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Atmospheric Chemistry and Physics Discussions

Supplement of

Characterization of a real-time tracer for Isoprene Epoxydiols-derived Secondary Organic Aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements

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Table S1. Pearson's correlation coefficients (R) between time series of organic ions and the PMF IEPOX-SOA factor for the SOAS study (SE US forest).

Ion Formula	Ion mass	Correlation coefficient (R)
Ions with R > 0.8		
$C_5H_6O^+$	82.0419	0.97
$C_5H_5O^+$	81.034	0.95
$C_4H_5^+$	53.0391	0.90
$C_4H_6O^+$	70.0419	0.88
$C_3H_7O_2^+$	75.0446	0.87
$C_3H_5O^+$	57.034	0.84
$C_4H_6^+$	54.047	0.84
CH_3O^+	31.0184	0.83
$C_4H_7O_2^+$	87.0446	0.83
$C_3H_6^+$	42.047	0.82
$C_4H_2^+$	50.0157	0.82
$C_5H_8O^+$	84.0575	0.82
$C_4H_5O^+$	69.034	0.82
C_4H^+	49.0078	0.82
$C_3H_3^+$	39.0235	0.82
$C_2H_3^+$	27.0235	0.81
C_3H^+	37.0078	0.80
$C_2H_5^+$	29.0391	0.80
$C_4H_3^+$	51.0235	0.80
$C_3H_2^+$	38.0157	0.80
$C_3H_5^+$	41.0391	0.80
CH_2O^+	30.0106	0.80
Ions with lowest R		
$CHNO^+$	43.0058	-0.37
CNO^+	41.998	-0.12
CN^+	26.0031	-0.11
Other common used ions in AMS		
$C_2H_3O^+$	43.0184	0.72
$C_3H_7^+$	43.0548	0.57
CO_2^+	43.9898	0.66
$C_3H_3O^+$	55.0184	0.72
$C_4H_7^+$	55.0548	0.68
$C_2H_4O_2^+$	60.0211	0.60

