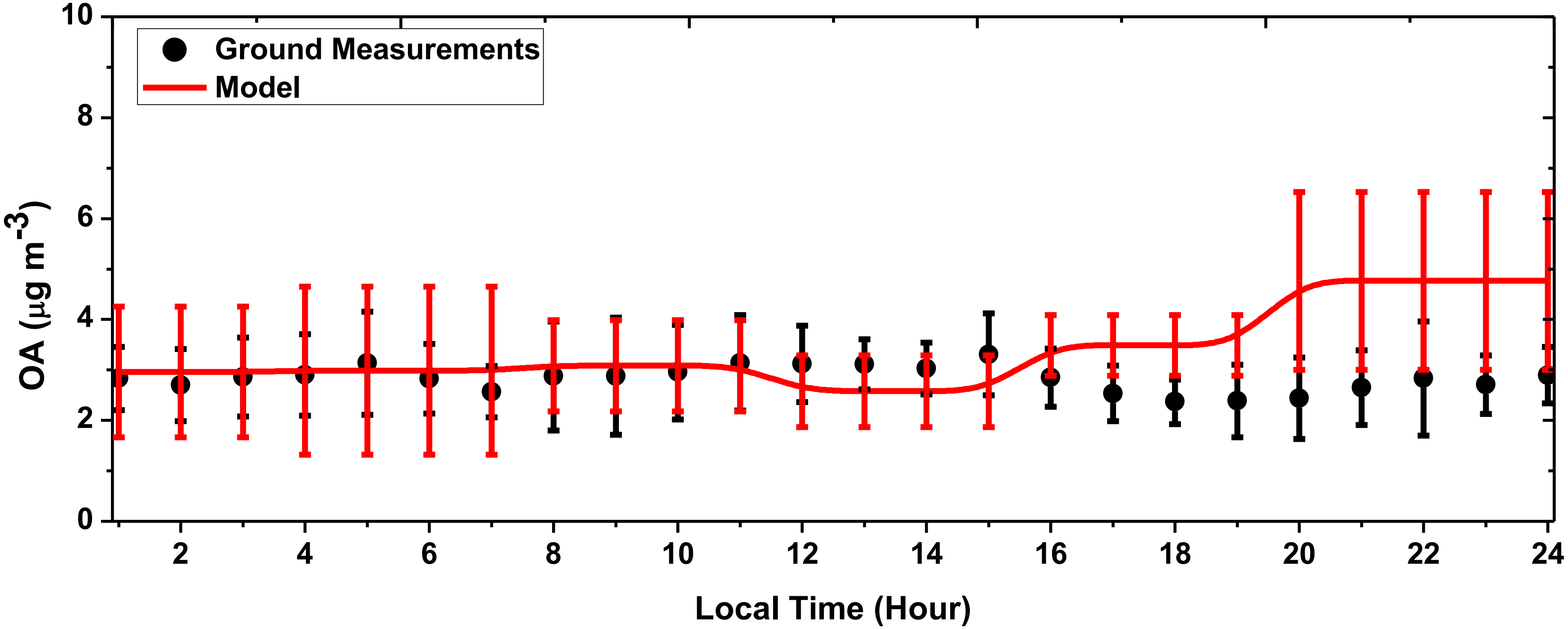


Average measured O:C = 0.58

Average predicted O:C = 0.62

Average Diurnal OA Concentration

(San Pietro Capofiume, Italy)

