Real-time Characterization of Isoprene-Derived Secondary Organic Aerosol Formation at the Look Rock Site, Tennessee during 2013 Southern Oxidant and Aerosol Study (SOAS)

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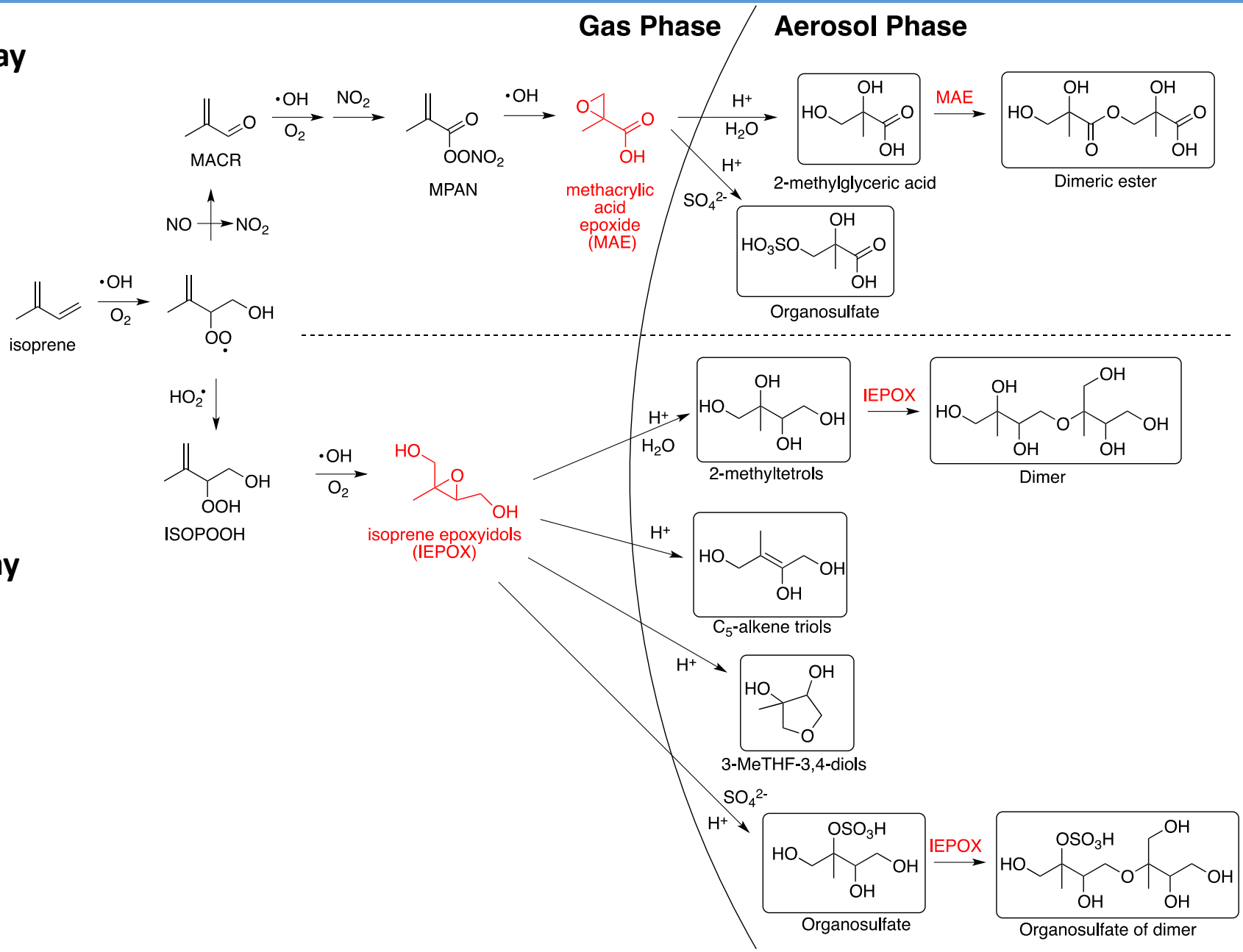
Isoprene Photooxidation Mechanism in the Atmosphere

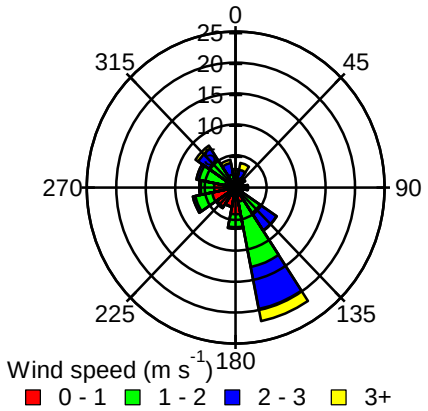


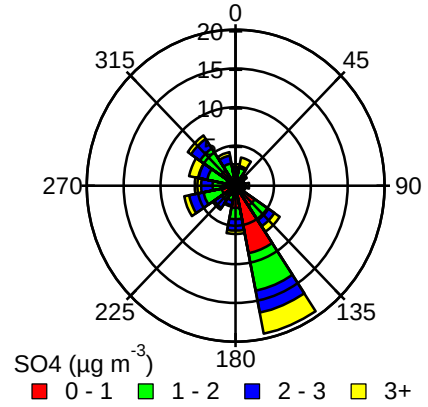
Lin et al. (2013)

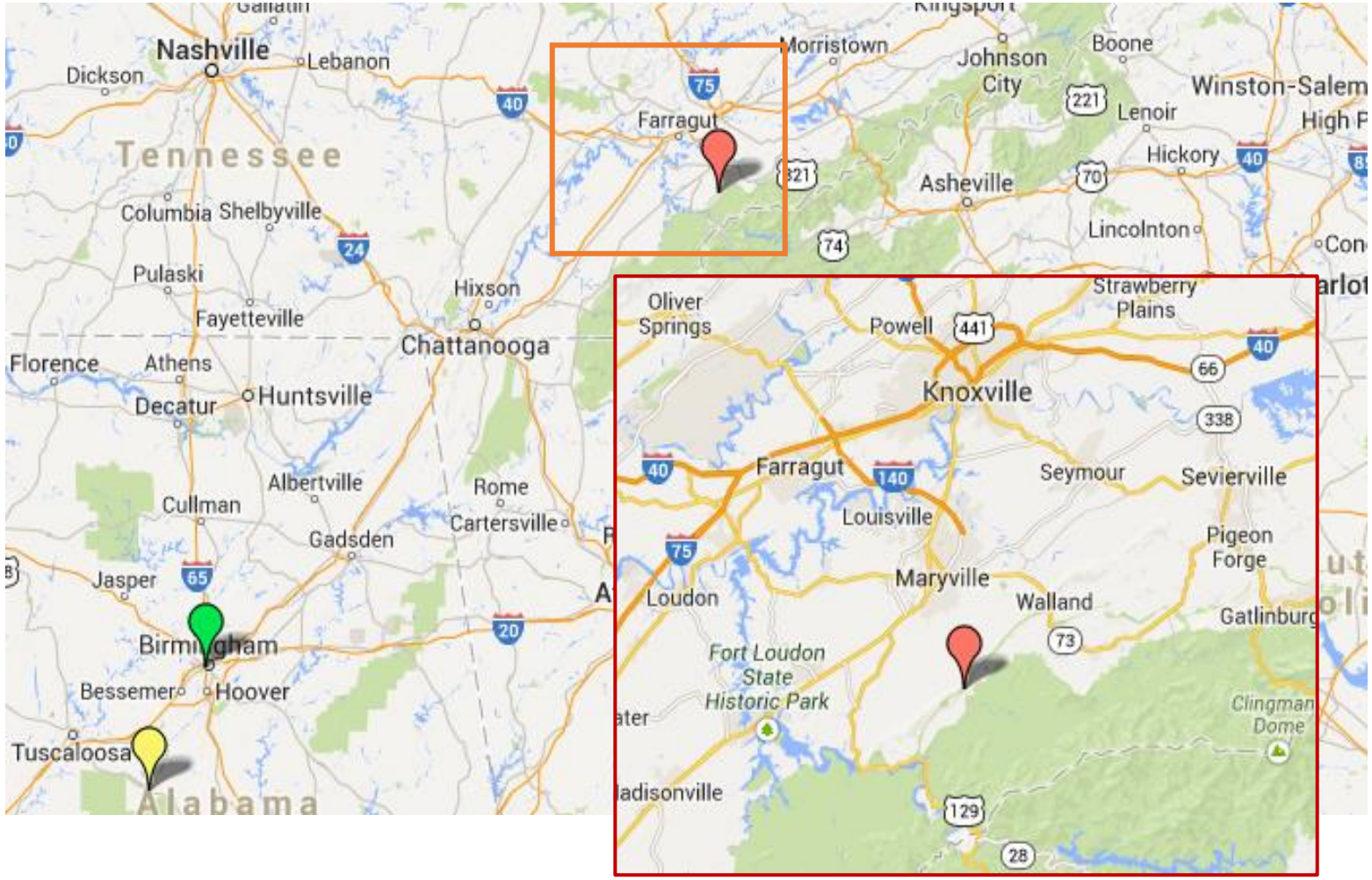
Paulot et al. (2009), Surratt et al. (2010), Lin et al. (2012), Zhang et al. (2012), Nguyen et al. (2014)