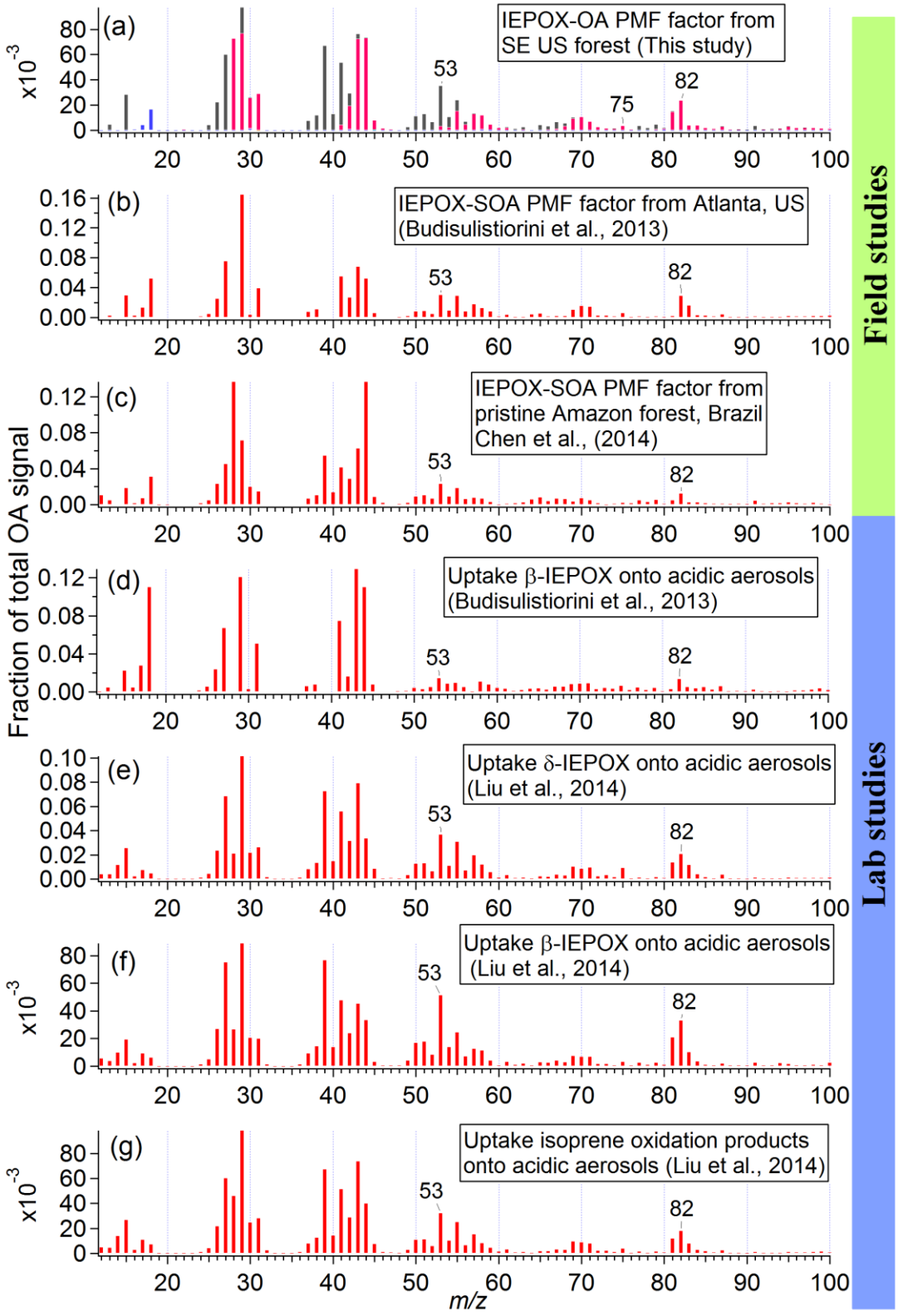
Table S2. Description of spectra which have higher $f_{C_5H_6O}$ than background $f_{C_5H_6O}$, labeled by number in Fig. 5.

Index	Spectra name	Description of spectra sources	References
1	HOA[a] from CARES campaign	Isoprene emission influenced, aerosol is neutralized	(Setyan et al., 2012)
2	OA from CA Central Valley	Isoprene emission influenced, aerosol is slightly acidic.	(Dunlea et al., 2009)
3	NO3+Δ–3–Carene reaction in Chamber	Biogenic SOA	Chamber study in CU
4	Ozonolysis a-terpene in Chamber	Biogenic SOA	(Chhabra et al., 2010)
5	SV-OOA[b] from SOAR	Slight biogenic influence	(Docherty et al., 2011)
6	SV-OOA from Paris summer campaign	Not mentioned in study, however, forests around the sampling site.	(Crippa et al., 2013)
7	NO3+Δ–3–Carene reaction in Chamber	Biogenic SOA	Chamber study in CU
8	SV-OOA from SOAS	Isoprene and monoterpene influenced	This study
	NO3+Δ–3–Carene reaction in Chamber	Biogenic SOA	Chamber study in CU
10	MO-OOA[c] in CARES campaign	Urban SOA with isoprene emission-influenced	(Setyan et al., 2012)
11	SV-OOA in MILAGRO	Urban SOA	(Aiken et al., 2009;Ulbrich et al., 2009)
12	LV-OOA in Paris summer	Urban-background SOA, forests around the sampling site.	(Crippa et al., 2013)
13	Adipic acid	Pure chemical OA standards	(Canagaratna et al., 2015)
14	3-Hydroxy-3-Methylglutaric Acid	Pure chemical OA standards	(Canagaratna et al., 2015)
15	4-ketopimelic acid	Pure chemical OA standards	(Canagaratna et al., 2015)
16	5-Oxoazelaic acid	Pure chemical OA standards	(Canagaratna et al., 2015)
17	Gamma ketopimelic acid dilactone	Pure chemical OA standards	(Canagaratna et al., 2015)