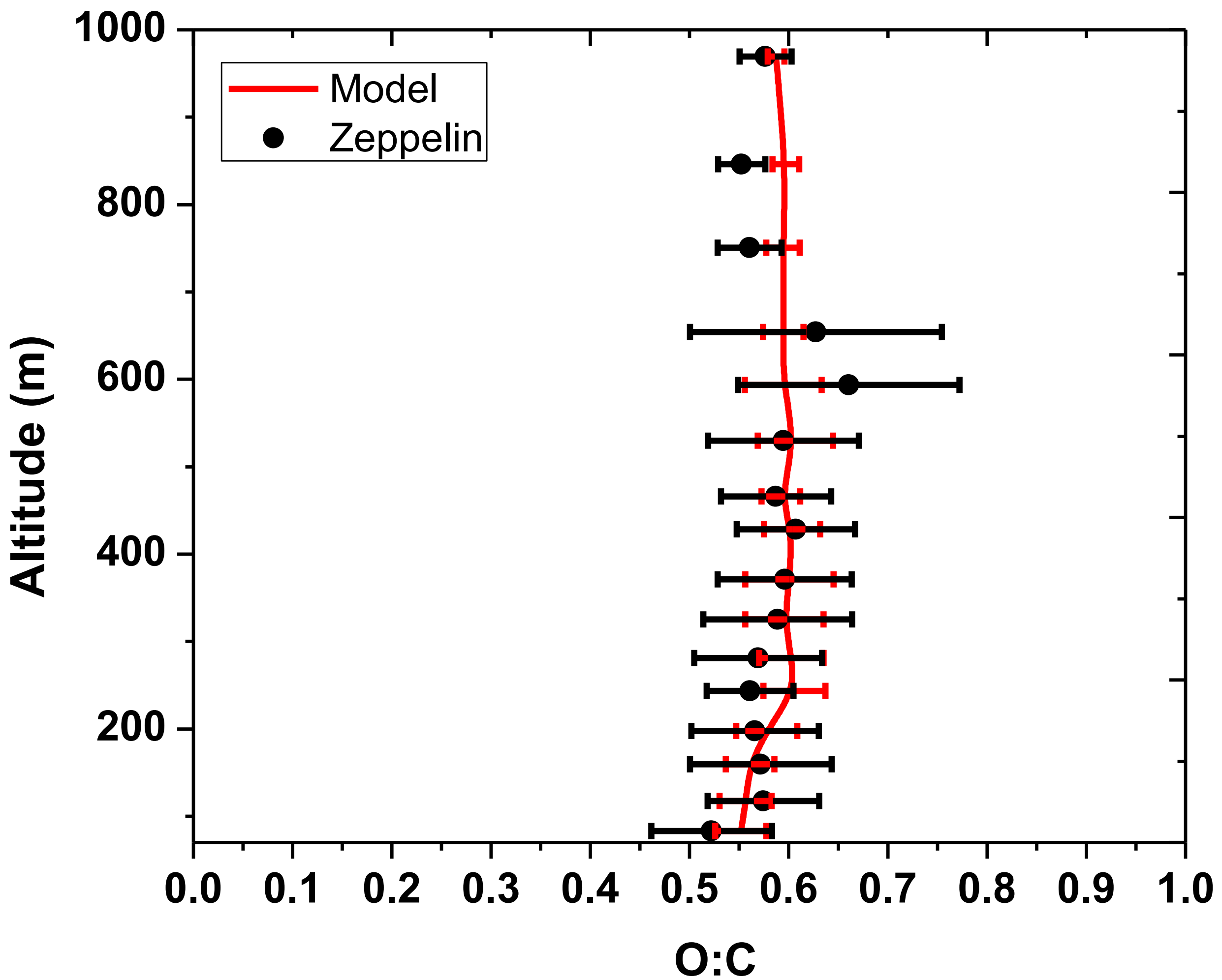


Average measured OA = 2.8 µg m^{-3}

Average predicted OA = 3.4 µg m^{-3}

