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Supplement of

Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements

W. W. Hu et al.

Correspondence to: J. L. Jimenez (jose.jimenez@colorado.edu)

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	NO_3 + Δ-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	NO_3 + Δ-Carene reaction in Chamber	Biogenic SOA	Chamber study in CU
8	SV-OOA from SOAS	Isoprene and monoterpene influenced	This study
	NO_3 + Δ-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

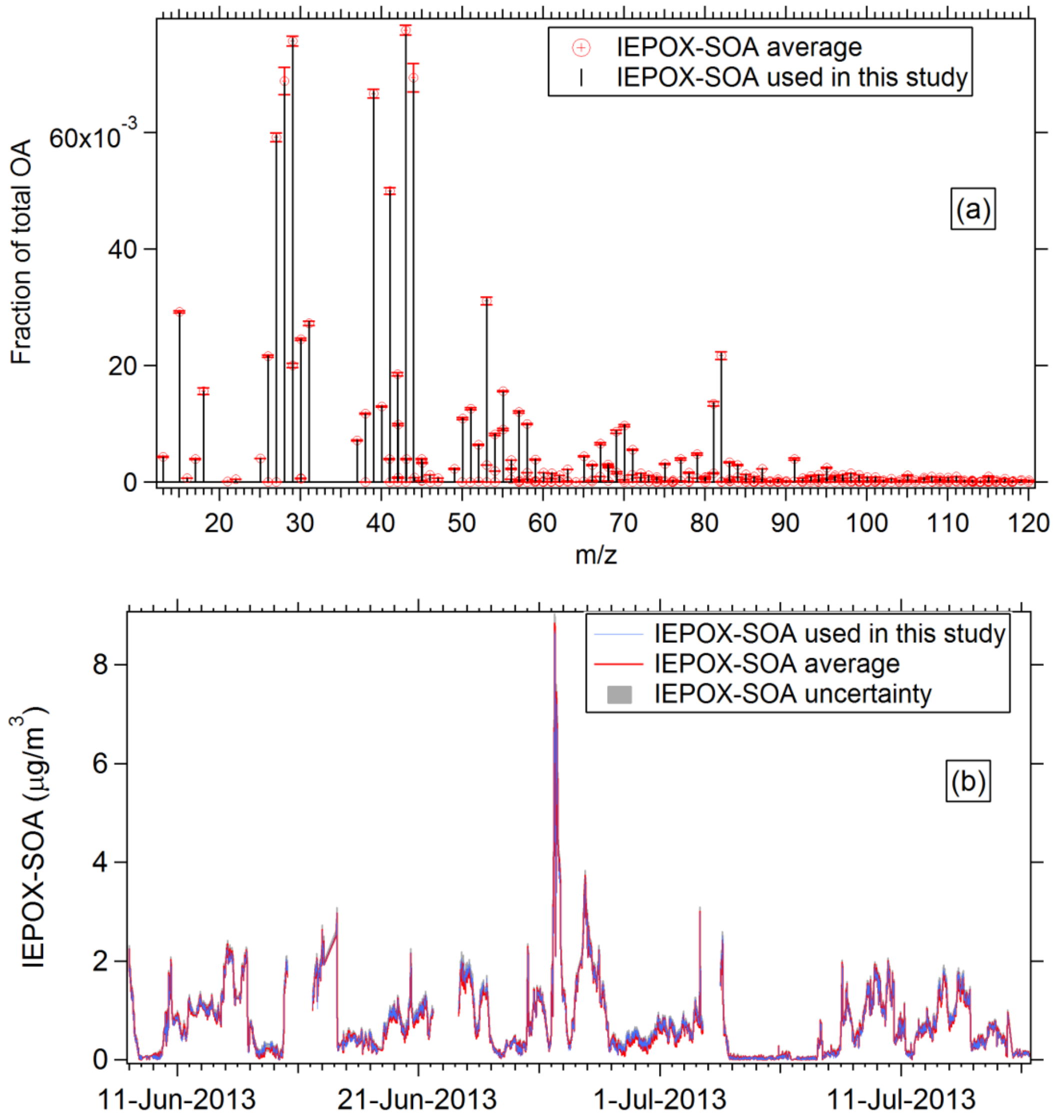

Figure S1. Results from bootstrapping analysis of the 4-factor solution of the SOAS dataset. Average IEPOX-SOA, with standard deviation, are shown for IEPOX-SOA (a) mass spectrum and (b) time series.