[a] HOA=Hydrocarbon-like OA

[b] SV-OOA=Semi-volatile oxygenated OA

[c] MO-OOA=More-oxidized oxygenated OA


(a)
IEPOX-OA PMF factor from SE US forest (This study)
53
82
75
x10^-3
(b)
IEPOX-SOA PMF factor from Atlanta, US (Budisulistiorini et al., 2013)
(c)
IEPOX-SOA PMF factor from pristine Amazon forest, Brazil Chen et al., (2014)
Fraction of total OA signal
(d)
Uptake β-IEPOX onto acidic aerosols (Budisulistiorini et al., 2013)
(e)
Uptake δ-IEPOX onto acidic aerosols (Liu et al., 2014)
(f)
Uptake β-IEPOX onto acidic aerosols (Liu et al., 2014)
(g)
Uptake isoprene oxidation products onto acidic aerosols (Liu et al., 2014)
m/z
Field studies
Lab studies

10

Figure S1. Mass spectra of IEPOX-SOA from different studies. Panel (a) − (c) are the results from field studies. Panel (d) − (g) are the results from lab studies.

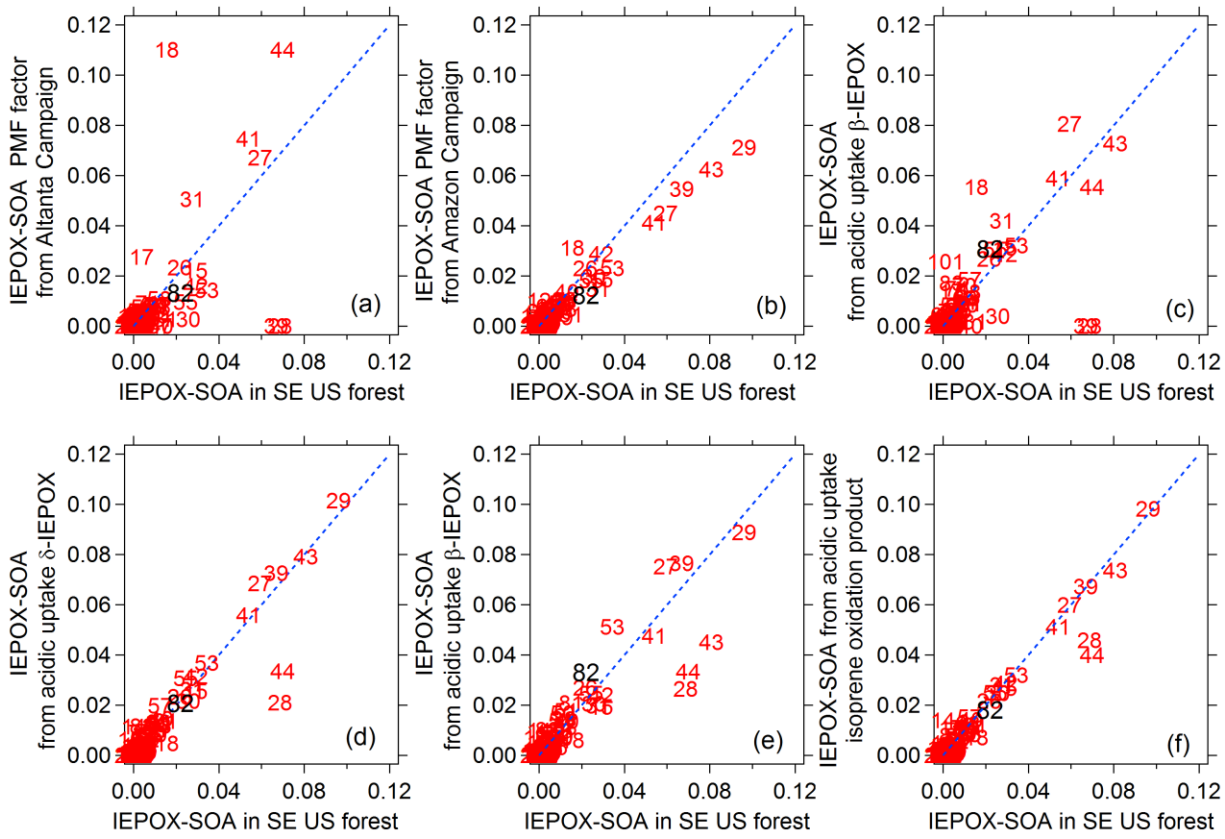


Figure S2. Scatter plots of IEPOX-SOA spectra in other studies vs IEPOX-SOA spectrum from this study (SOAS, SE US forest). The spectra on the y-axes are in the same order as Figures S1 (b) to (g).