Average Vertical O:C Profile

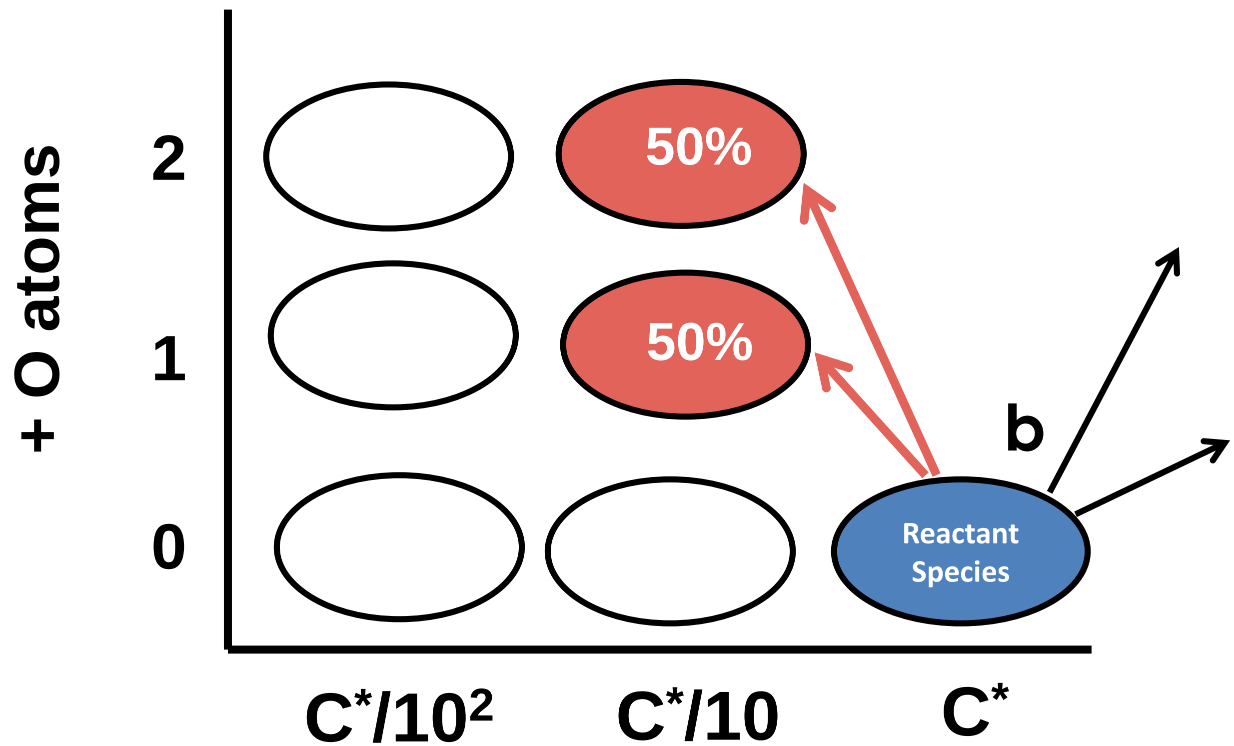
(All Zeppelin flights)



