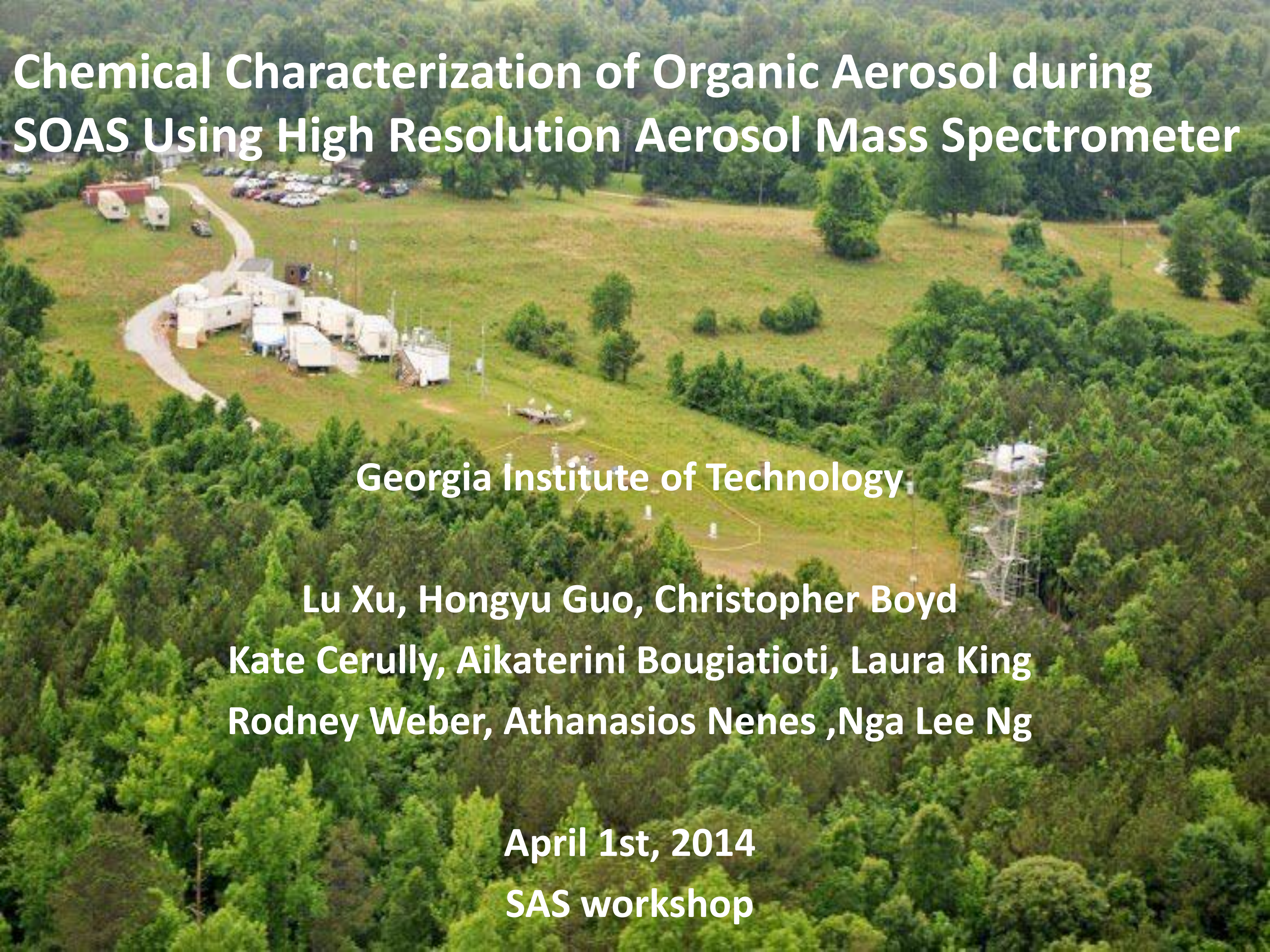

# Chemical Characterization of Organic Aerosol during SOAS Using High Resolution Aerosol Mass Spectrometer

Georgia Institute of Technology

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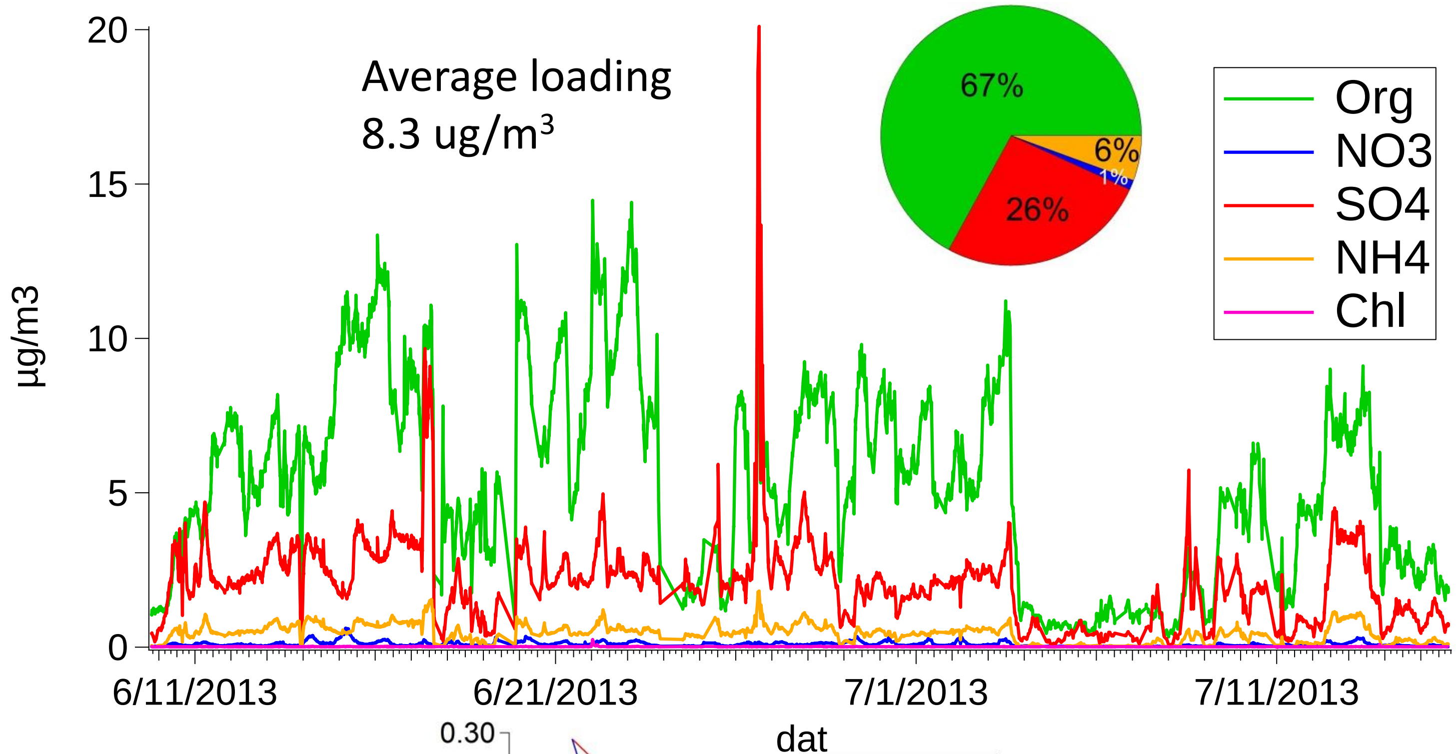
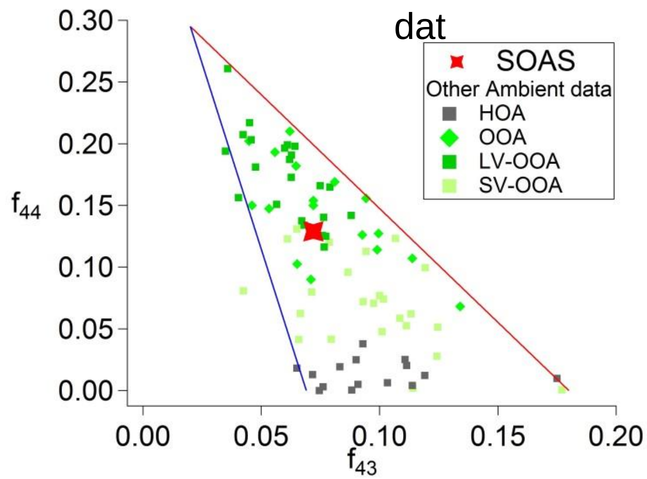
Kate Cerully, Aikaterini Bougiatioti, Laura King
Rodney Weber, Athanasios Nenes ,Nga Lee Ng