Study Aims and Location

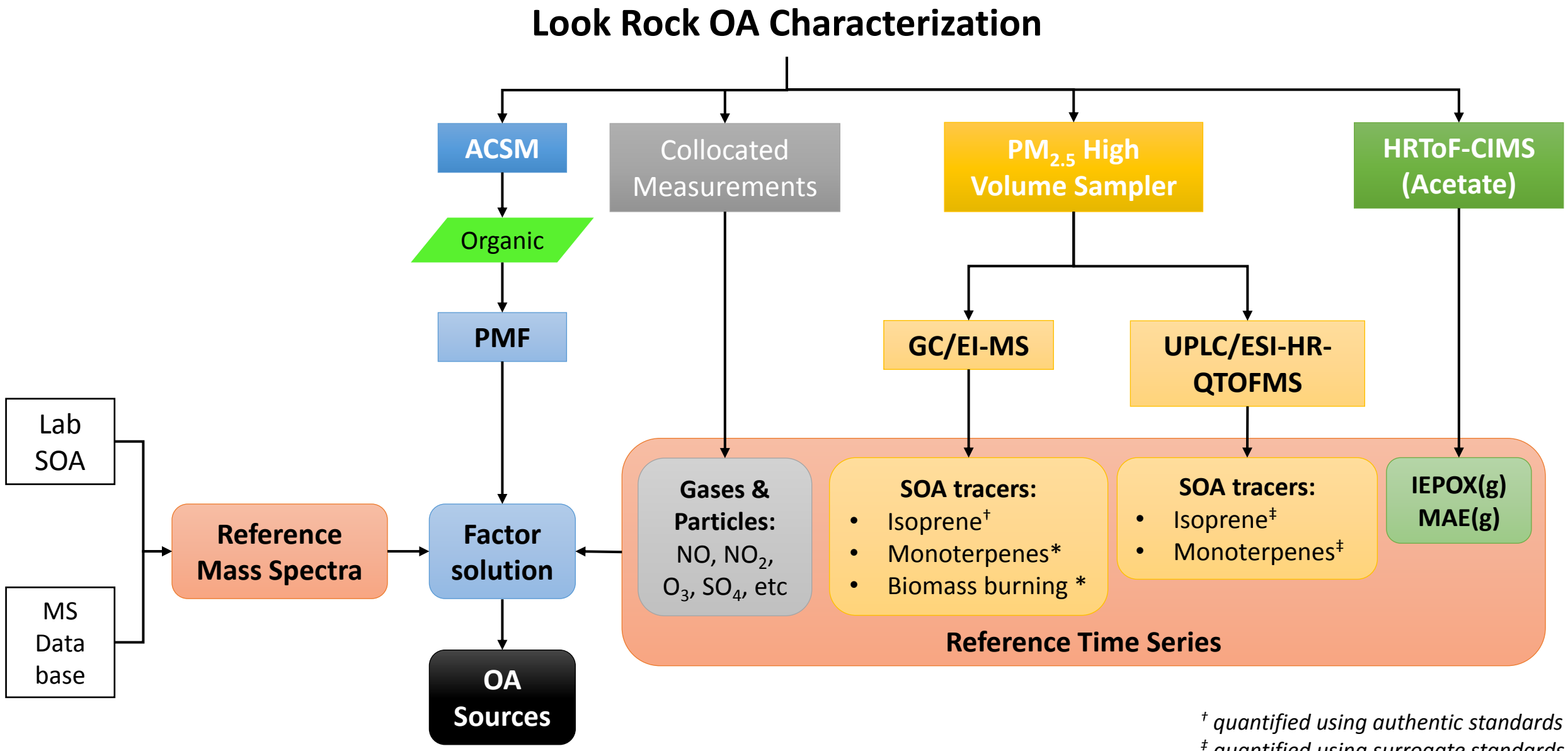
1. Measure isoprene-derived SOA tracers to aid in source apportionment of OA.
2. Evaluate the effects of aerosol acidity and NOx on the heterogeneous chemistry of isoprene-derived epoxides leading to SOA
3. Evaluate formation of gaseous epoxides from isoprene oxidation in the atmosphere