Average measured O:C = 0.58

Average predicted O:C = 0.59

Homogeneous chemical aging (with OH) Functionalization- Fragmentation

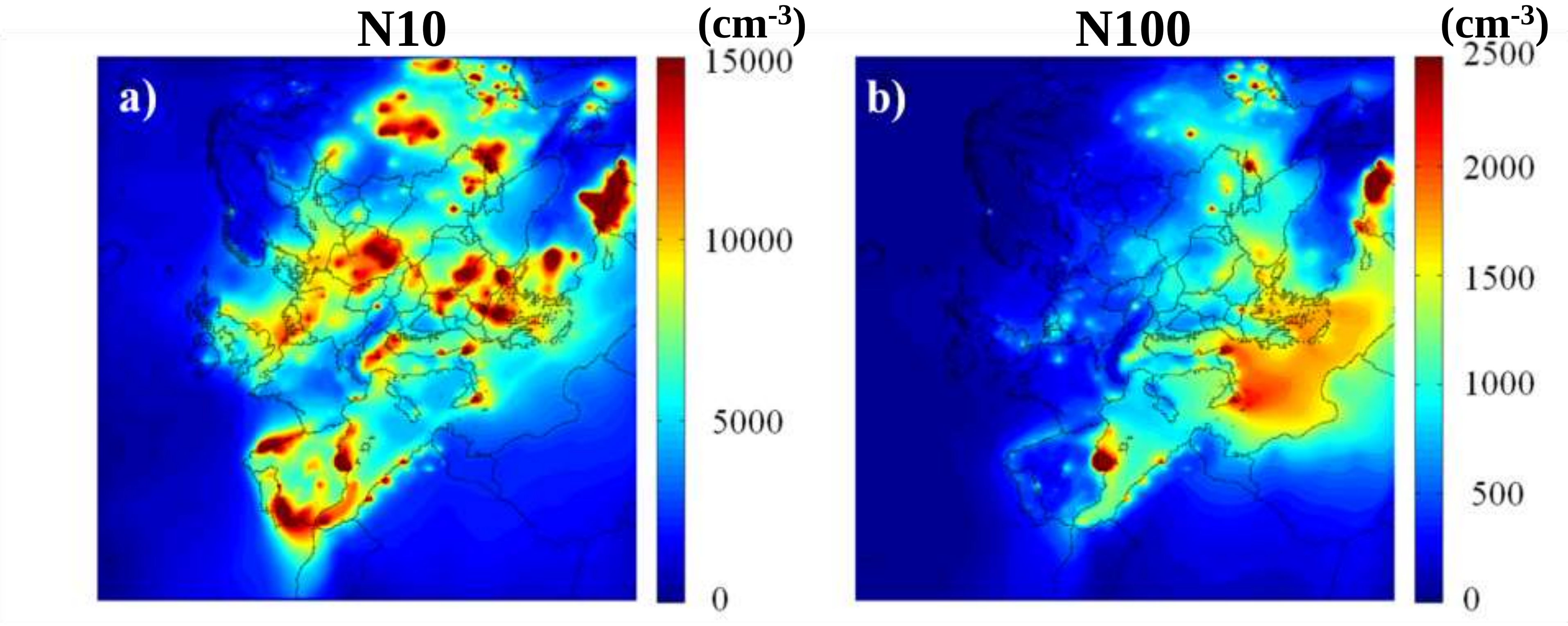


SOA Effects on Particle Number

Particle number concentration fields

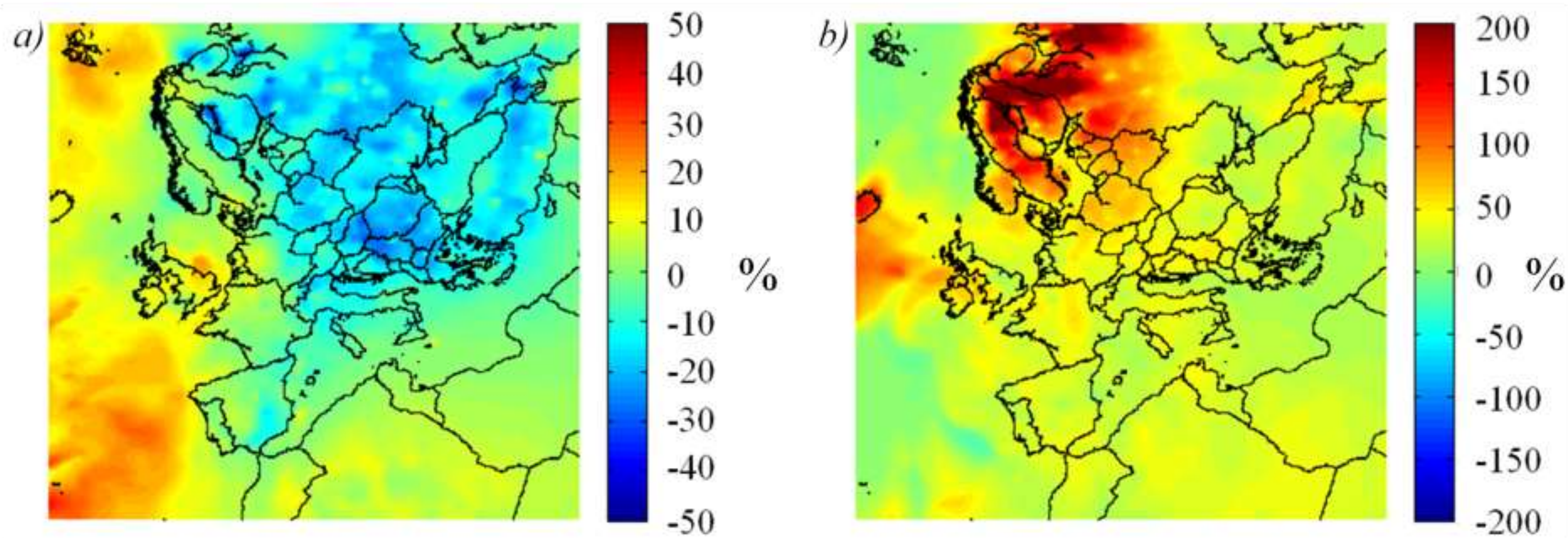
(June 2012)