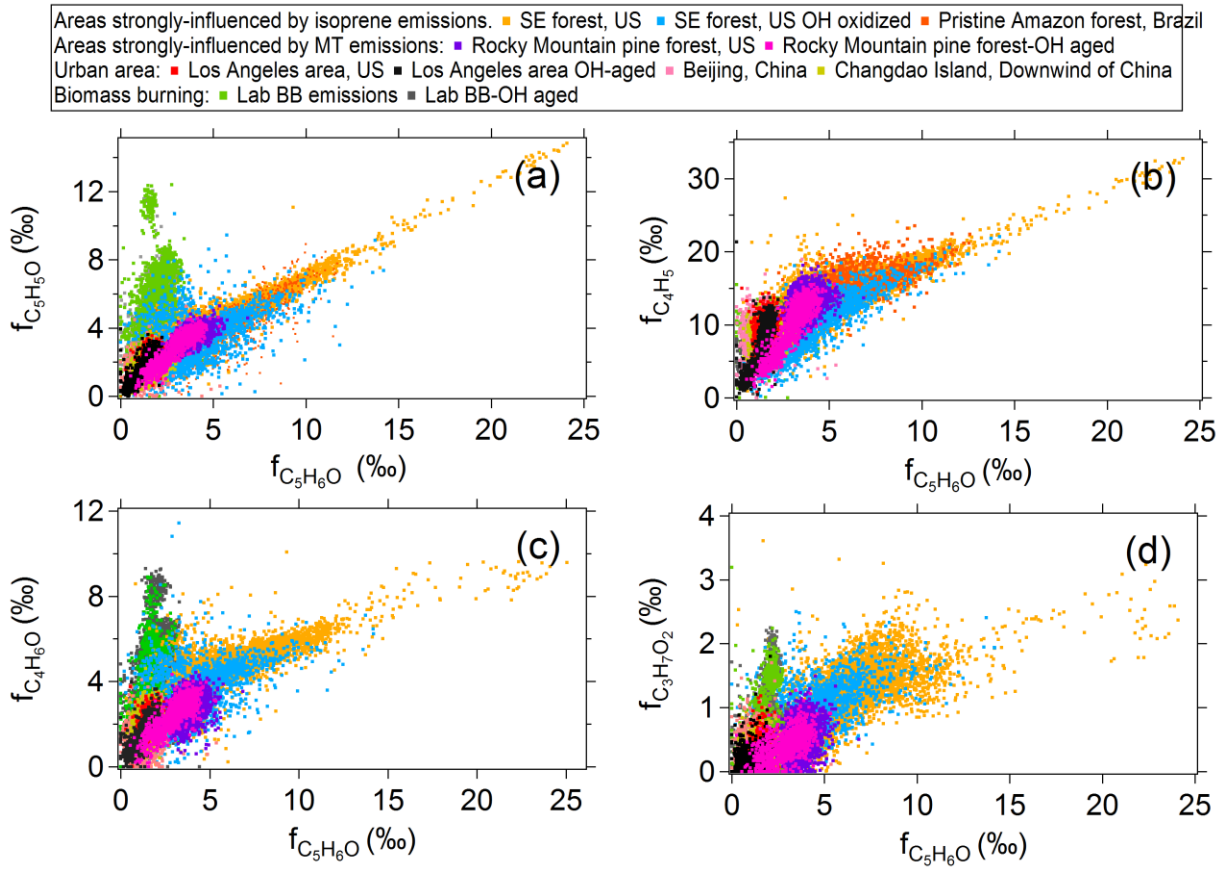


Figure S3. Scatter plots of abundance of ions versus $f_{C_5H_6O}$ obtained in different studies: (a) $f_{C_5H_5O}$,(b) $f_{C_4H_5}$, (c) $f_{C_4H_6O}$, and (d) $f_{C_3H_7O_2}$. Compared to $C_5H_6O^+$, $f_{C_4H_5}$, $f_{C_4H_6O}$, and $f_{C_5H_5O}$ have high background levels in urban and biomass-burning emissions. The signal to noise of $f_{C_3H_7O_2}$ measured in AMS is very low.

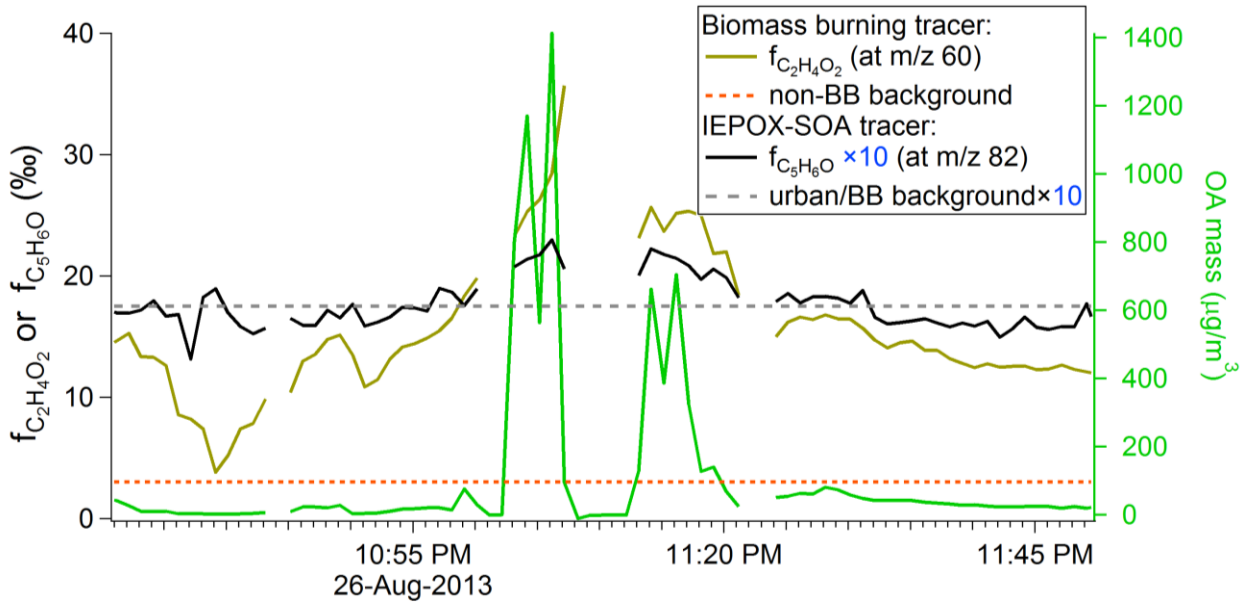


Figure S4. Time series of OA mass concentration, and of tracers for IEPOX-SOA ($f_{C_5H_6O}$) and biomass-burning ($f_{C_2H_4O_2}$, *m/z* 60.0211) compared to their respective backgrounds on the research flight on Aug 26, 2013 during the SEAC4RS campaign. The biomass-burning tracer indicates extensive fire influence during this period, while the IEPOX-SOA tracer stays at background levels across widely varying OA concentrations.