April 1st, 2014
SAS workshop

# Ambient Non-refractory PM1 composition

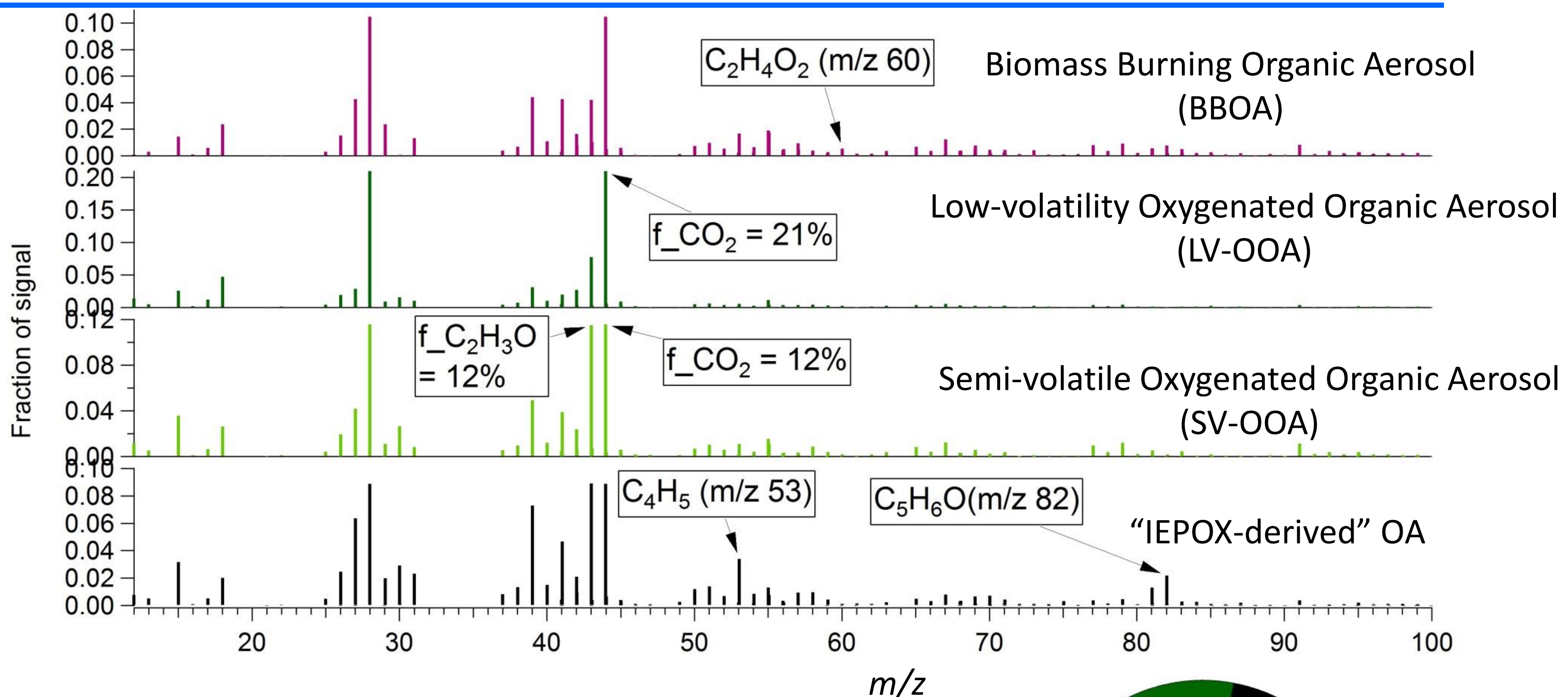
## (High-Resolution Time-of-Flight Aerosol Mass Spectrometer)

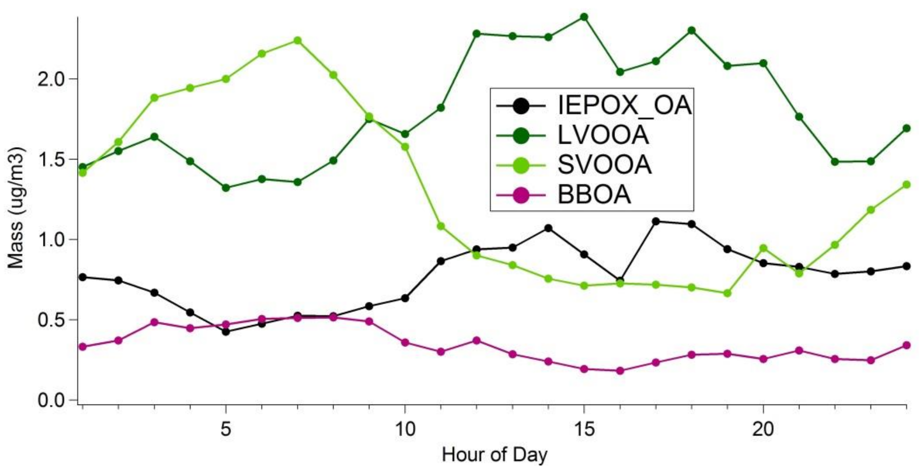


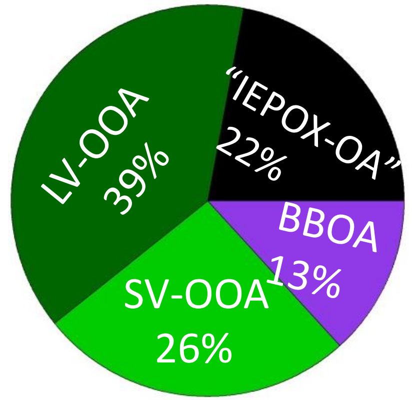




Ng et al., 2010 ACP

# Positive Matrix Factorization (PMF) – ambient total OM



# PMF factors correlation

*All OA factors are correlated with at least one anthropogenic component*

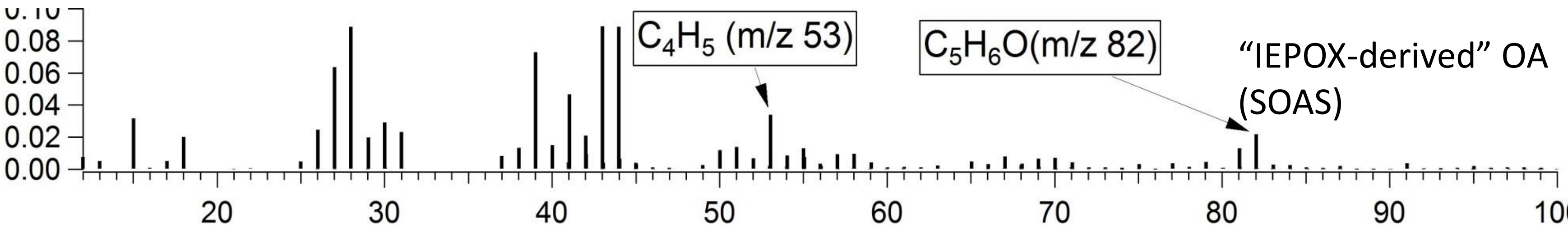
*Table. R between species*

| | $SO_4^{2-}$ | AMS $NO_3^-$ | $NO_x$ | BC | $O_3$ | BrnC |
|---|---|---|---|---|---|---|
| "IEPOX_OA" | **0.79** | 0.12 | -0.06 | 0.38 | 0.30 | 0.26 |
| SVOOA | 0.11 | **0.81** | **0.61** | 0.46 | -0.22 | 0.43 |
| LVOOA | 0.42 | 0.33 | 0.01 | **0.61** | **0.61** | 0.44 |
| BBOA | 0.34 | 0.67 | 0.39 | **0.70** | 0.14 | **0.74** |

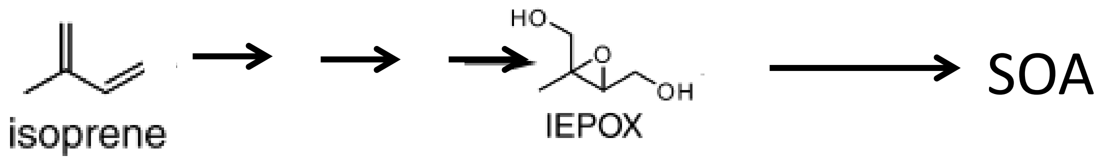
Weber et al, JGR 2007 → WSOC correlates with CO.

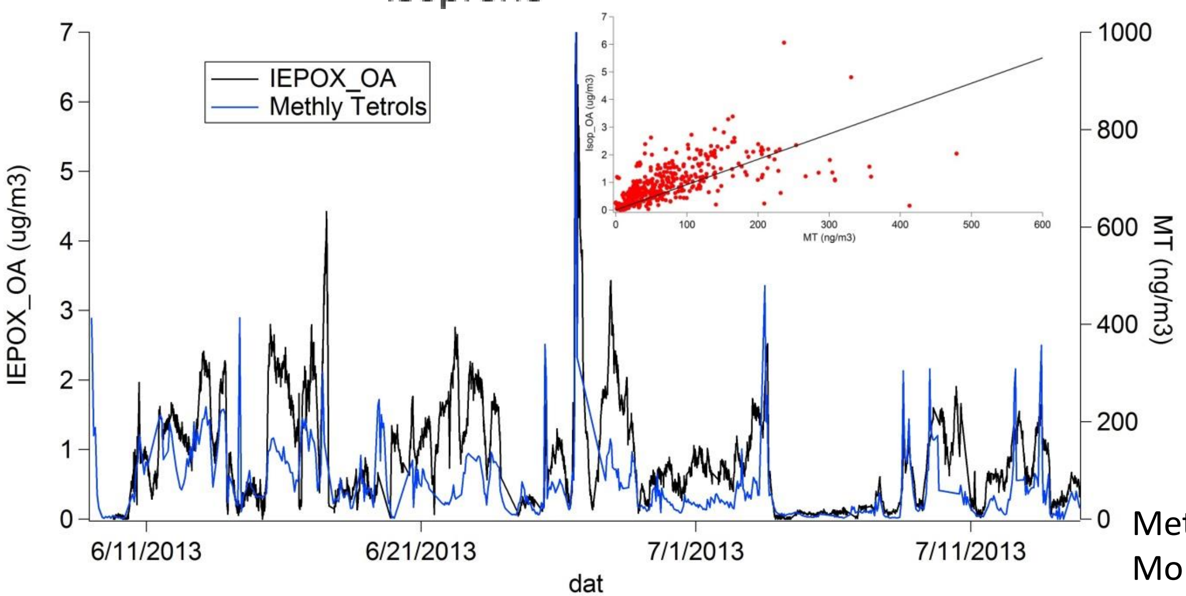
*Q: How do anthropogenic components affect SOA formation?*

# "IEPOX-OA"




- Characterized by Ion $C_4H_5^+$ and $C_5H_6O^+$.
- Robinson et al. (2011), Lin et al. (2012) → related to Isoprene (IEPOX) chemistry.