Without organic condensation



Changes due to condensation of organic vapors (no chemical aging)

N10 **N100**

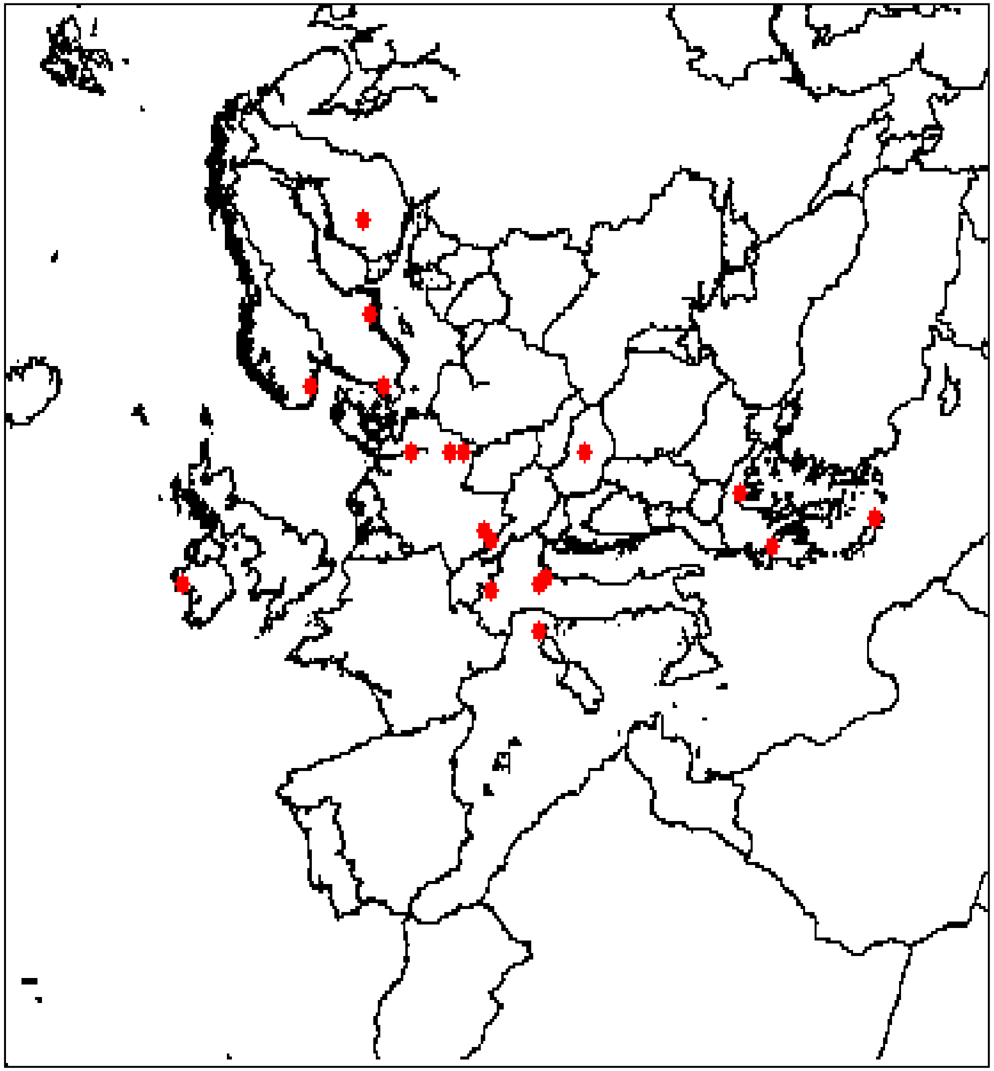


$$\% = 100\,\frac{ORG - NO\,ORG}{NO\,ORG}$$

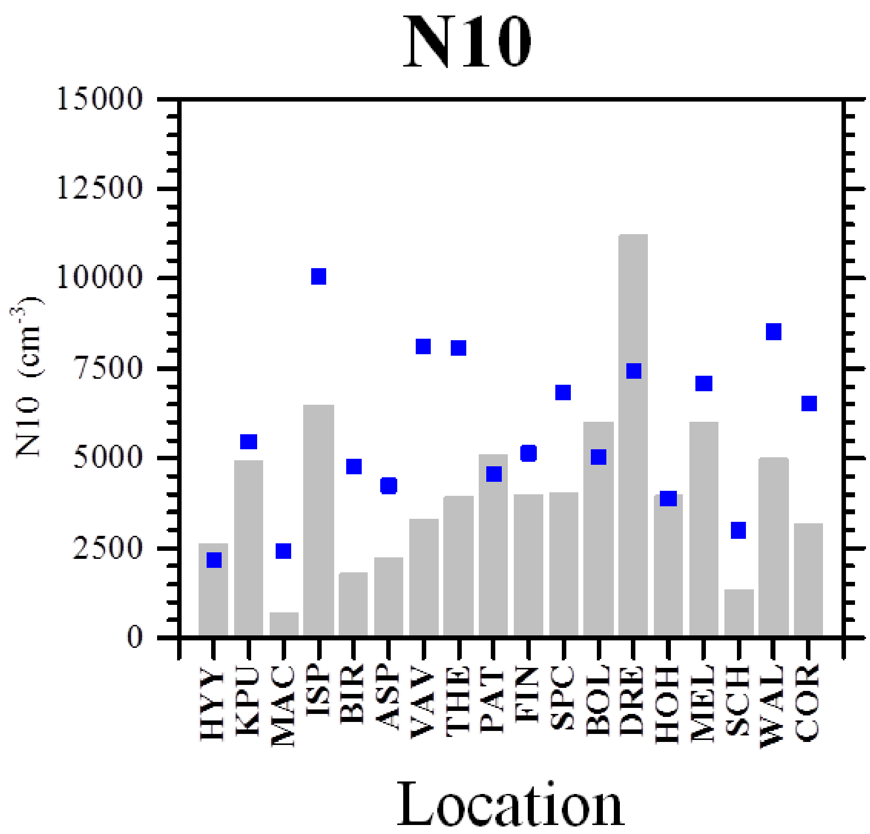
Comparison with field observations