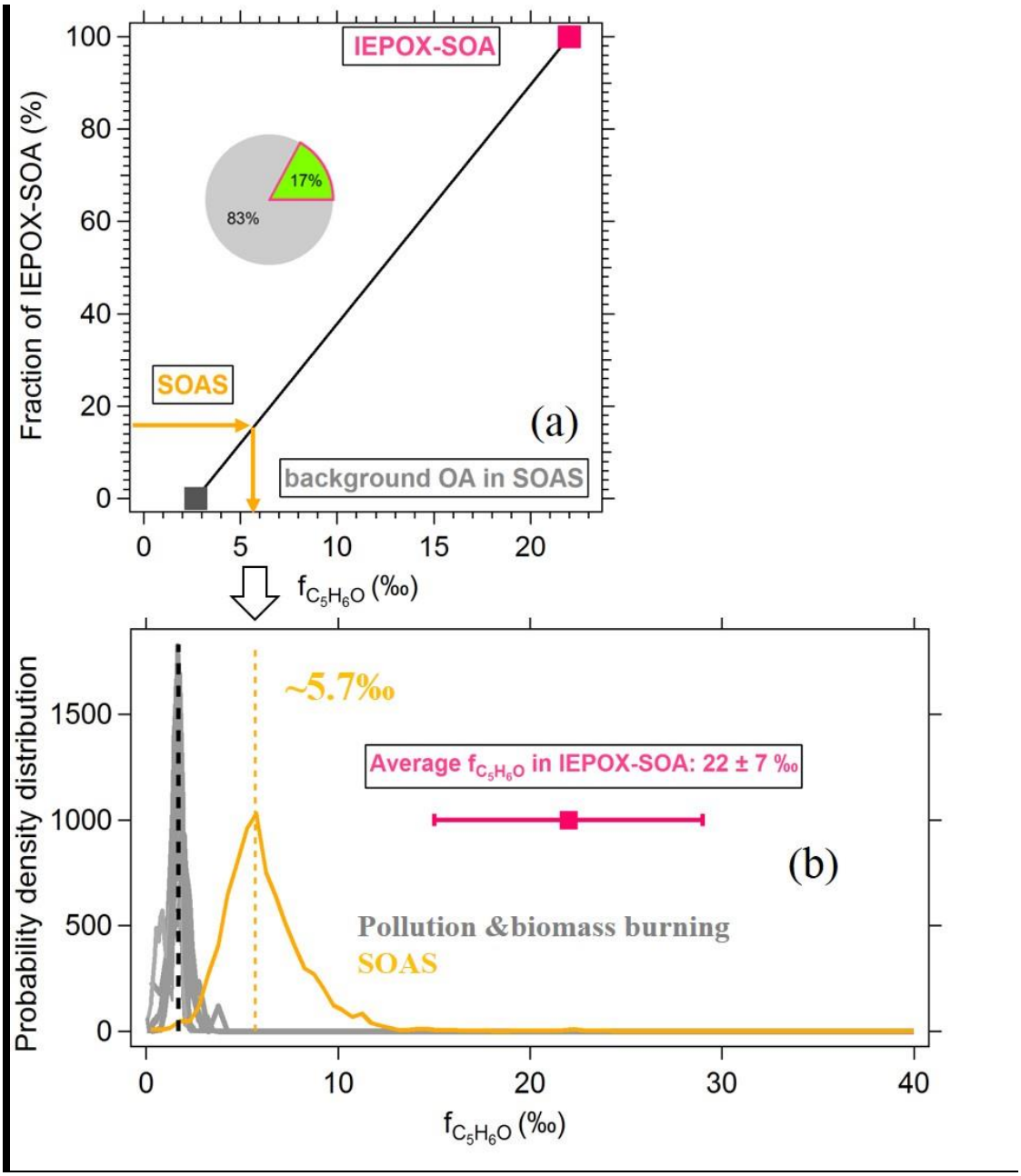