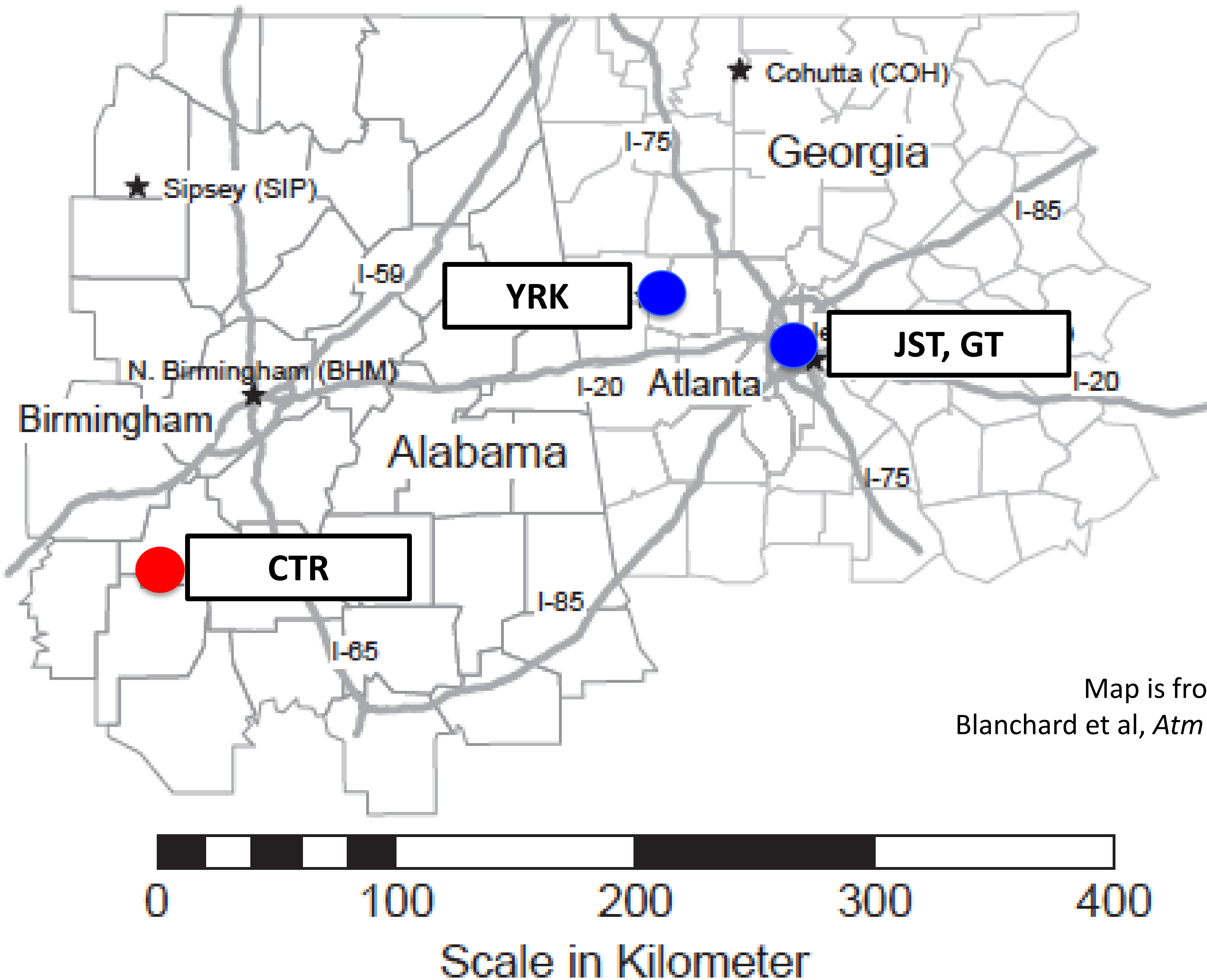



SOAS: IEPOX-OA correlates with Methyl Tetrols (R=0.7) → This factor is related to isoprene OA

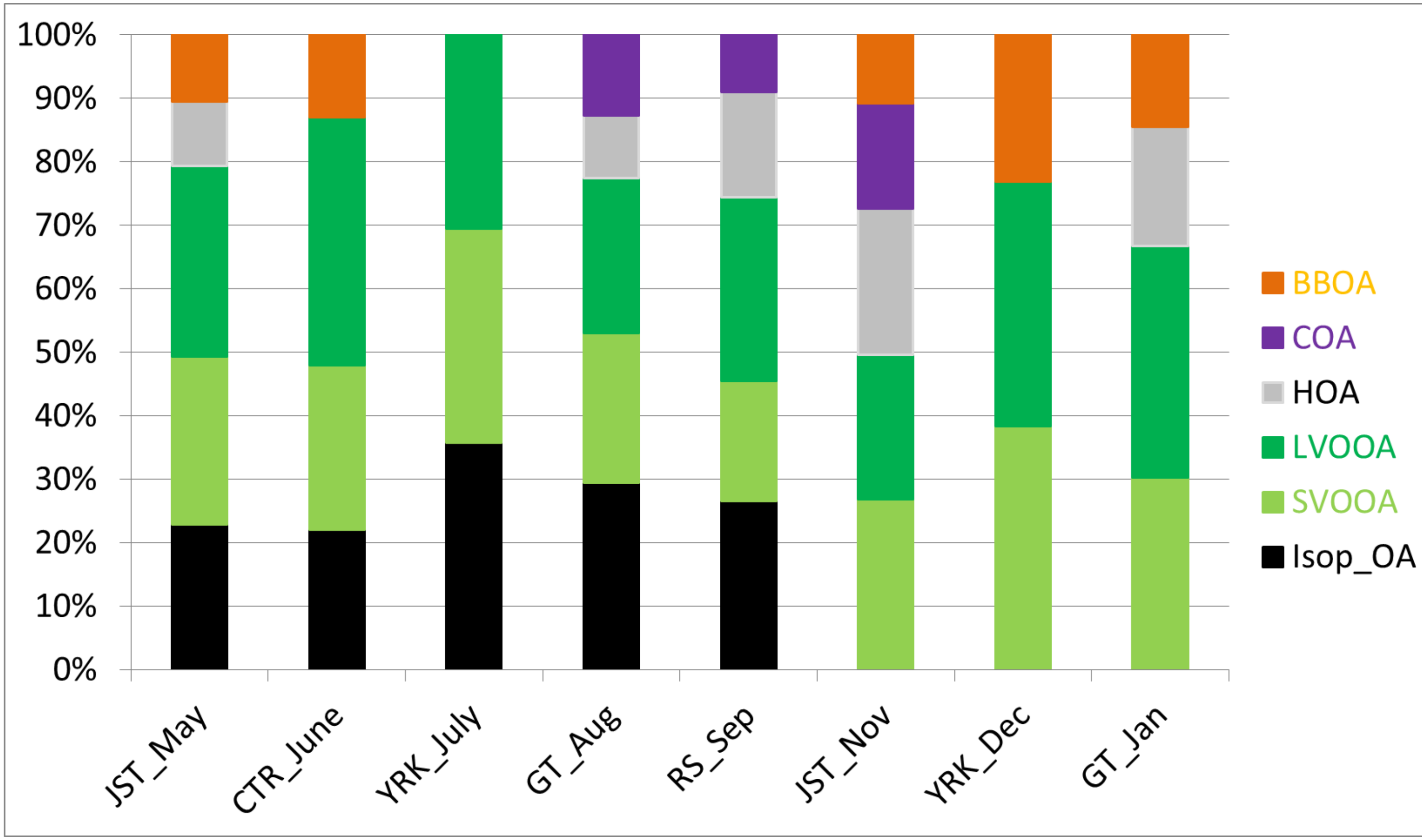
Methly Tetrols data are from Goldstein group.
More details: poster by Gabriel Isaacman.

# Greater Atlanta Area (EPA Clean Air Center: SCAPE)




Map is from
Blanchard et al, *Atm Env* 2011.

# "IEPOX-OA"



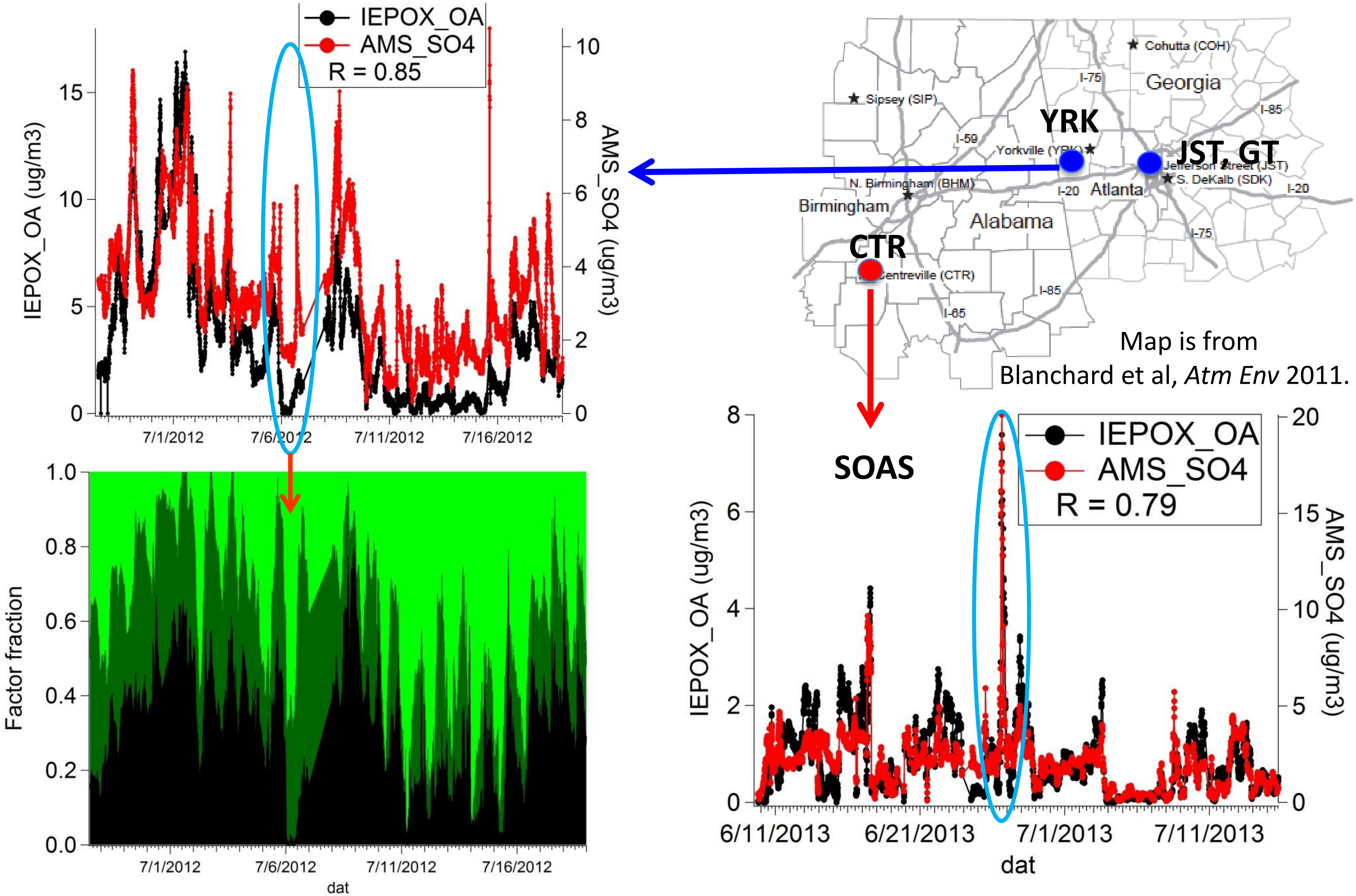

Our study (SOAS + Atlanta):
Isoprene OA was only observed from May to September.