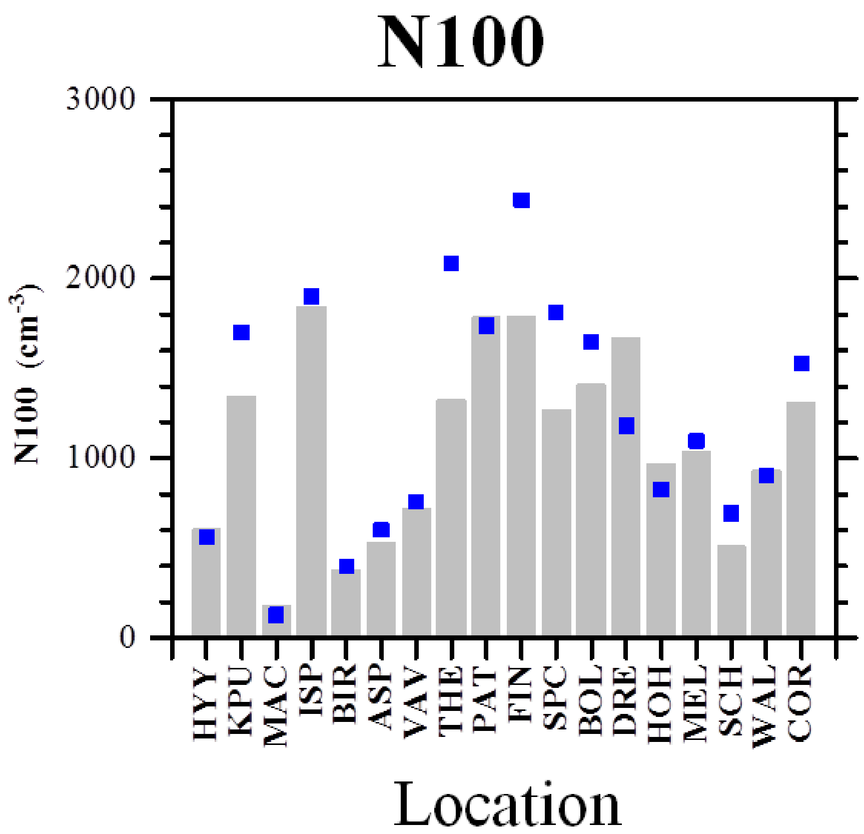
- **Ground stations:**

BIRkenes	- Norway
MACe Head	- Ireland
HYYtiala	- Finland
K-PUszta	- Hungary
CORsica	- France
ASPvreten	- Sweden
VAVhill	- Sweden
ISPra	- Italy
San **P**ietro **C**apofiume	- Italy
BOLogna	- Italy
PATra	- Greece
FINokalia	- Greece