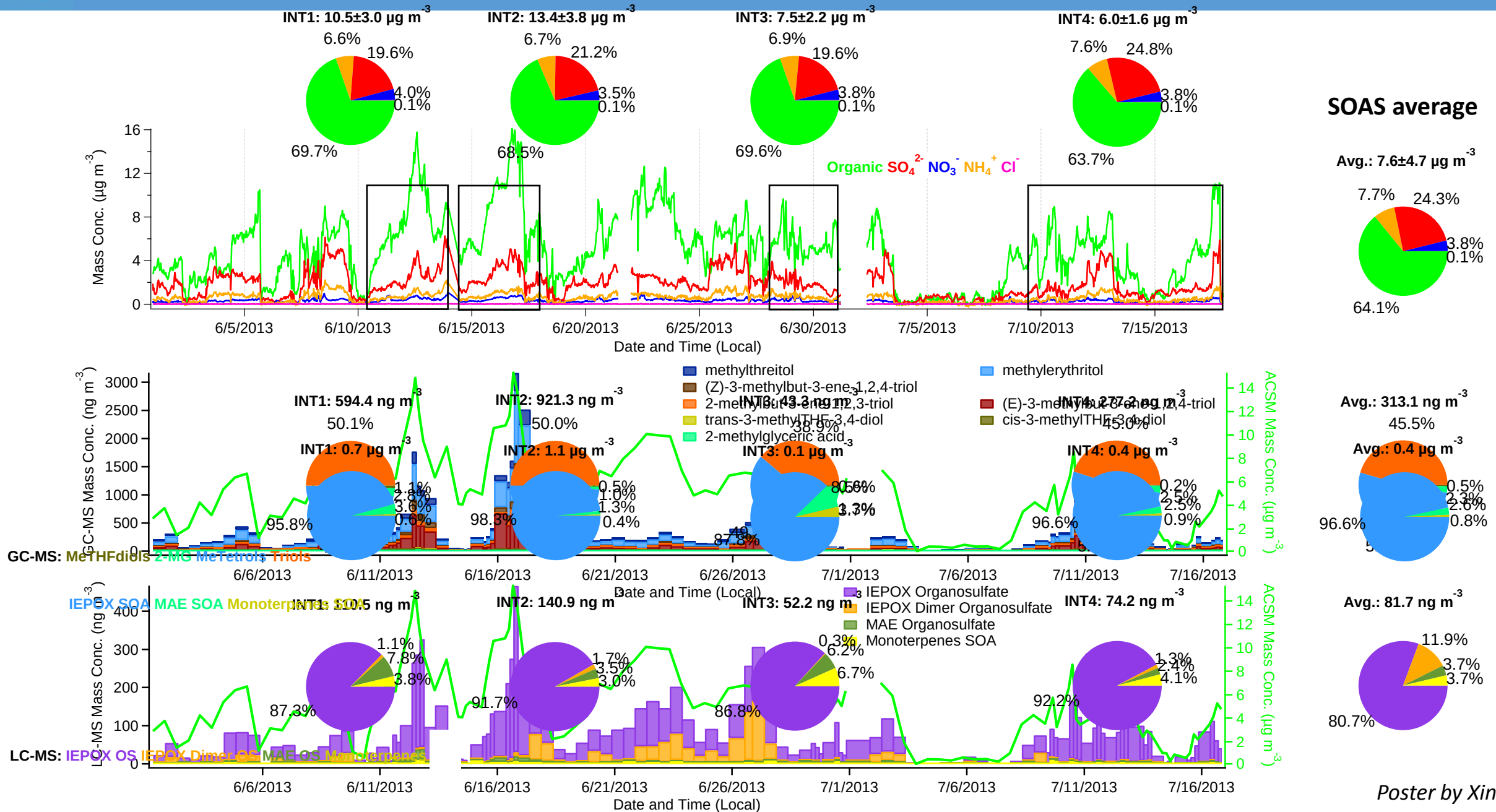


Methods



† *quantified using authentic standards*
‡ *quantified using surrogate standards*
* *in process*