Consistency ⟷

Guenther et al (2006 ACP):
seasonal variation of isoprene emission (high in summer)

Ding et al. (ES&T 2008):
methytetrols only exist from May to October in US SE.

# “IEPOX-OA”

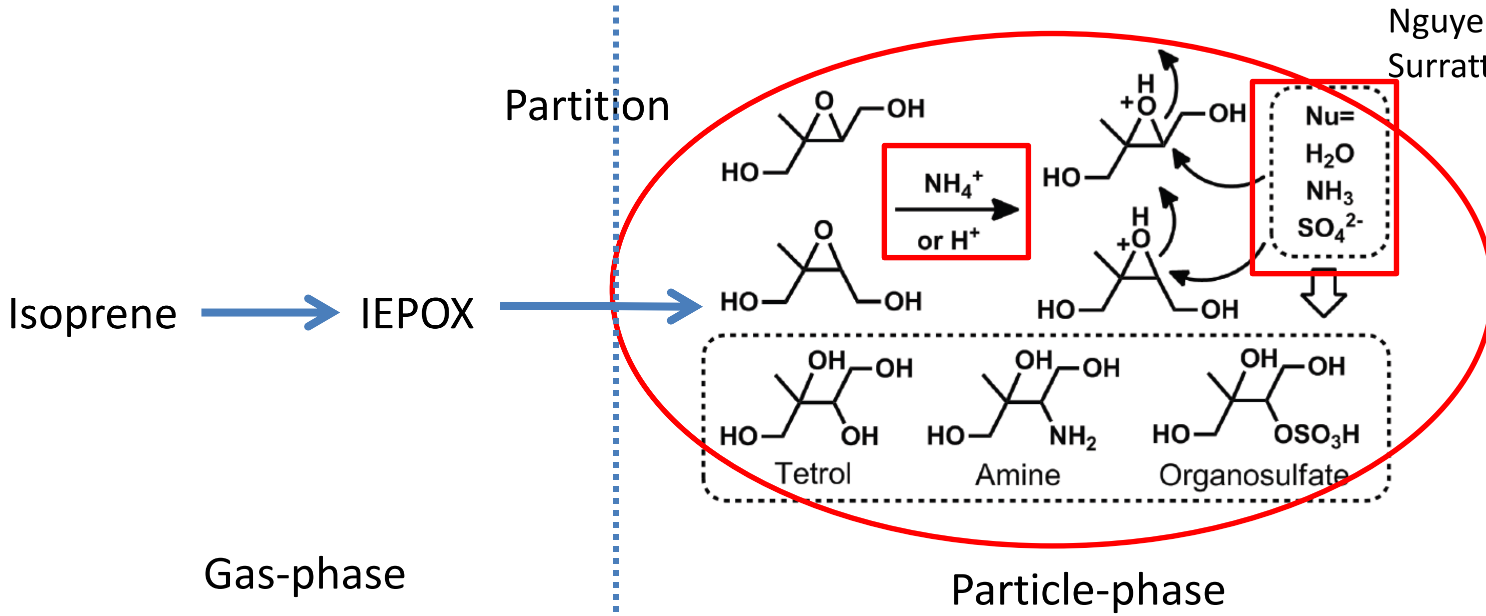



**Low $SO_4$ limits “IEPOX_OA” formation.**

**High $SO_4$ enhances “IEPOX_OA” formation**

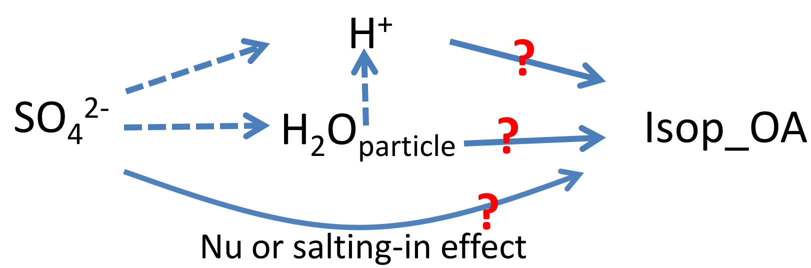
# Mechanism of IEPOX_OA formation

Nguyen et al. 2013 ACPD
Surratt et al. 2010 PNAS




Requirement (Nguyen et al.)

1. Particle water
2. Proton donor: $H^+$; $NH_4^+$
3. Nucleophile: $SO_4$; $H_2O$




Question: how exactly does SO4 influence isoprene SOA?
Through affecting acidity?
Through affecting particle water?
Or directly as a nucleophile or salting-in effect?

# Effect of SO4 on IEPOX_OA formation -- Multivariate Linear Regression

$$IEPOX\_OA = \beta_0 + \beta_1 * H_2O + \beta_2 * [H^+] + \beta_3 * SO_4$$

Adjusted $R^2 = 0.66$

| Variable | β-coefficient | Standard error | t Value | P value |
|---|---|---|---|---|
| Intercept | 0.054 | 0.115 | 0.47 | 0.6365 |
| $H_2O$ | 0.006 | 0.010 | 0.65 | 0.5141 |
| $H^+$ | -0.106 | 0.057 | -1.86 | 0.0641 |
| $SO_4$ | 0.450 | 0.018 | 24.35 | <0.0001 |

- Particle water and H+ are predicted by ISORROPIA (II).
- SO4 has the strongest association with IEPOX_OA
- IEPOX_OA vs $H_2O$/acidity → not significant (same for organic water)
- Water and Acidity are important in IEPOX_OA formation, but they are not limiting factors.

(More details about water and pH: poster by Hongyu Guo)

# Effect of water and acidity on IEPOX_OA formation

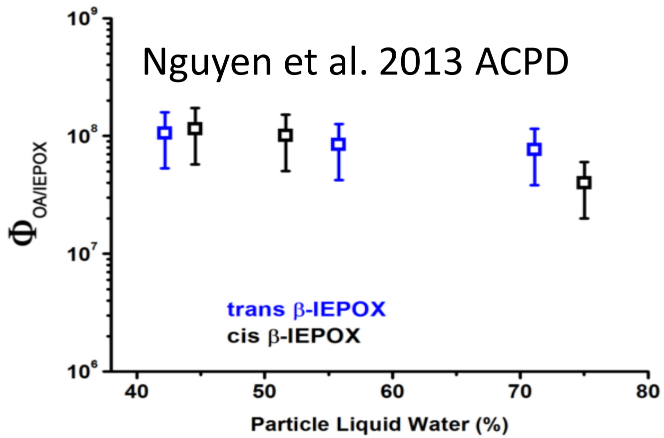
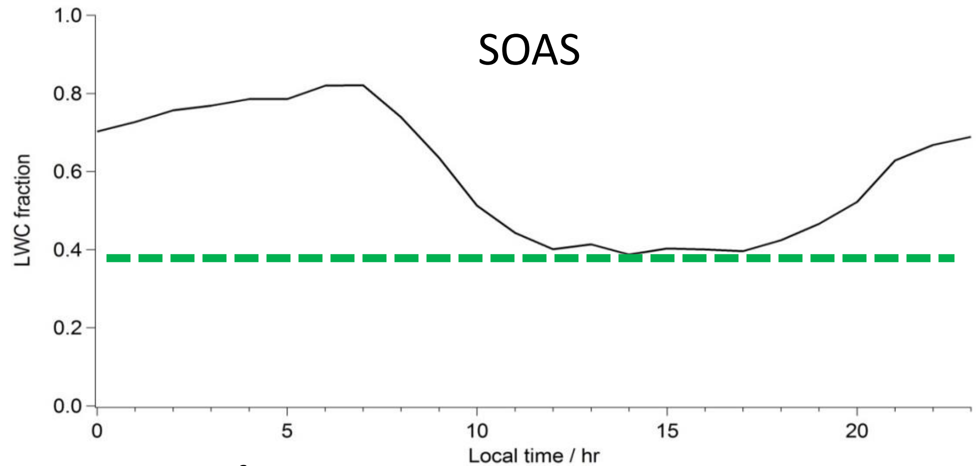



**Fig. 2.** Reactive partitioning coefficients ($\Phi_{OA/IEPOX}$) during the gas-phase IEPOX injection phase for the *trans* and *cis* isomers as a function of the particle liquid water concentration. Error bars indicate an estimated combined 50 % error.