THEssaloniki	- Greece
DREsden	- Germany
HOHenpeissenberg	- Germany
MELpitz	- Germany
SCHneefernerhaus	- Germany
WALdhof	- Germany



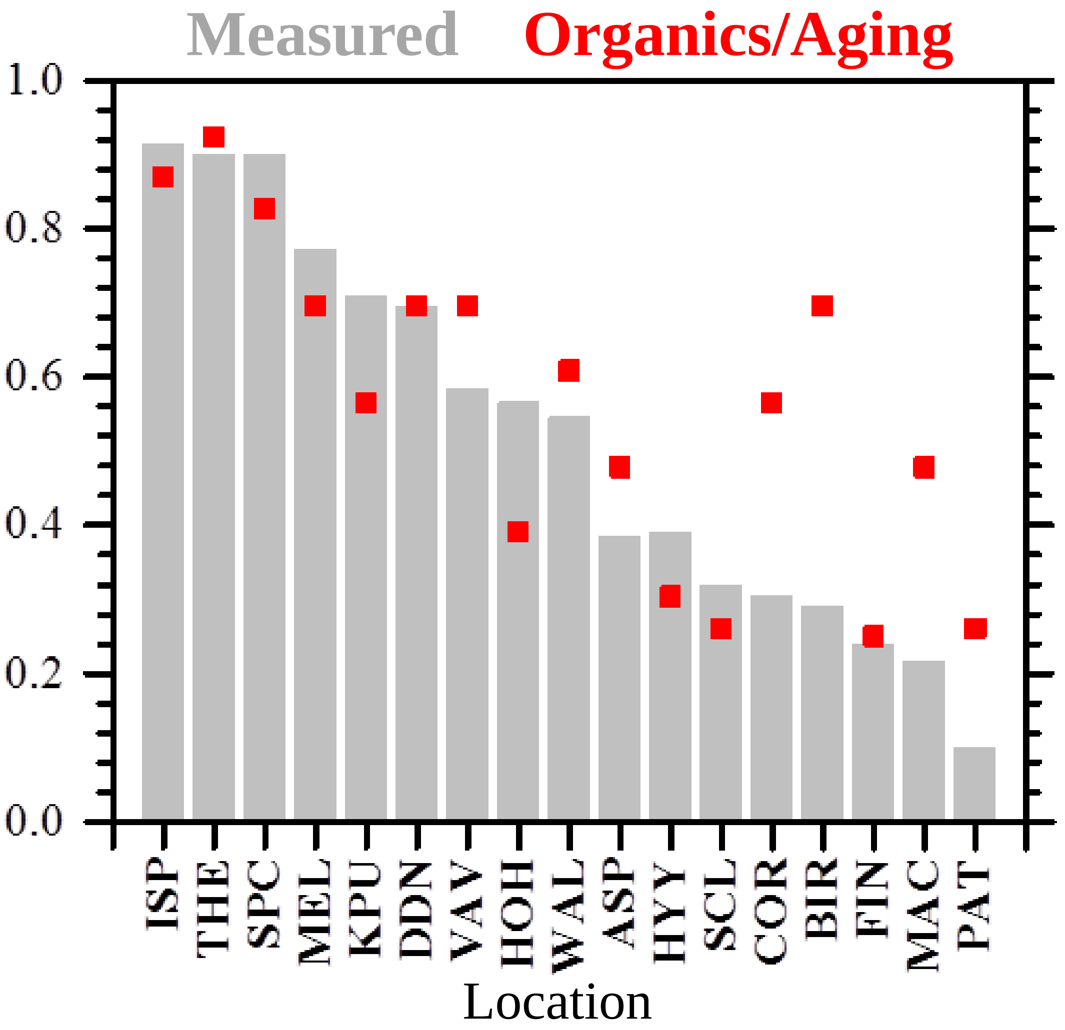
Evaluation of PMCAMx-UF





Measured With organics and aging

Nucleation Frequency (June 2012)