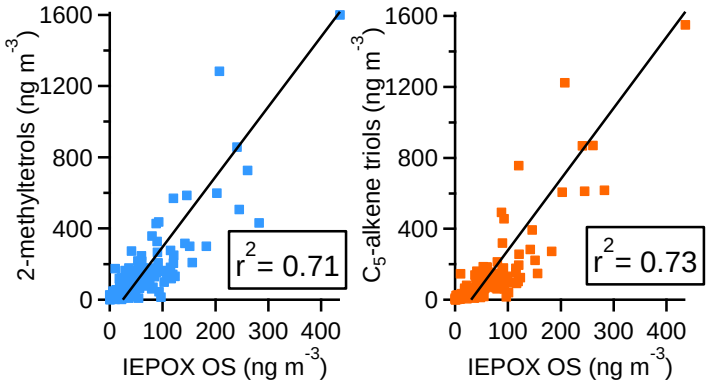
(1a) SOA Tracers Quantification

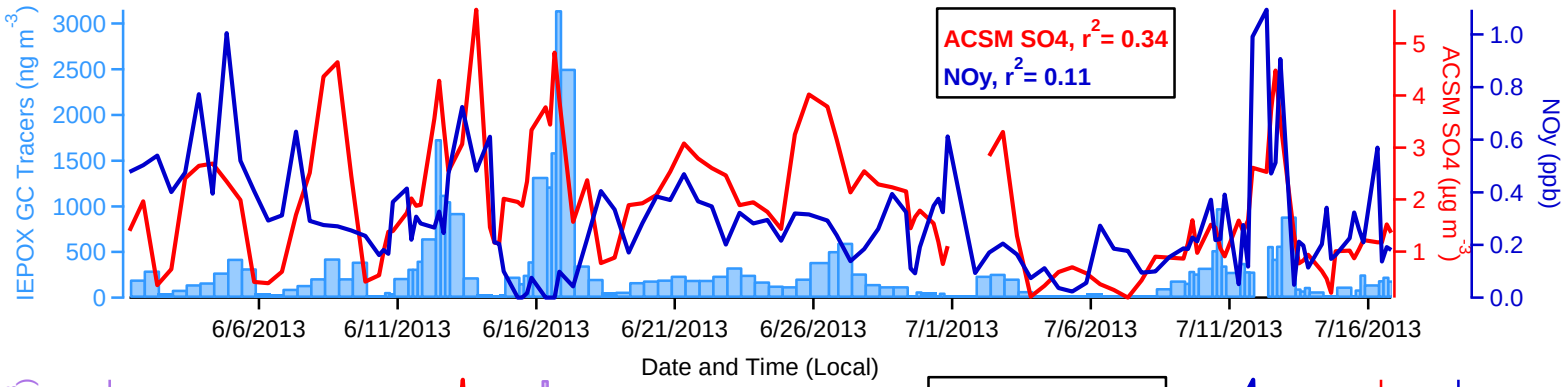


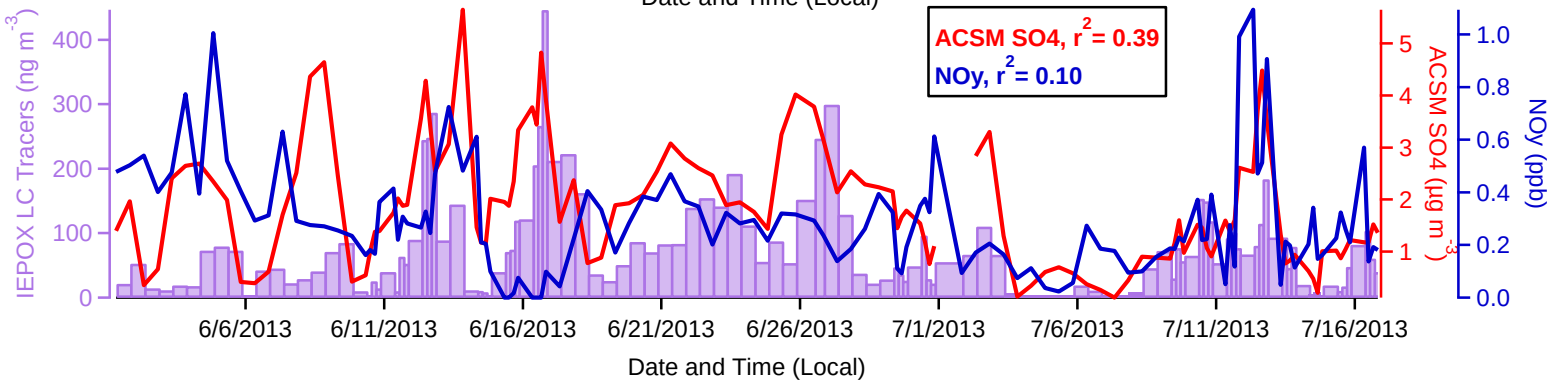
Poster by Xinxin Li

(1a) SOA Tracers Quantification: Tracers Comparison

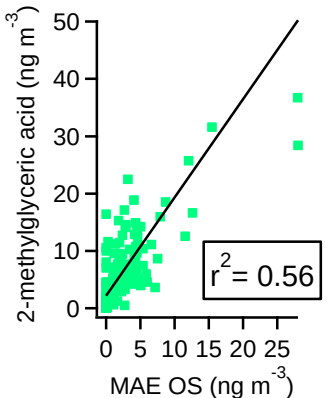
IEPOX-derived SOA Tracers

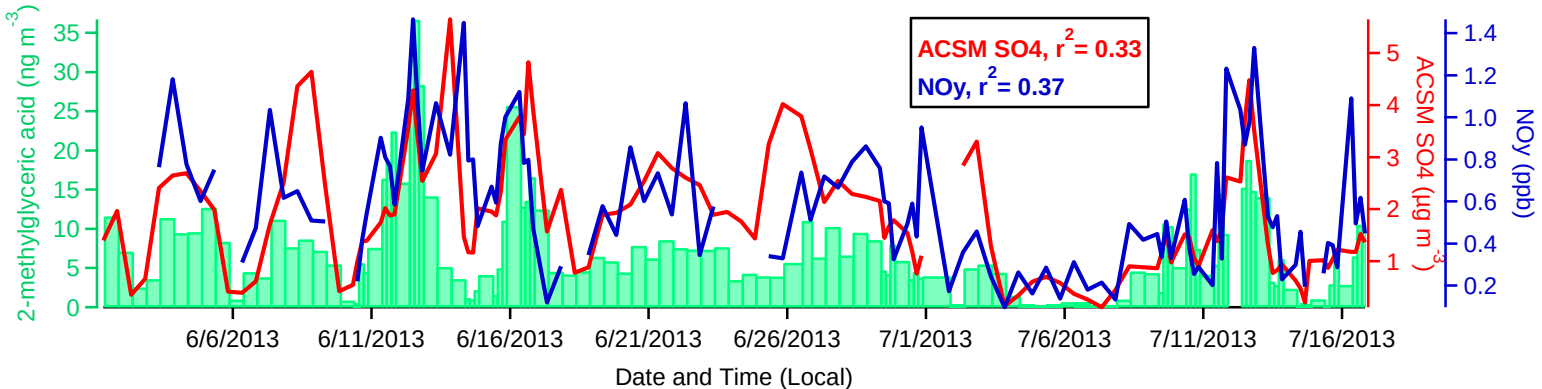






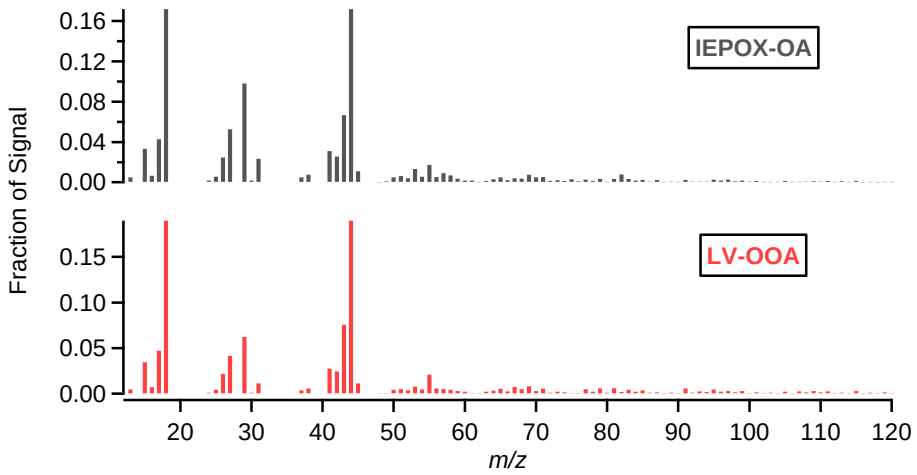
MAE-derived SOA Tracers

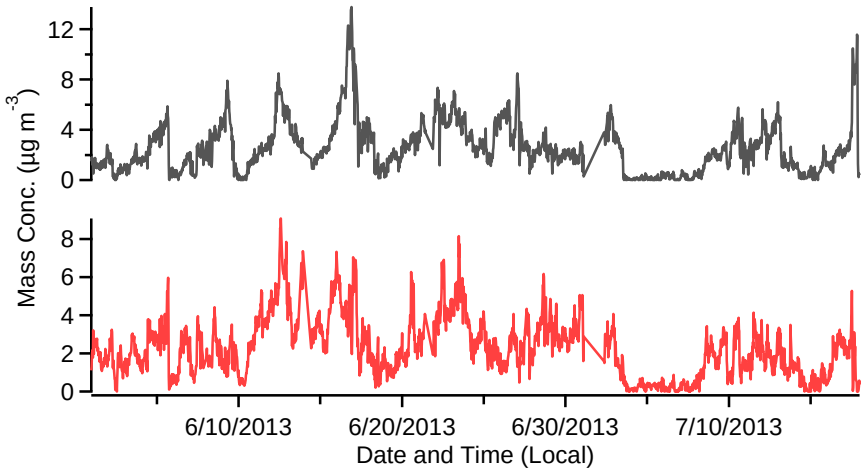




(1b) OA Characterization

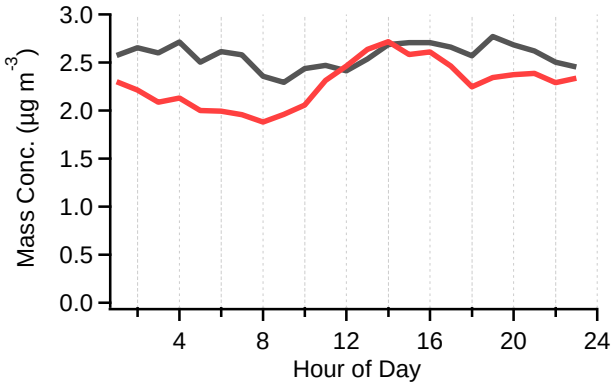
PMF: 2 Factor Fpeak = -0.05

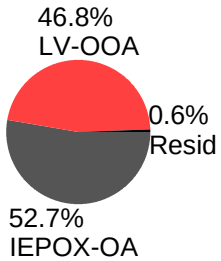




r_{MS}	Borneo 82Fac	ATL IEPOX-OA	Lab IEPOX-SOA
IEPOX-OA	0.926	0.883	0.701
LV-OOA	0.858	0.830	0.581

r_{TS}	ACSM SO4	Ox	NOx
IEPOX-OA	0.790	0.097	0.020
LV-OOA	0.481	0.066	0.086

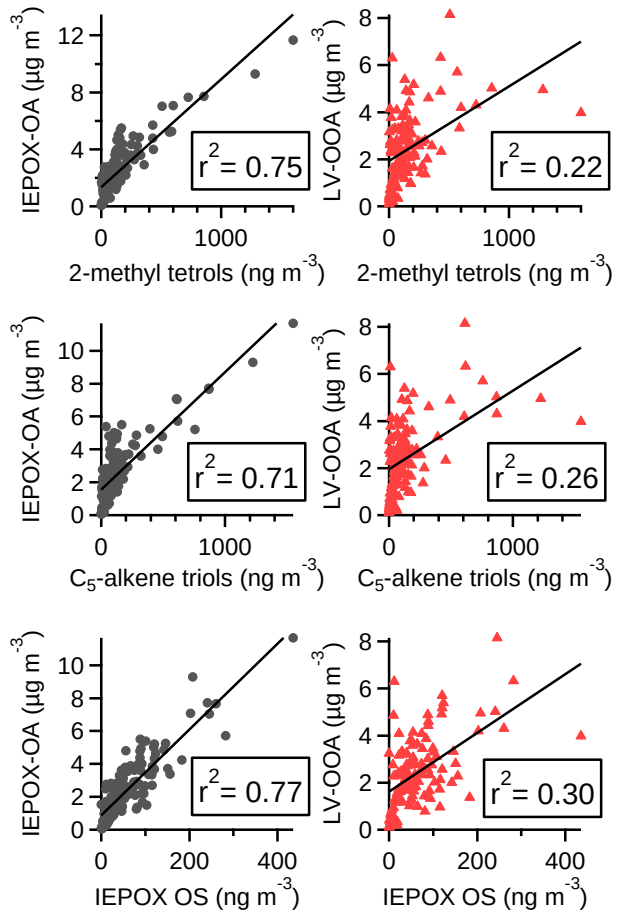




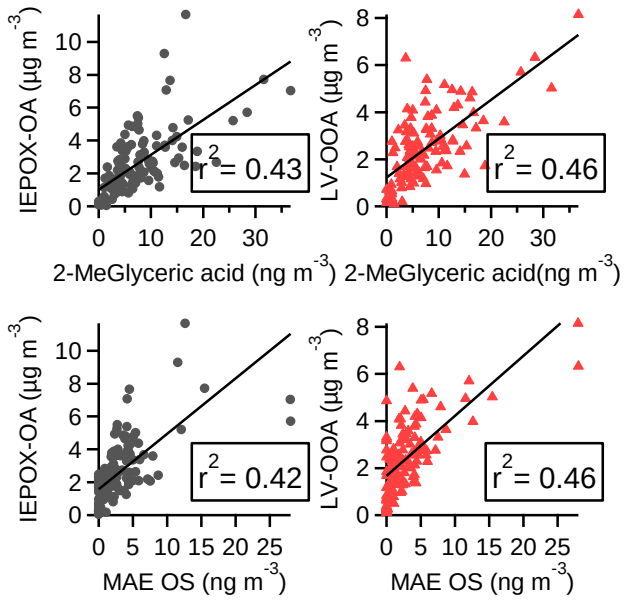
IEPOX-OA factor is consistent with Budisulistiorini et al. (2013, ES&T), Robinson et al. (2011, ACP), and Slowik et al. (2011, ACP) which characterized by *m/z* 82 ion.