Note: for consistency

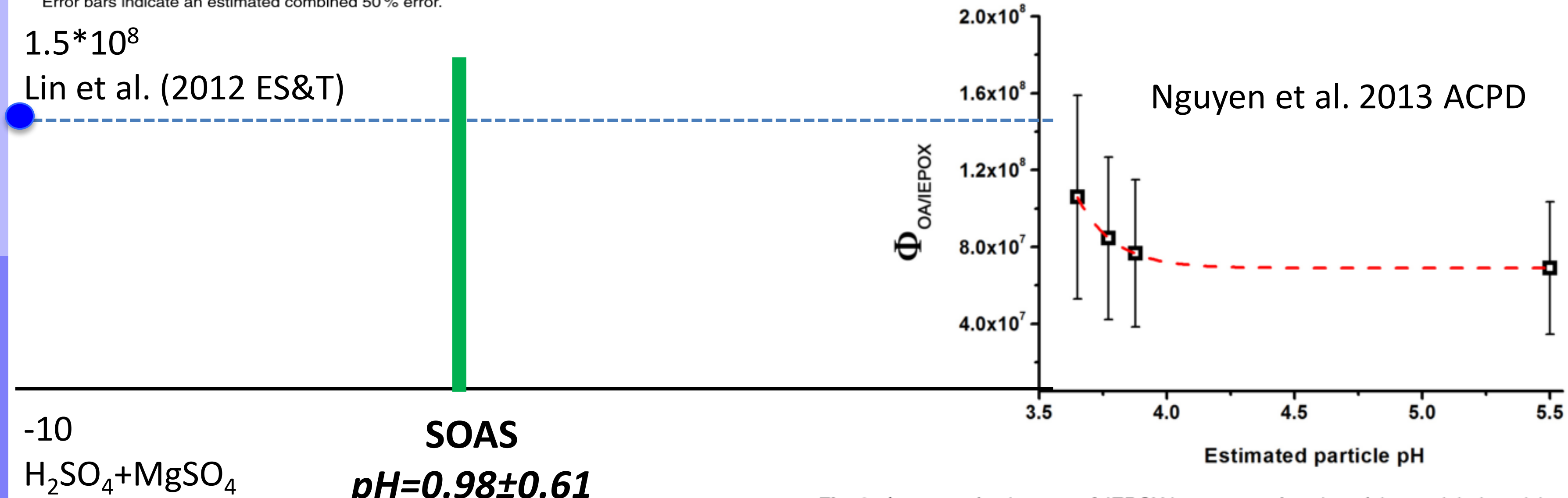
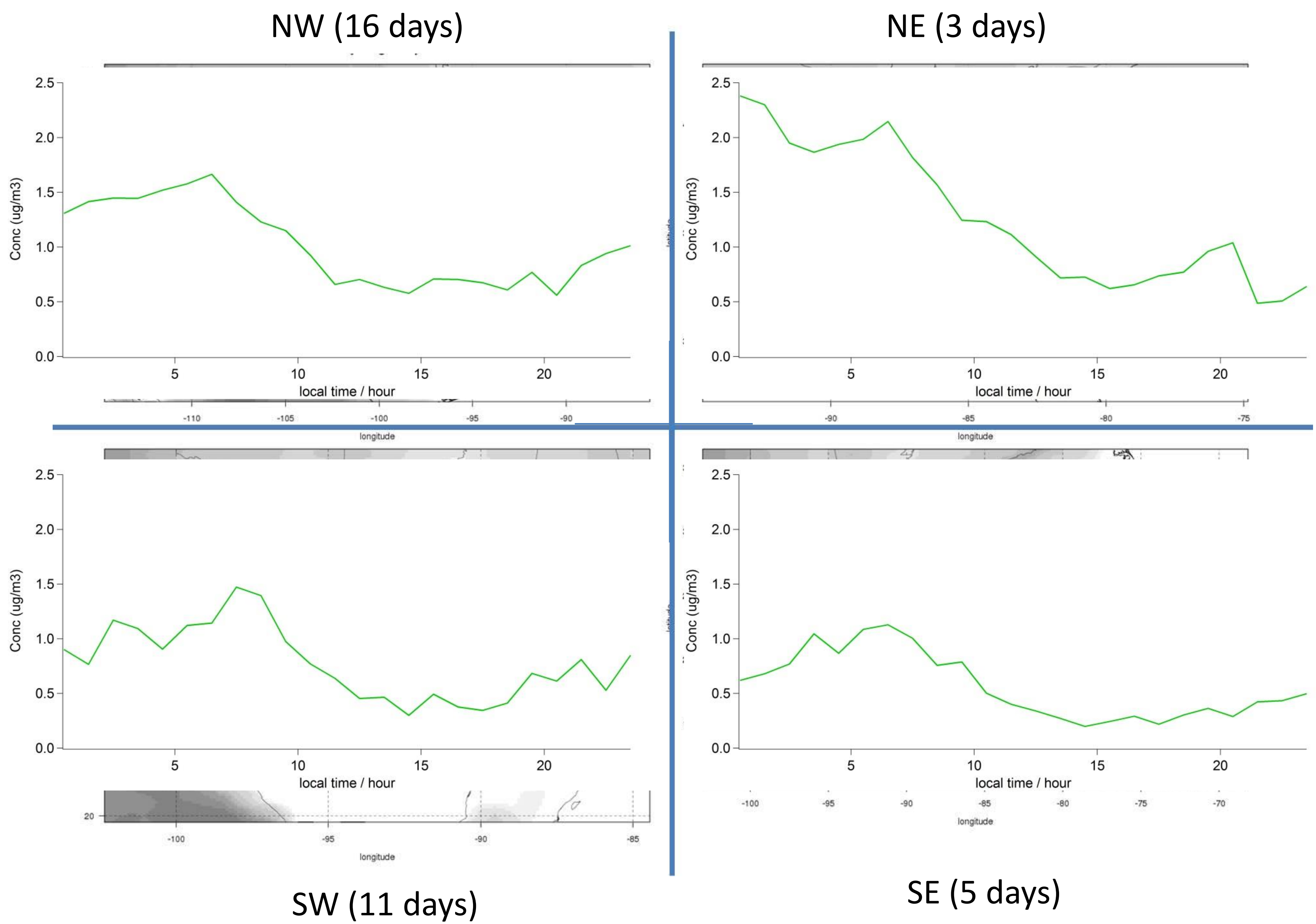



**Fig. 3.** $\Phi_{OA/IEPOX}$ for the *trans* β-IEPOX isomer as a function of the modeled particle pH.

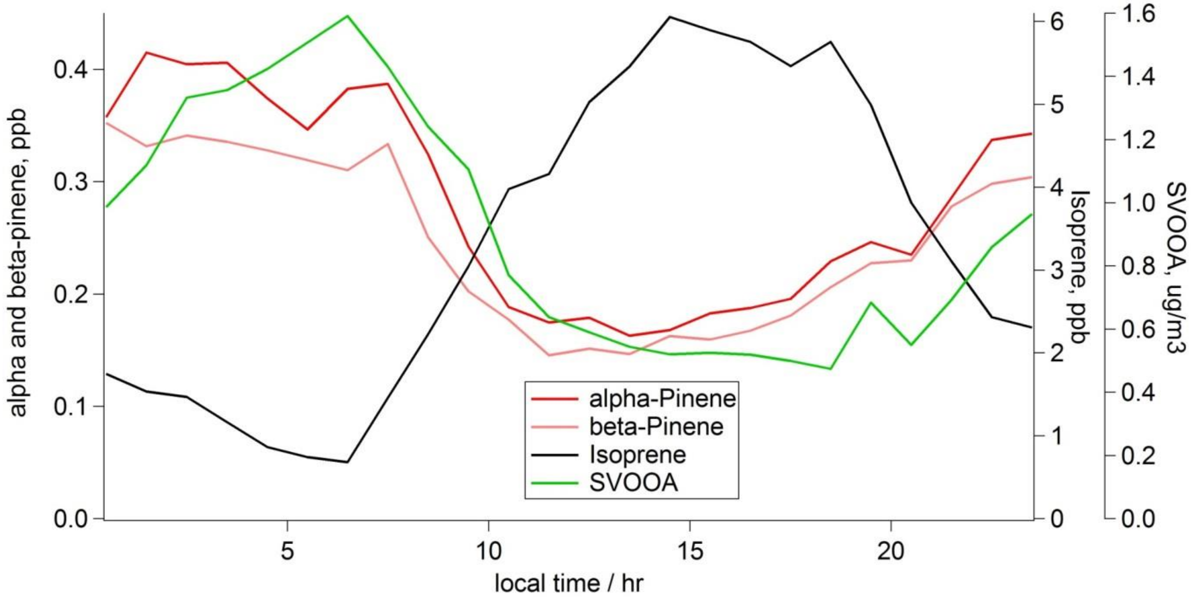
$SO_4^{2-}$ —Salting in effect→ Enhance IEPOX uptake —Nucleophile / $H_2O/SO_4^{2-}$→ IEPOX_OA

# Source of SVOOA: local or long-range transport?



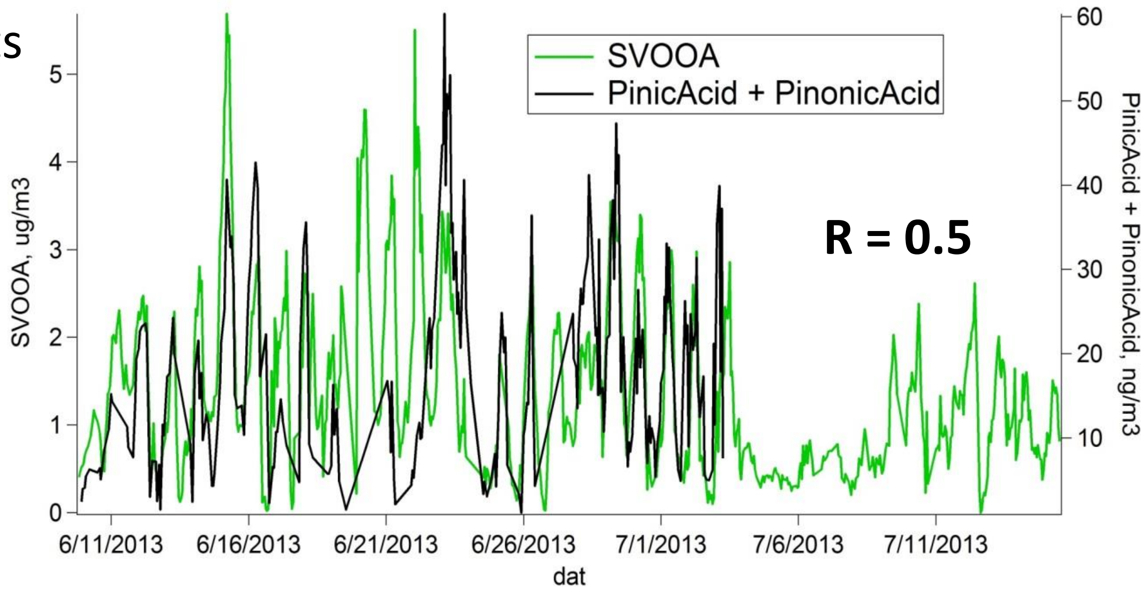

Data provided by NCAR/EOL under sponsorship of the National Science Foundation

# Source of SVOOA: Monoterpenes




SVOOA has similar diurnal trend as monoterpenes.