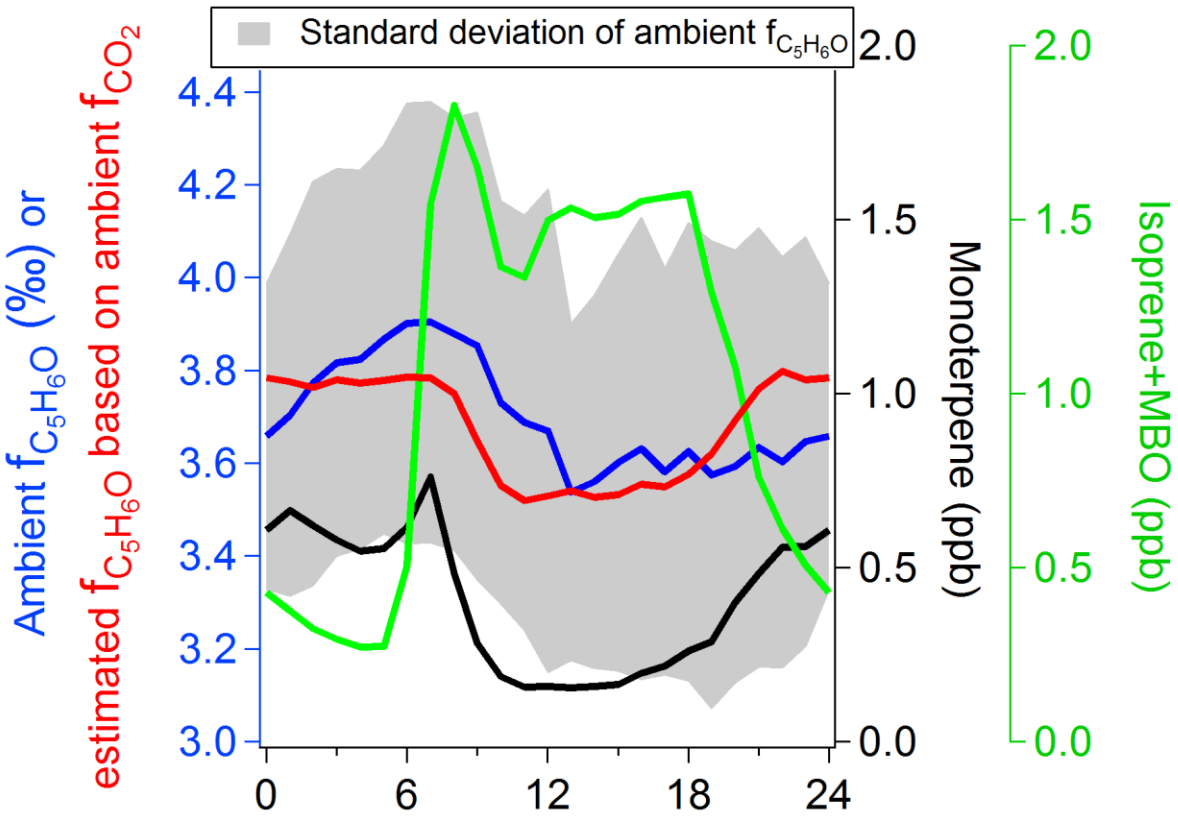