(1b) OA Characterization: Identification of PMF Factors

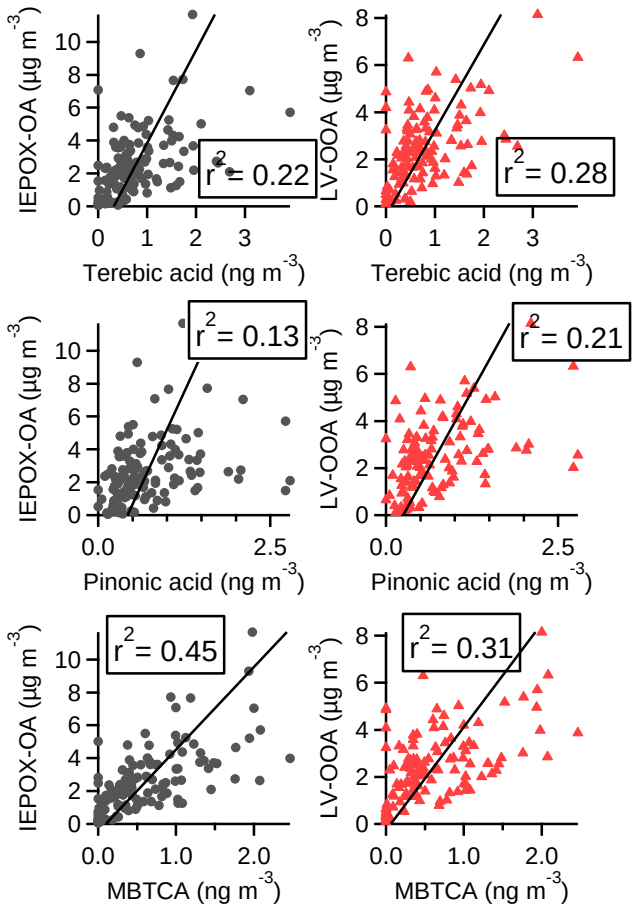
IEPOX-derived SOA Tracers



MAE-derived SOA Tracers

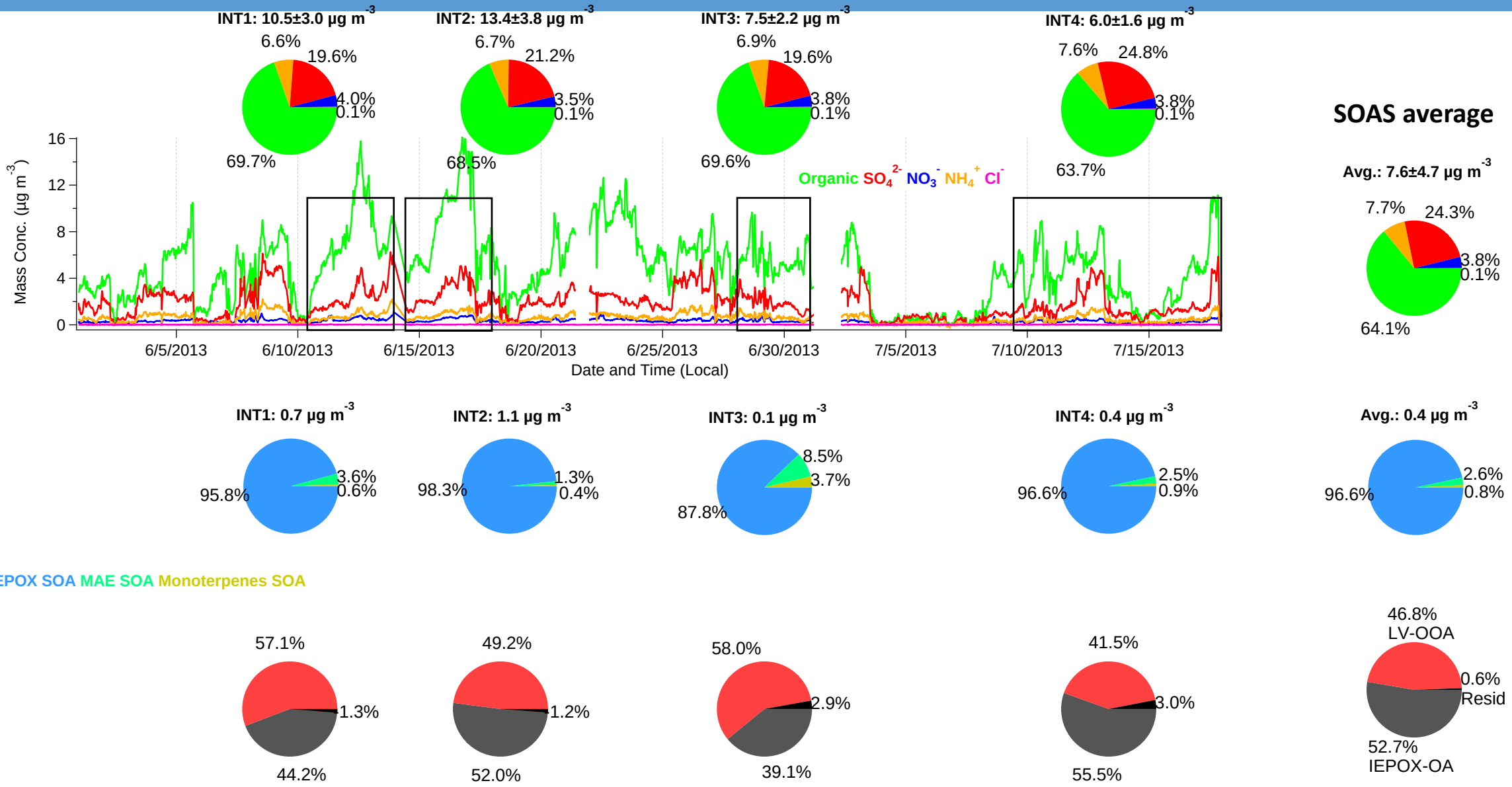


Monoterpenes-derived SOA Tracers

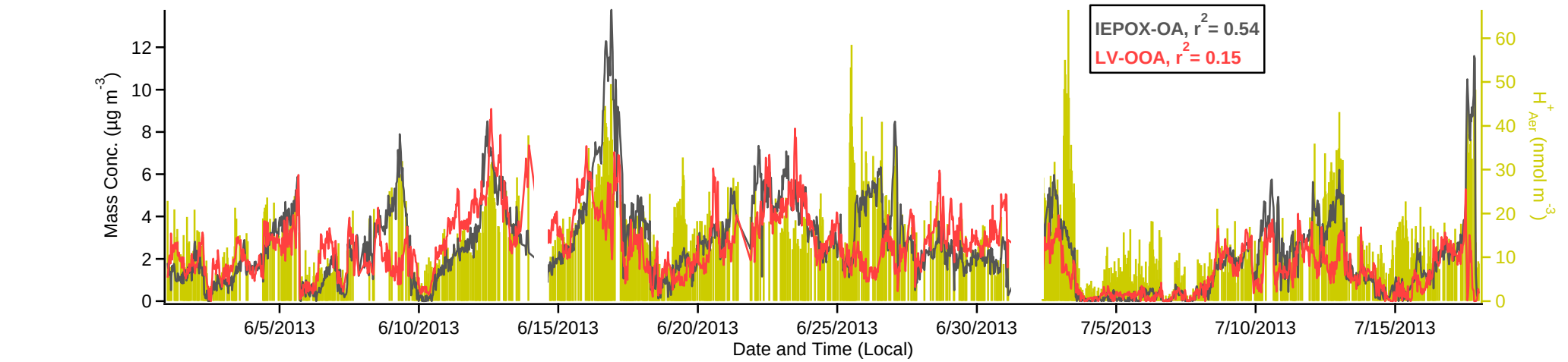


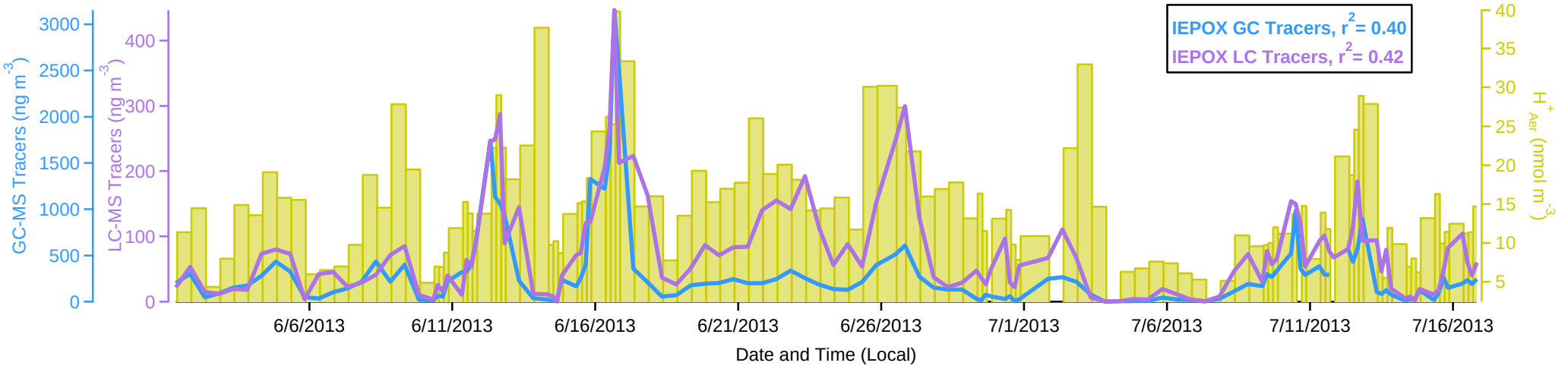
Strong correlation between IEPOX-OA factor and IEPOX-derived SOA tracers provides evidence supporting that IEPOX is the major source.

(1b) OA Characterization: Contributions to OM



(2) Effect of Aerosol Acidity on Isoprene-derived SOA Formation

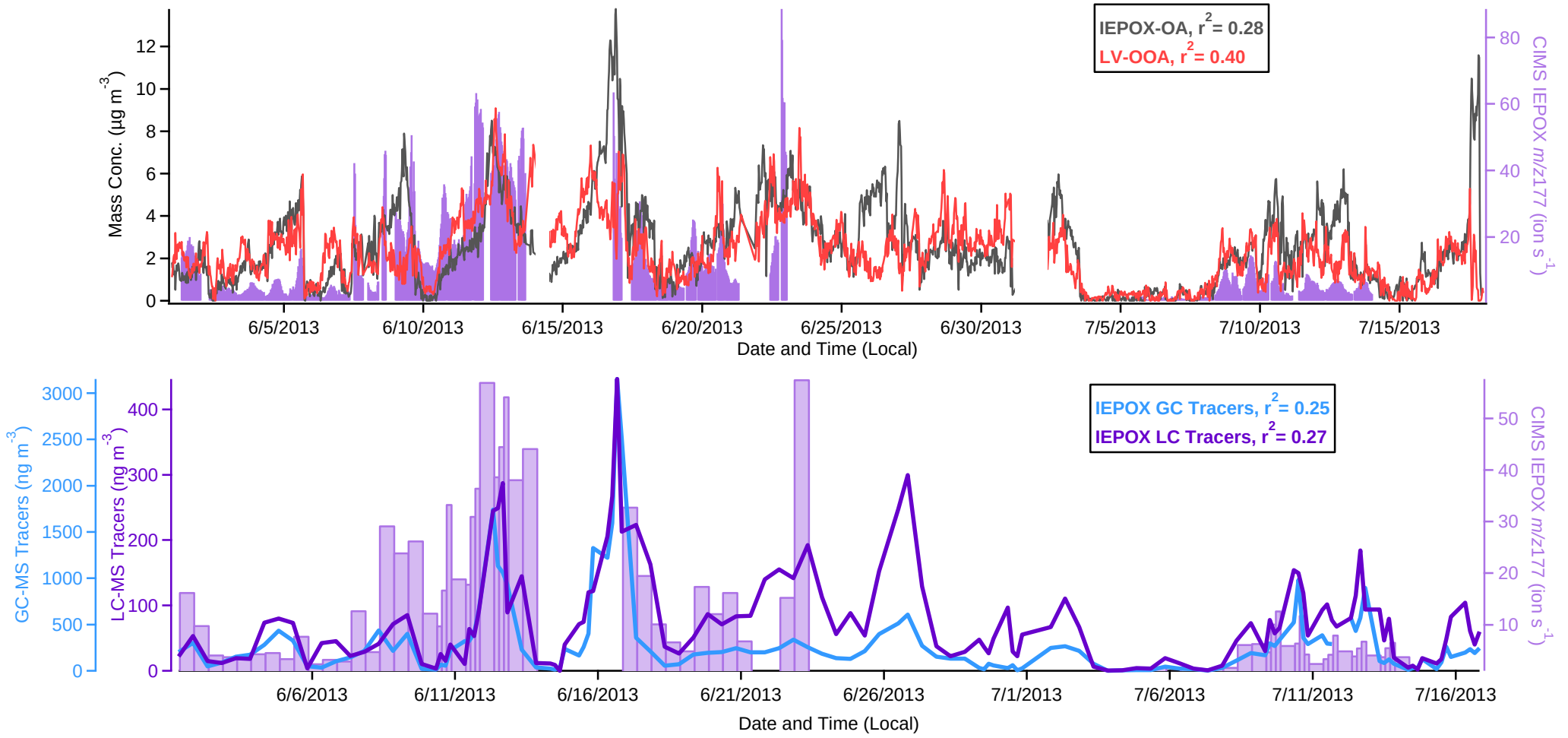




During **more acidic period*** some variations in IEPOX-OA and IEPOX SOA molecular tracers can be explained by H^+ present in aerosol, suggesting that aerosol acidity might play important role in their formation.

**H^+_{Aer} and $NH_4^+{}_{meas}/NH_4^+{}_{neu}$ were estimated using aerosol indicator approaches in Zhang et al. (2007). More acidic period is determined from $NH_4^+{}_{meas}/NH_4^+{}_{neu} < 0.75$*

(3) Gaseous Epoxides Formation from Isoprene Oxidation Measurements



Weaker correlations between CIMS IEPOX and IEPOX-OA factor and IEPOX SOA tracers could be explained due to upwind chemical processing.

Summary

- Isoprene-derived SOA tracers comprise on average ~10% of total OM measured by ACSM
  - IEPOX-reactive uptake dominates the isoprene-derived SOA fraction at Look Rock during SOAS, whereas monoterpene-derived SOA contribute minimally
  - Difference in correlations of IEPOX-derived and MAE-derived SOA tracers with NO_y provides some indications that MAE forms under high NO_2/NO conditions

- IEPOX-OA factor resolved from PMF analysis is highly correlated with IEPOX-derived SOA tracers.