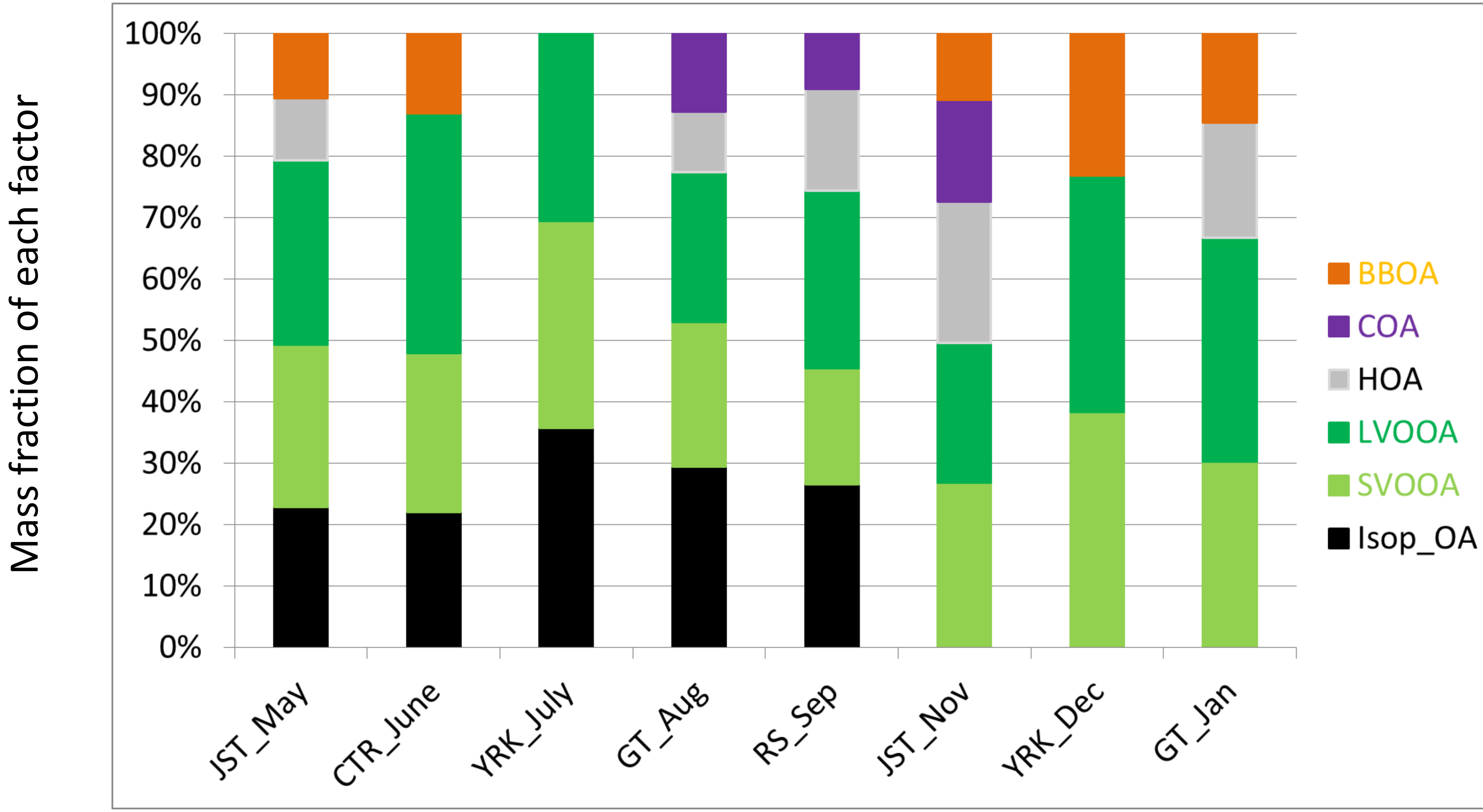
SVOOA correlates with monoterpene oxidation products (Pinic Acid and Pinonic Acid).




SVOOA could be related to SOA from monoterpenes.

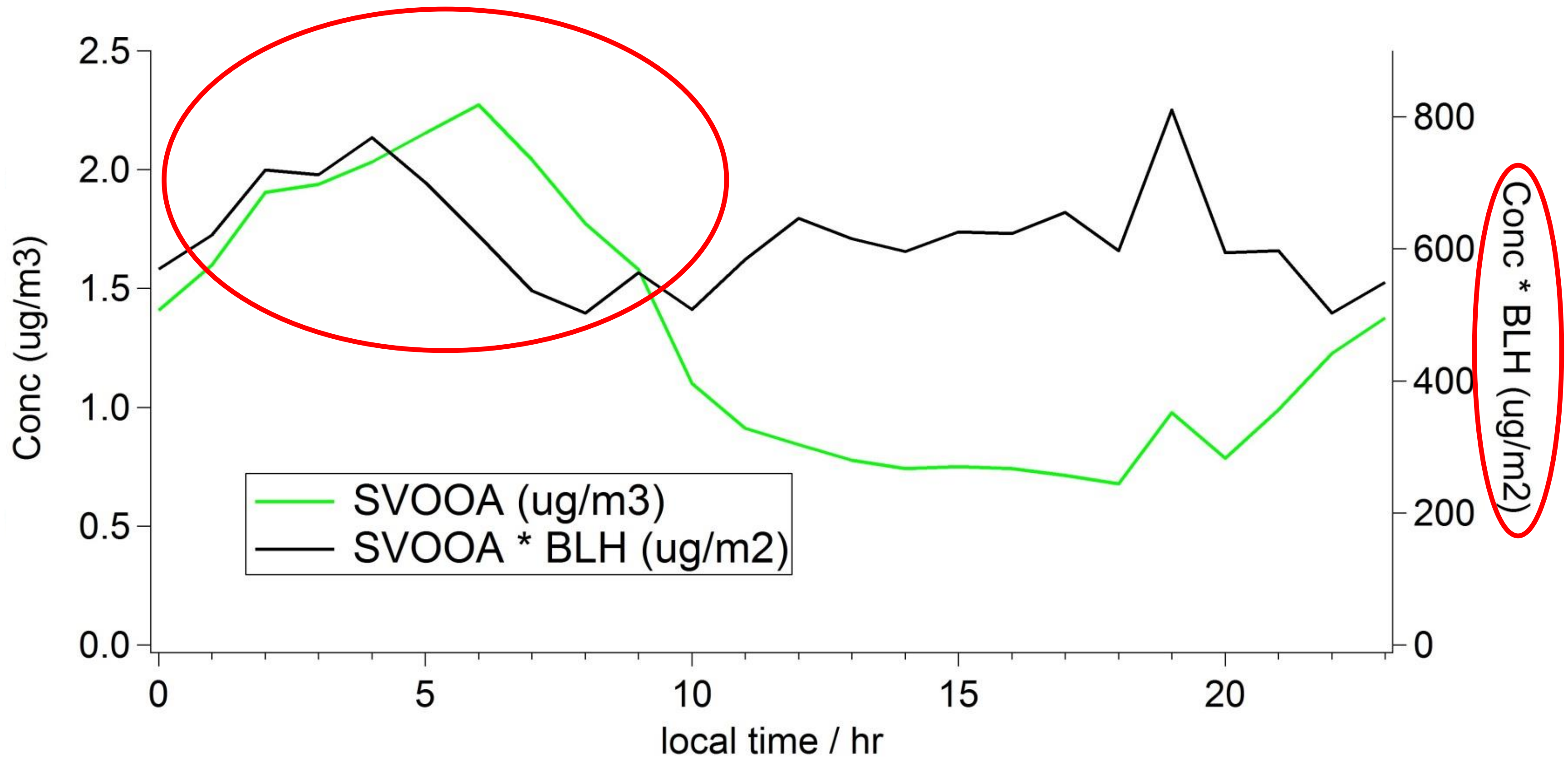
Pinic/Pinonic acids are from Goldstein group

# Evidence for "SVOOA is from Monoterpenes"



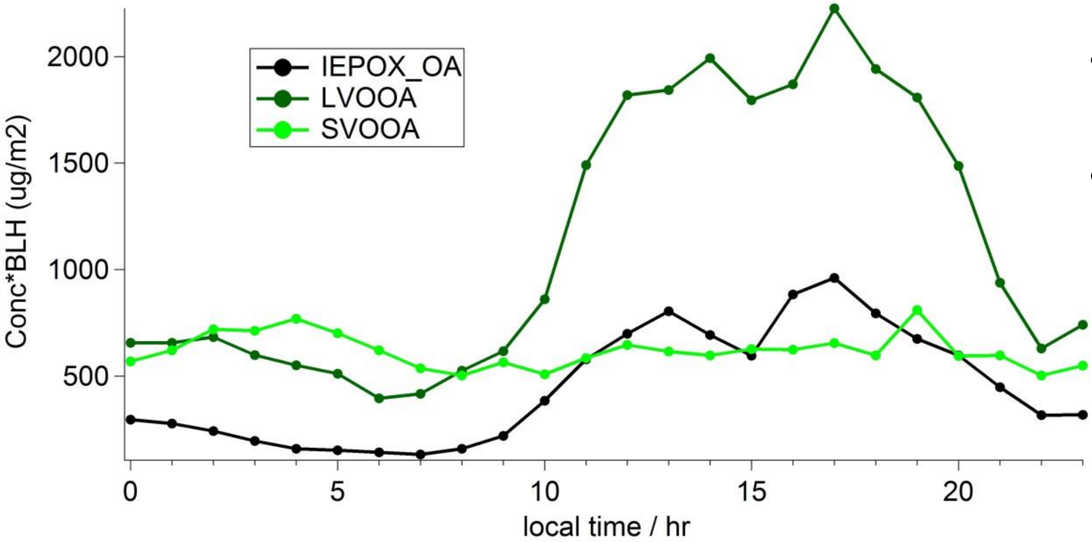

- Greater Atlanta Area: SVOOA was observed throughout the year.
- Unlike Isoprene, monoterpenes exist throughout the year.
- Ding et al. (ES&T 2008) showed that oxidation products of monoterpenes exist in US SE throughout the year.