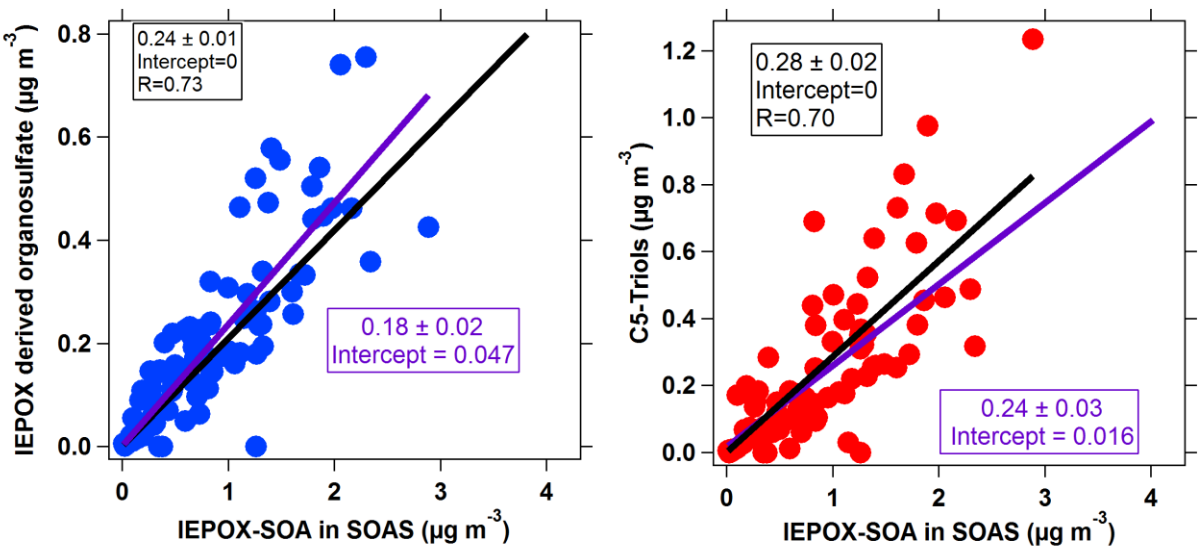

Figure S2. Scatter plots between IEPOX-derived organosulfate and C5-triols vs IEPOX-SOA_{PMF} in the SOAS study. The IEPOX-derived organosulfate and C5-triols were measured in GC/MS and LC/MS analysis of filter extracts (Lin et al., 2014;Budisulistiorini et al., 2015).