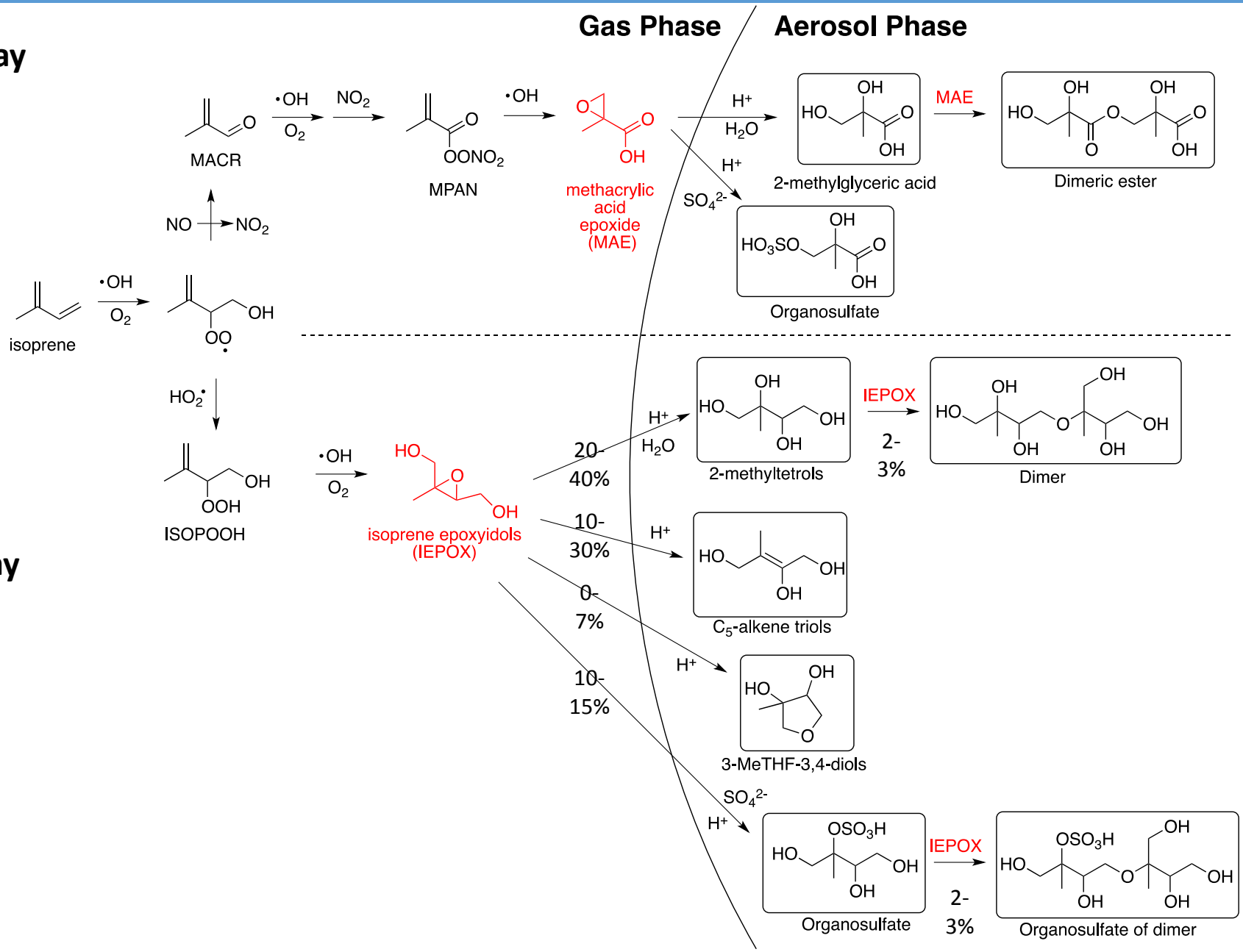
- Effect of acidity on SOA formation was moderate for IEPOX-OA factor and IEPOX-derived SOA tracers.

Future Work

- Aerosol acidity and liquid water content analysis
  - E-AIM, ISORROPIA
- Back trajectory analysis
  - HYSPLIT
- Modeling SOA formation
  - CMAQ (Pye et al., 2013), GAMMA (McNeill et al., 2012)
- Aerosol light absorption analysis
  - UV-Vis
  - UPLC/DAD and UPLC/ESI-HR-QTOFMS molecular characterization
- Complete synthesis of IEPOX-derived organosulfate
- HRToF-CIMS calibration

Look Rock Sorority

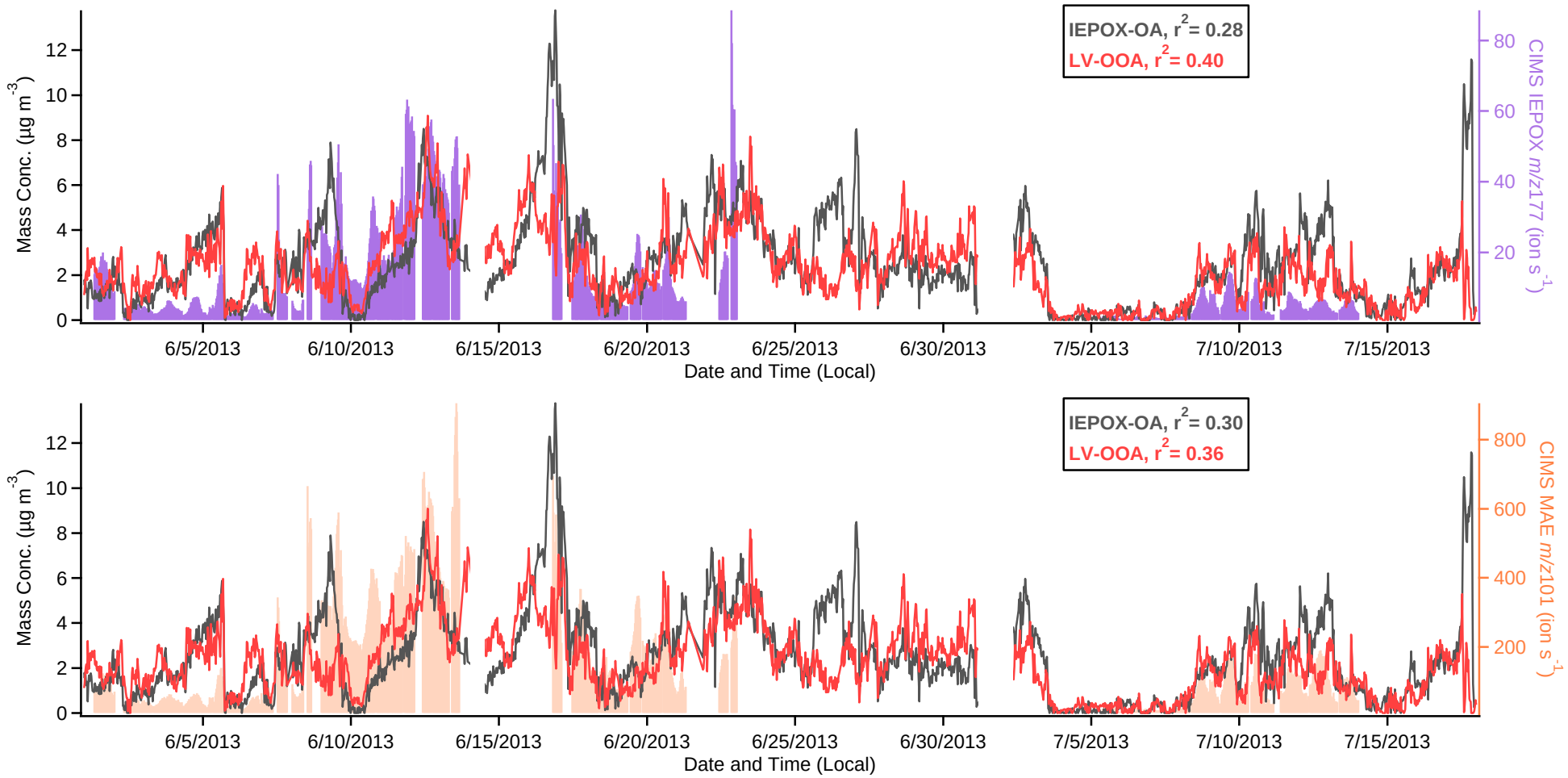
Isoprene Photooxidation Mechanism in the Atmosphere