Figure S5. Schematic of the estimation method of IEPOX-SOA based on ambient $f_{C_5H_6O}$. (a) Fraction of IEPOX-SOA in total OA vs ambient $f_{C_5H_6O}$ (b) probability distribution of $f_{C_5H_6O}$ in SOAS and in background studies. The average background of $f_{C_5H_6O}$ in OA from SOAS-CTR should be between the $f_{C_5H_6O}$ from urban and biomass burning emissions (~1.7‰) and $f_{C_5H_6O}$ strongly influenced by monoterpene emissions, which we can use 3.7‰ from Rocky Mountain site as representative value. An average $f_{C_5H_6O}$ value of 2.7‰ was used here for the background $f_{C_5H_6O}$ for SOAS-CTR. $f_{C_5H_6O}$ in PMF resolved IEPOX-SOA is 22‰. Two values corresponding to 0% and 100% IEPOX-SOA in total OA, are shown as two square points shown in Fig. S5a. If we assume the air containing these two types of OA are mixed with each other,

then we can draw a line between these two points in Fig. S5a. Ambient $f_{C_5H_6O}$ in OA partially contributed by IEPOX-SOA should vary along this line. Take SOAS as an example, 17% of OA in SOAS was composed by IEPOX-SOA, then it corresponds to an expected average $f_{C_5H_6O}$ of ~5.7 ‰, which is consistent with what was observed (Fig. S5b). The peak of the probability distribution of $f_{C_5H_6O}$ in ambient OA in SOAS is around 5.7‰.