# SVOOA



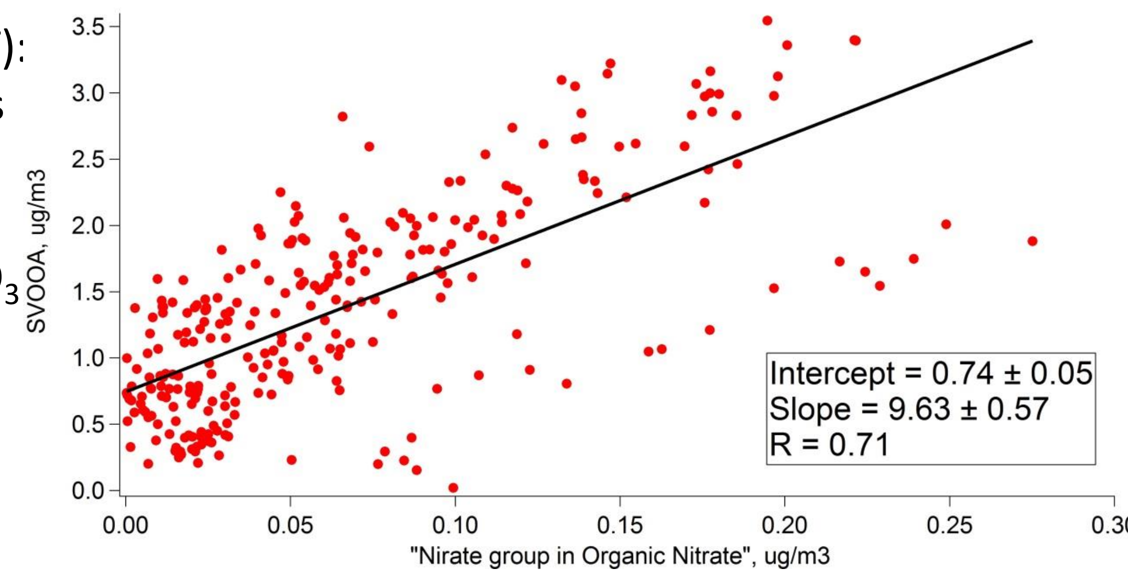

Nighttime increase: change in BLH or production?
Production

# Effects of $NO_x$ on SVOOA formation




- SVOOA is the only factor with nighttime production.
- NO2 + O3 → NO3 (major oxidant at night)

- Concurrent chamber studies (GT): SOA yield of beta-pinene+NO3 is ~70% and the molar fraction of organic nitrate is up to 80%
- Estimate ON based on ($AMS\_NO_3$ – $PILS\text{-}IC\_NO_3$)
- SVOOA has a strong association with "ON" → NO3 (originating from NOx) affects SVOOA formation




More details about nighttime chemistry: poster by Chris Boyd

# Conclusions

- Submicron non-refractory PM1 in SOAS dominated by organics (67%), followed by $SO_4$ (26%).
- All OA factors are correlated with at least one anthropogenic component.
- (22%) IEPOX_OA: Water and acidity are important, but not limiting IEPOX_OA in US SE (highly acidic and abundant water). IEPOX_OA formation is greatly and directly regulated by SO4 (e.g., nucleophile, salting-in effect).
- (26%) SVOOA: likely originates from monoterpenes, and its formation could be controlled by nighttime $NO_3$ chemistry (NOx effect).

*Q: How do anthropogenic components affect SOA formation?*

**$NO_x$ and $SO_4$ together can potentially control at least 46% of the total organic aerosols measured at SOAS**

# Acknowledgement

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R834799

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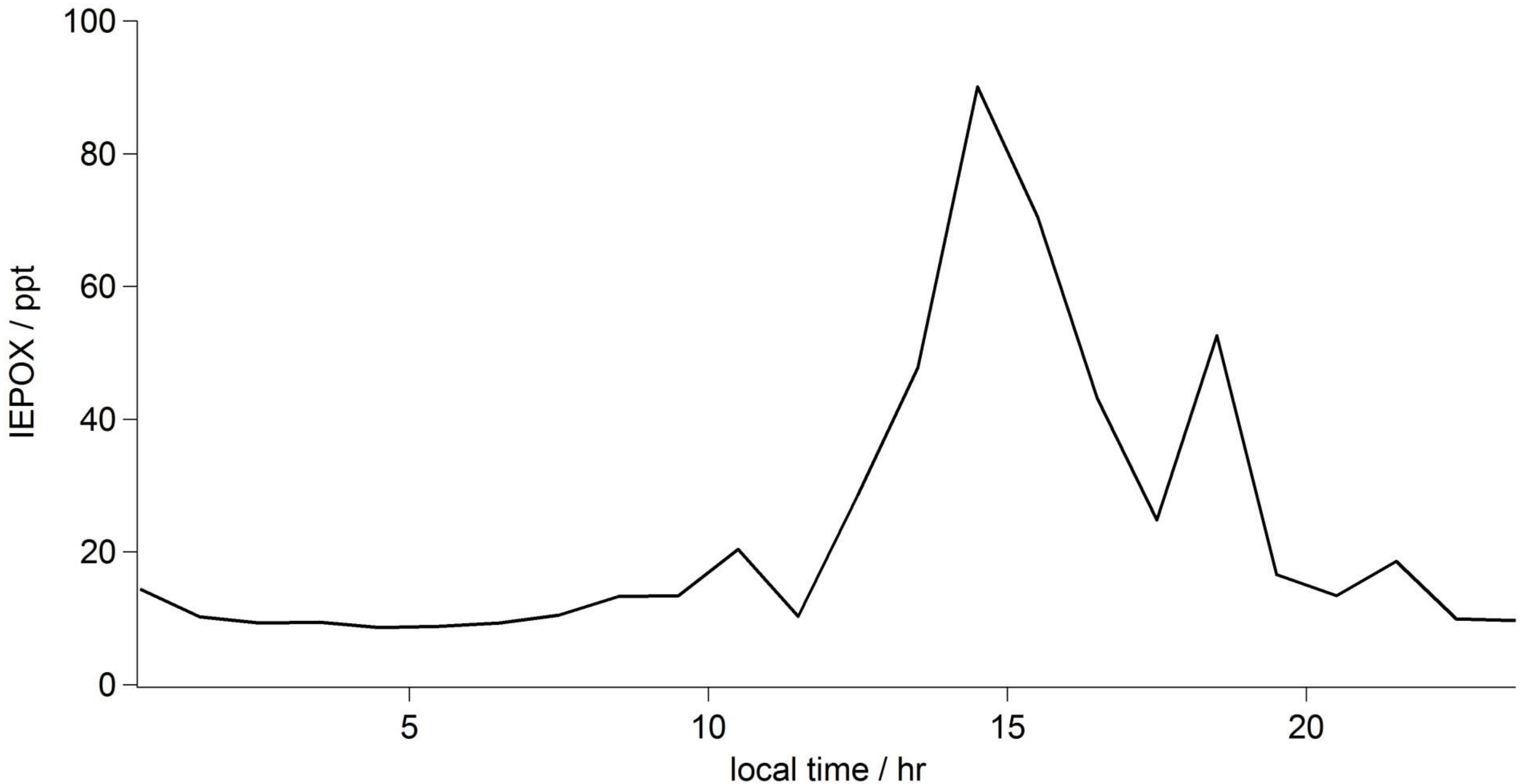
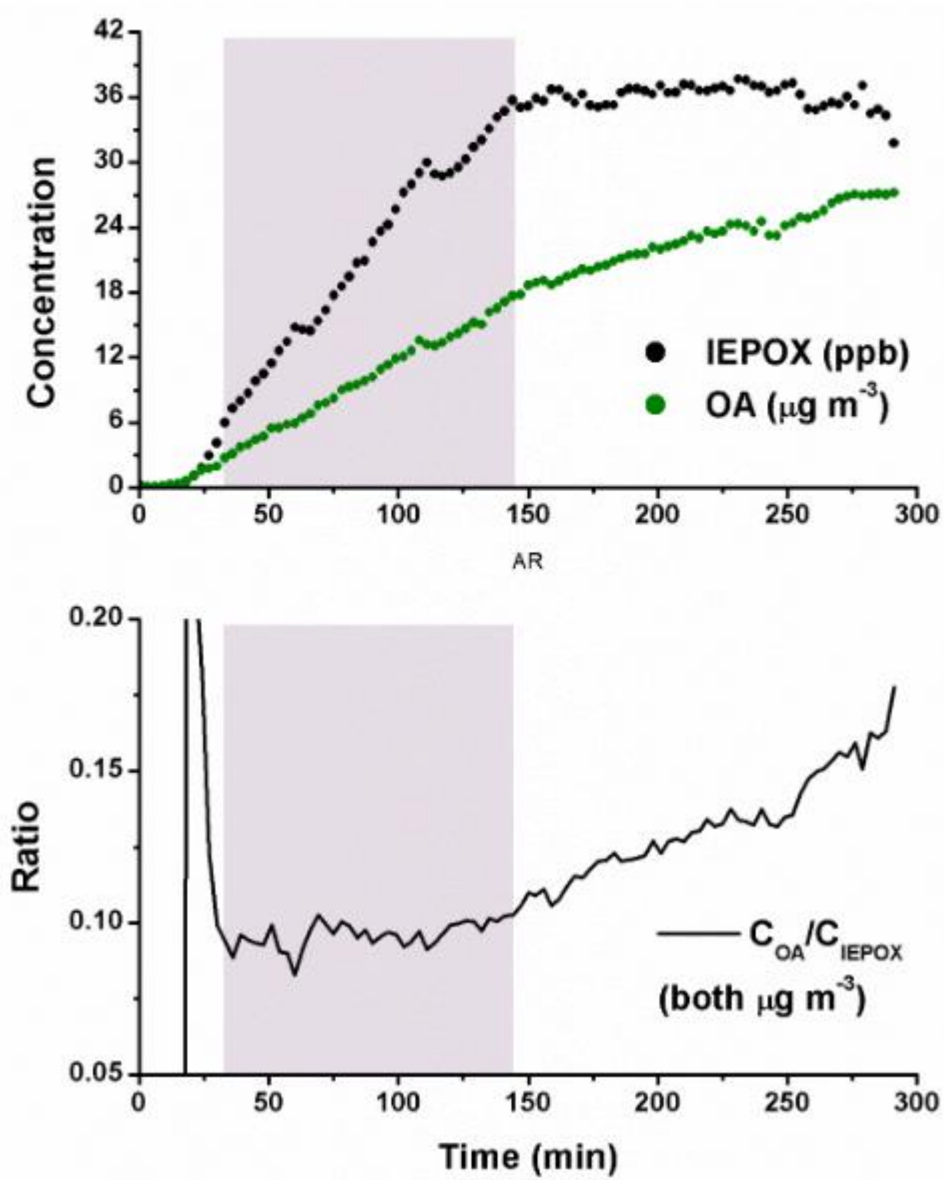
**Thank You!**

This work was made possible by US EPA grant R834799 and 83540301. The contents are solely the responsibility of the grantee and do not necessarily represent the official views of the US EPA. Further, US EPA does not endorse the purchase of any commercial products or services mentioned in the work.