Lin et al. (2012), Lin et al. (2013)

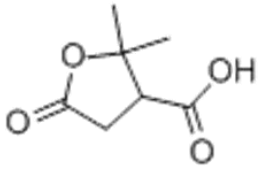
Paulot et al. (2009), Surratt et al. (2010), Lin et al. (2012), Zhang et al. (2012)

(3) Gaseous Epoxides Formation from Isoprene Oxidation Measurements

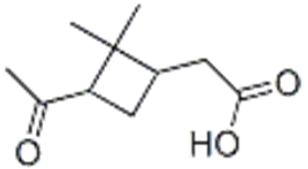


Monoterpenes-derived SOA Tracers

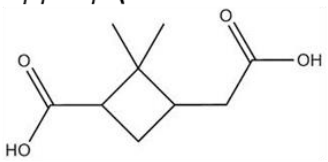
Terebic acid
$C_7H_{10}O_4$ (M-H$^-$: 157 m/z)



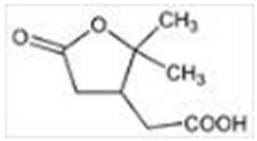
Pinonic acid
$C_{10}H_{16}O_3$ (M-H$^-$: 183 m/z)



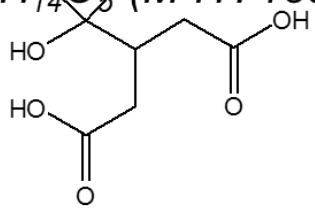
Pinic acid
$C_9H_{14}O_4$ (M-H$^-$:185 m/z)



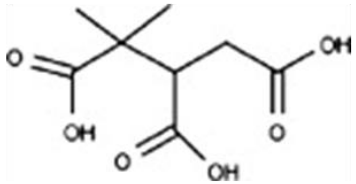
Terpenylic acid
$C_8H_{12}O_4$ (M-H$^-$:171 m/z)



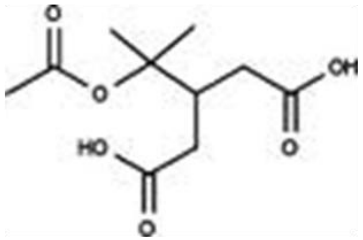
Diaterpenylic acid (DTA)
$C_8H_{14}O_5$ (M-H$^-$: 189 m/z)



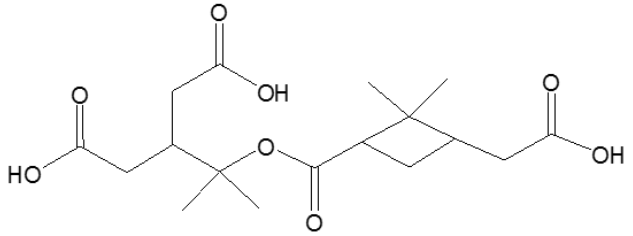
3 Methyl-1,2,3-butanetricarboxylic acid (MBTCA) $C_8H_{12}O_6$ (M-H$^-$: 203 m/z)



Diaterpenylic acid acetate (DTAA)
$C_{10}H_{16}O_6$ (M-H$^-$: 231 m/z)



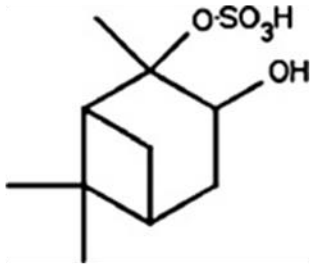
Pinyl-diaterpenyle ester
$C_{17}H_{26}O_8$ (M-H$^-$: 357 m/z)



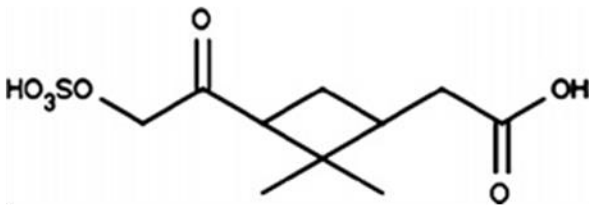
Acid compounds

Monoterpenes-derived SOA Tracers

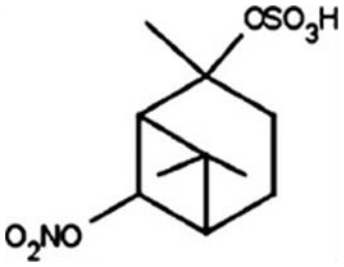
$C_{10}H_{18}O_5S$ (M-H$^-$: 249 m/z)



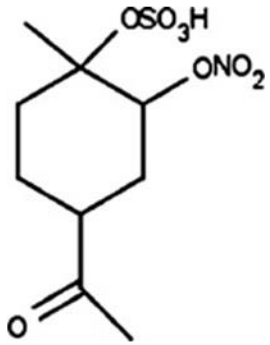
$C_{10}H_{16}O_7S$ (M-H$^-$: 279 m/z)



$C_{10}H_{17}NO_7S$ (M-H$^-$: 294 m/z)



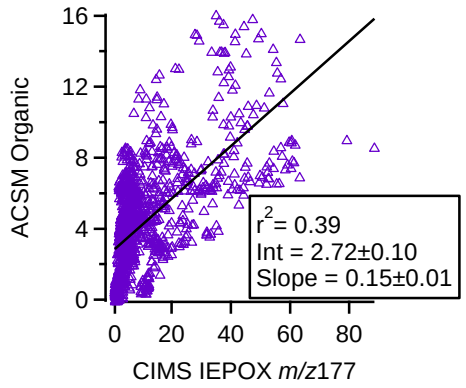
$C_9H_{15}NO_8S$ (M-H$^-$: 296 m/z)

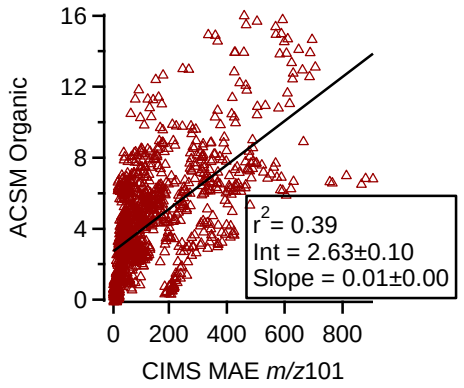


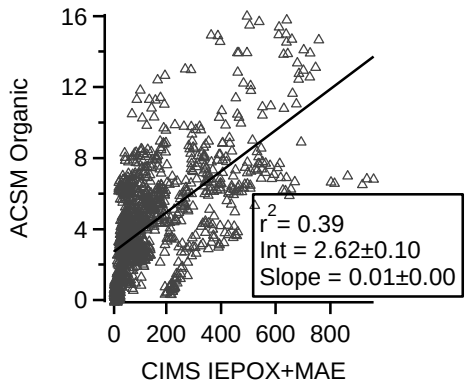
$C_{10}H_{17}NO_{10}S$ (M-H$^-$: 343 m/z)

Unknown

Organosulfates


ACSM Organic
16
12
8
4
0
0
20
40
60
80
CIMS IEPOX m/z177
r2= 0.39
Int = 2.72±0.10
Slope = 0.15±0.01


ACSM Organic
16
12
8
4
0
0
200
400
600
800
CIMS MAE m/z101
r2= 0.39
Int = 2.63±0.10
Slope = 0.01±0.00


ACSM Organic
16
12
8
4
0
0
200
400
600
800
CIMS IEPOX+MAE
r2 = 0.39
Int = 2.62±0.10
Slope = 0.01±0.00