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53 **Figure S6.** Diurnal variation of ambient $f_{C_5H_6O}$ in OA at the Manitou Forest pine forest site in
54 the Rocky Mountains during the BEACHON-RoMBAS 2011 field study, together with diurnal
55 variations of estimated $f_{C_5H_6O}$ from f_{CO_2} based on regression results between $f_{C_5H_6O}$ and f_{CO_2}
56 (ambient+Oxidation flow reactor) in this study. The diurnal variation of monoterpene and
57 isoprene+MBO are also shown.

58

59

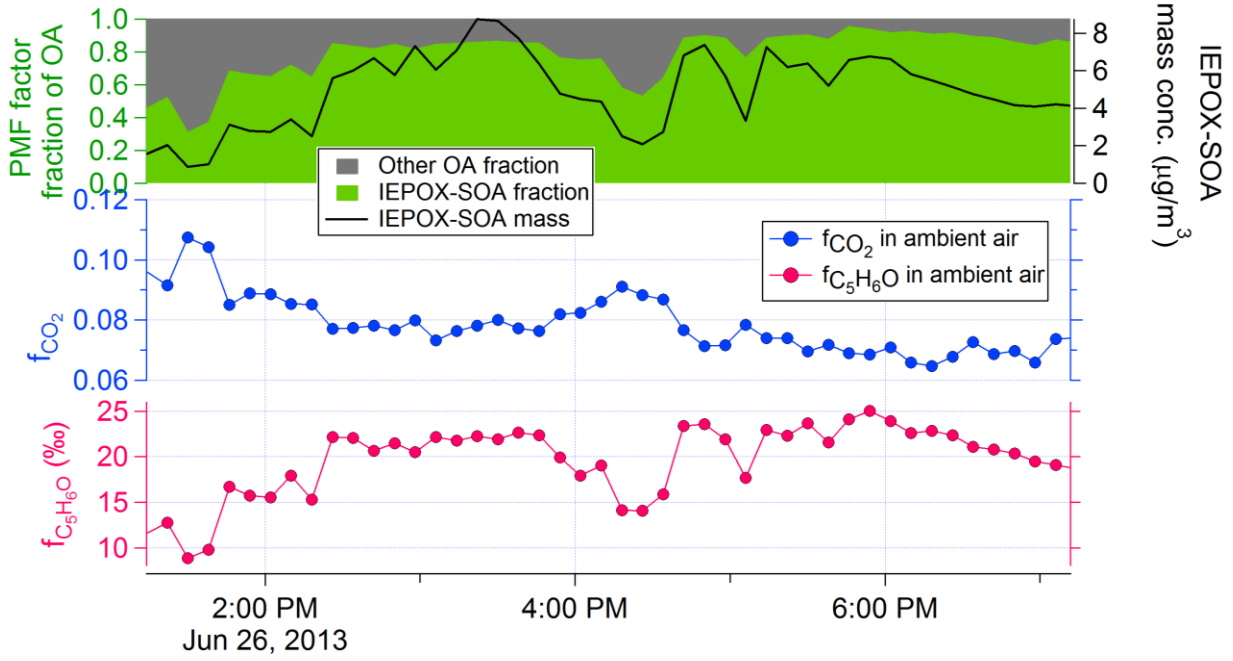

Figure S7. Time series of ambient $f_{C_5H_6O}$, f_{CO_2}, and IEPOX-SOA mass concentrations, together with the IEPOX-SOA fraction of OA during the SOAS-CTR campaign in a SE US forest. During this period, high sulfate and IEPOX-SOA mass concentrations and mass fractions are observed.

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