100ppt IEPOX = 0.5ug/m3 IEPOX
OA/IEPOX = 0.2

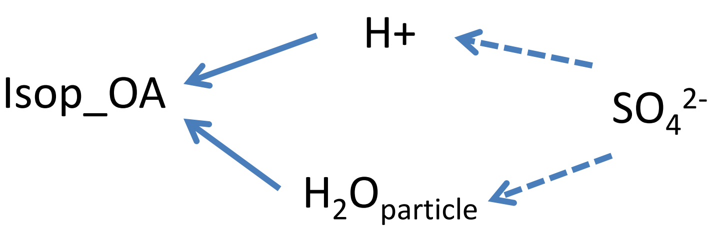
**Figure S3:** Top panel: OA grows in response to IEPOX gas-phase injection, but continues to grow after halting IEPOX injection, an indication that the system is not at equilibrium. Bottom panel: the ratio of the OA to gas-phase IEPOX starts off noisy and levels out as IEPOX is injected. The ratio continues to grow as gas-phase IEPOX stabilizes and OA continues to grow. The shaded panel where the ratio levels out is used in $\Phi_{OA/IEPOX}$ calculations.



# Effect of SO4 on Isop_OA formation:
# -- Multivariate Linear Regression

Reduced model

Isop_OA = intercept + B1*H2O + B2*acid




$R2 = 0.24$

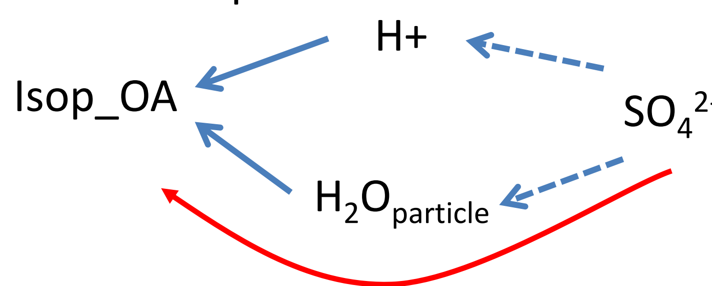
| Variable | parameter estimate | Standard error | t Value | P value |
|---|---|---|---|---|
| Intercept | 0.065 | 0.172 | 0.38 | 0.7041 |
| H2O | 0.142 | 0.012 | 11.94 | <0.0001 |
| H+ | 0.333 | 0.081 | 4.12 | <0.0001 |

expected change in Isop_OA per unit change in water holding everything else constant

Statistical significance < 5% → significant

Full model

Isop_OA = intercept + B1*H2O + B2*acid + B3*SO4

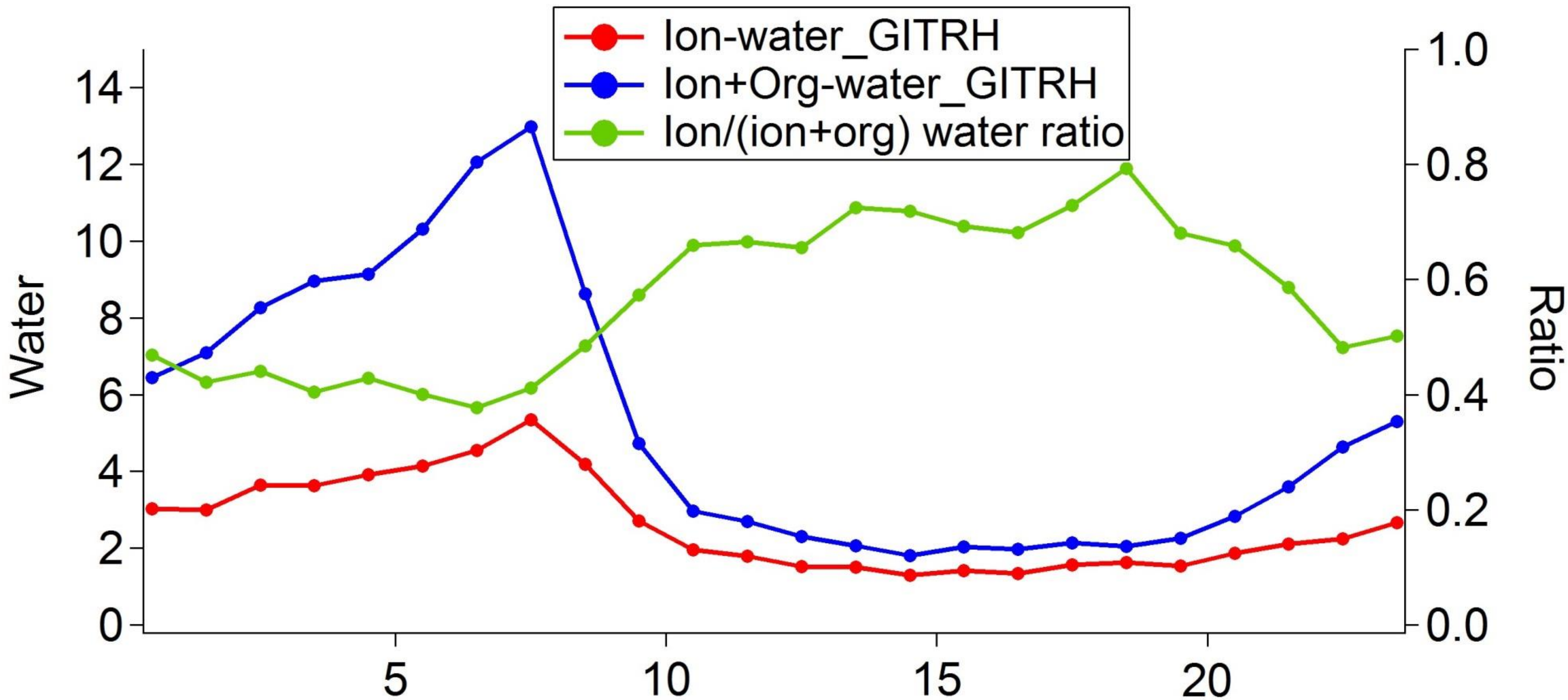



$R2 = 0.66$

| Variable | parameter Estimate | Standard error | t Value | P value |
|---|---|---|---|---|
| Intercept | 0.054 | 0.115 | 0.47 | 0.6365 |
| H2O | 0.006 | 0.010 | 0.65 | 0.5141 |
| H+ | -0.106 | 0.057 | -1.86 | 0.0641 |
| SO4 | 0.450 | 0.018 | 24.35 | <0.0001 |

Adding SO4 in the model changes the association between water and Isop_OA →

SO4 → water → Isop_OA << SO4 → Isop_OA



Ion-water_GITRH
Ion+Org-water_GITRH
Ion/(ion+org) water ratio
Water
Ratio
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0
5
10
15
20

- I'd remove slide 2 (general characteristics of organics) - you can briefly mention it when presenting slide #3.
  slide 14, 15 (put for support slides). Slide 12,18 can also be removed, intermediate conclusions are good for
  a longer talk. Just summarize with the current conclusions slide you have at the end - it is great actually as is.
  With these deletions, you have 15 slides counting the cover an thank you slides. That means 13 slides, where you
  can really present the results carefully and with sufficiently slow pace. This has to be done for people to
  soak all the results in: less is more.

# Use organic water only

## Linear Regression Results

The REG Procedure
Model: Linear_Regression_Model
Dependent Variable: IsopOA

| | |
|---|---|
| Number of Observations Read | 503 |
| Number of Observations Used | 503 |

| Analysis of Variance | | | | | |
|---|---|---|---|---|---|
| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
| Model | 3 | 324.71569 | 108.23856 | 304.66 | <.0001 |
| Error | 499 | 177.28487 | 0.35528 | | |
| Corrected Total | 502 | 502.00056 | | | |

| | | | |
|---|---|---|---|
| Root MSE | 0.59605 | R-Square | 0.6468 |
| Dependent Mean | 0.00000300 | Adj R-Sq | 0.6447 |
| Coeff Var | 19870176 | | |

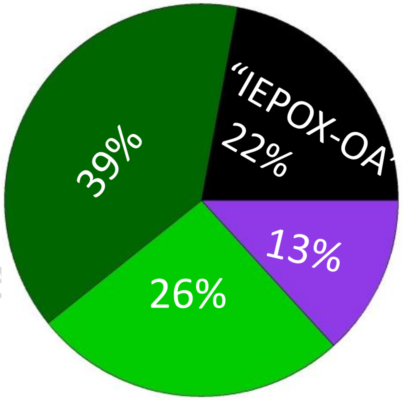
| Parameter Estimates | | | | | |
|---|---|---|---|---|---|
| Variable | DF | Parameter Estimate | Standard Error | t Value | Pr > \|t\| |
| Intercept | 1 | 0.00000462 | 0.02658 | 0.00 | 0.9999 |
| SO4 | 1 | 0.81580 | 0.02837 | 28.76 | <.0001 |
| water | 1 | 0.03013 | 0.02762 | 1.09 | 0.2758 |
| H | 1 | -0.04928 | 0.02909 | -1.69 | 0.0909 |

# Conclusions

- Overall

1) Submicron non-refractory PM1 in SOAS domin cs (67%), followed by $SO_4$ (26%).

2) All SOA factors are correlated with at least one c component.




- IEPOX_OA – 22% of OA

1) Water and acidity are important, but not limiting IEPOX_OA formation in US SE.

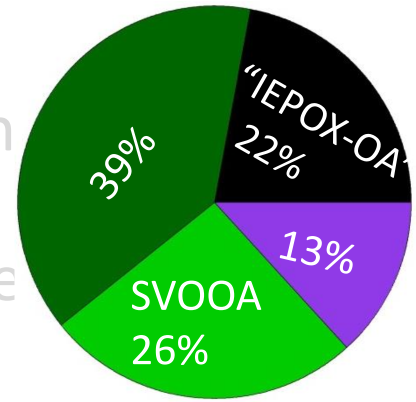
2) IEPOX_OA has strong association with SO4.
3) SO4 regulates IEPOX_OA formation directly (e.g., nucleophile, salting-in) in US SE.

- SVOOA – 26% of OA

1) SVOOA likely originates from monoterpenes, and its formation could be controlled by nighttime $NO_3$ chemistry (NOx effect).

- $NO_x$ and $SO_4$ together can potentially control about up to 50% of the total organic aerosols measured at SOAS

# Conclusions

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