Conclusions

- Rapid mixing of aromatic and biogenic SOA for RH exceeding 20%
  - Reductions of anthropogenic SOA will help reduce biogenic SOA
- Small change in biogenic SOA produced under low NO_x conditions as it keeps reacting with OH
- Significant later generation production of SOA if the first generation of reactions has taken place under high NO_x conditions.
- Results of MBTCA oxidation by OH and ambient perturbation experiments consistent with the above conclusions.
- Condensation of SOA on BC containing particles increases absorption by as much as a factor of two.
  - Core-shell Mie theory model reproduces this effect

Conclusions

- Updated PMCAMx predictions for a polluted area with both anthropogenic and biogenic influences consistent with the simple VBS parameterizations of SOA formation and chemical aging.
- A number of 2-D VBS schemes can explain OA and O:C observations.
- Additional constraining expected from ongoing application of PMCAMx to the SOAS campaign.
- SOA condensation leads often to reduction of particle number but to increases of the CCN concentrations.
  - Significant progress in simulating particle number concentrations
- Future work: Estimation of effects of controls of anthropogenic emissions on biogenic and anthropogenic OA in the Eastern US.

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- Colleagues

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Publications

- Donahue N. M., W. Chuang, S. A. Epstein, J. H. Kroll, D. R. Worsnop, A. L. Robinson, P. J. Adams, and S. N. Pandis (2014) Why do organic aerosols exist? Understanding aerosol lifetimes using the 2D VBS, Environ. Chem., 10, 151-157.
- Murphy B. N., N. M. Donahue, A. L. Robinson, and S. N. Pandis (2014) A naming convention for atmospheric organic aerosol, Atmos. Chem. Phys., 14, 5825-5839.
- Tasoglou A. and S. N. Pandis (2014) Formation and chemical aging of secondary organic aerosol during the b-caryophyllene oxidation, Atmos. Chem. Phys., 15, 6035-6046.
- Hildebrandt-Ruiz L., A. Paciga, K. Cerully, A. Nenes, N. M. Donahue, and S. N. Pandis (2014) Formation and aging of secondary organic aerosol from toluene: changes in chemical composition, volatility, and hygroscopicity, Atmos. Chem. Phys., 15, 8301-8313.
- Day M. C., M. Zhang, and S. N. Pandis (2015) Evaluation of the ability of the EC tracer method to estimate secondary organic aerosol carbon, Atmos. Environ., 112, 317-325.
- Pandis S. N., K. Skyllakou, K. Florou, E. Kostenidou, E. Hasa, and A. A. Presto (2015) Urban particulate matter pollution: A tale of five cities, Faraday Discussions, in press.
- Ye Q., E. S. Robinson, X. Ding, P. Ye, R. C. Sullivan, and N. M. Donahue (2016) Secondary organic aerosols are crunchy when dry but runny when wet, submitted.
- Tasoglou A., G. Saliba, R. Subramanian, and S. N. Pandis (2016) Absorption of chemically aging biomass burning carbonaceous aerosol, to be submitted.
- Wang N., E. Kostenidou, N. M. Donahue, and S. N. Pandis (2015) Chemical aging of a-pinene first-generation ozonolysis products by reactions with OH: I: Low NOx conditions, in prep.
- Kaltsonoudis C., E. Kostenidou, E and S. N. Pandis (2015) Development and evaluation of a mobile dual two-chamber system for atmospheric field perturbation experiments, in prep.
- Karnezi E. and S. N. Pandis (2015) Simulation of organic aerosol formation in a polluted area with the 2-D Volatility Basis Set, in preparation.