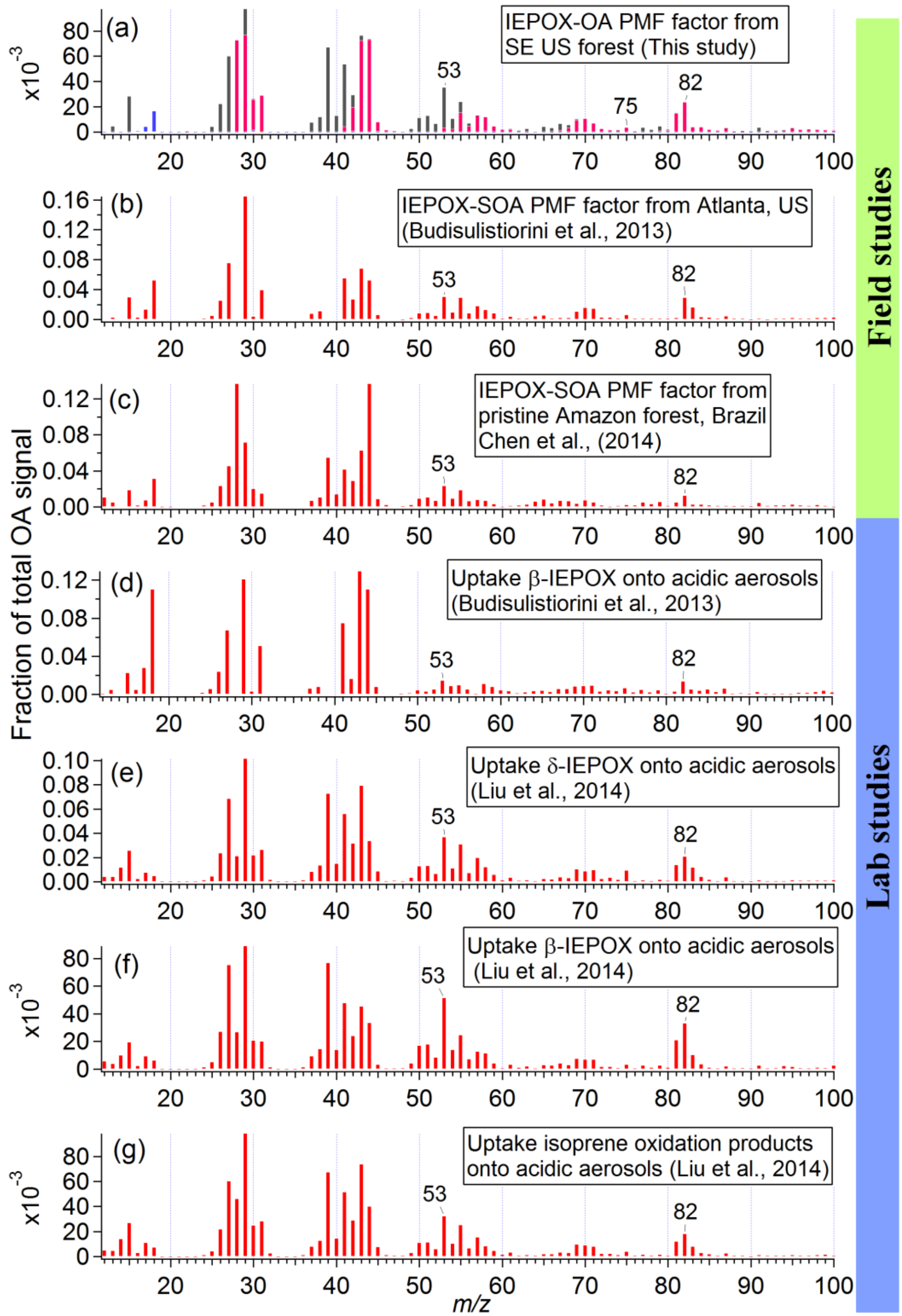

Figure S3. Mass spectra of IEPOX-SOA from different studies. Panel (a) − (c) are the results from field studies. Panel (d) − (g) are the results from lab studies.

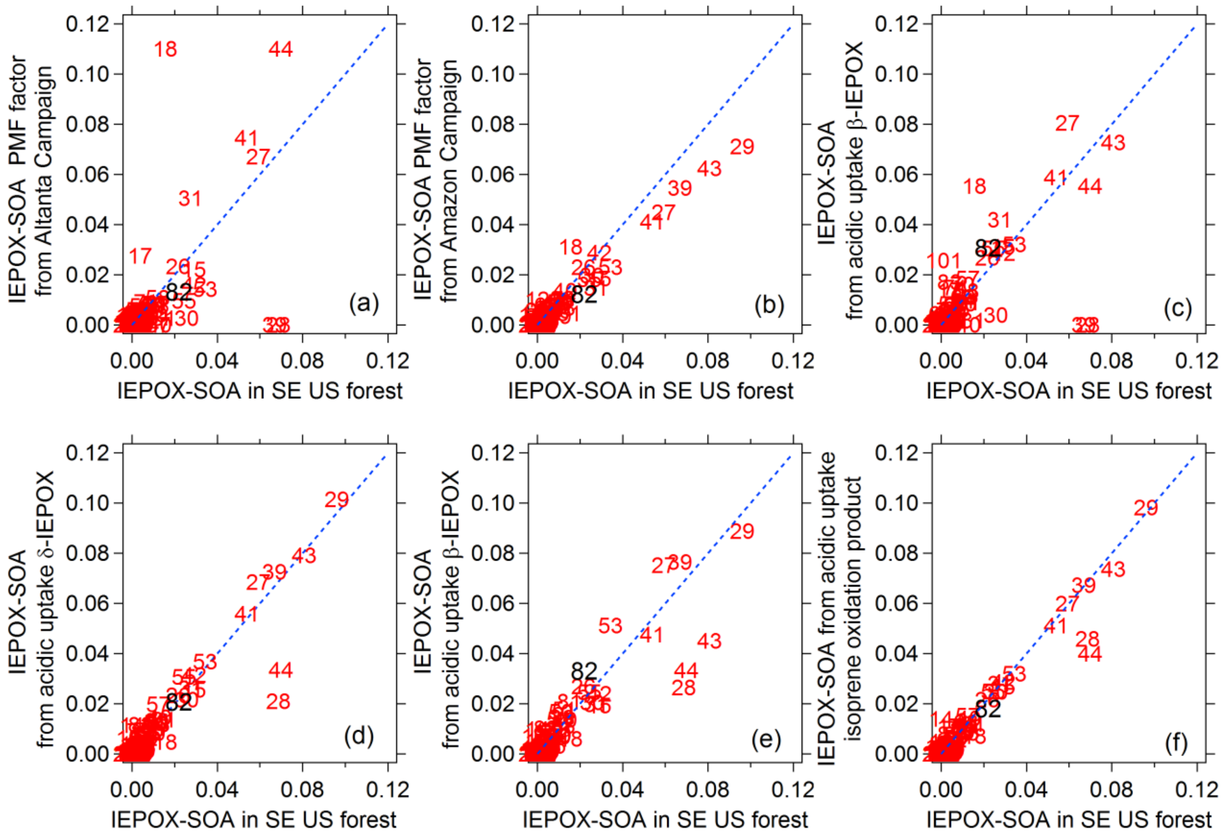

Figure S4. Scatter plots of IEPOX-SOA spectra in other studies vs IEPOX-SOA spectrum from this study (SOAS, SE US forest). The spectra on the y-axes are in the same order as Figures S1 (b) to (g).

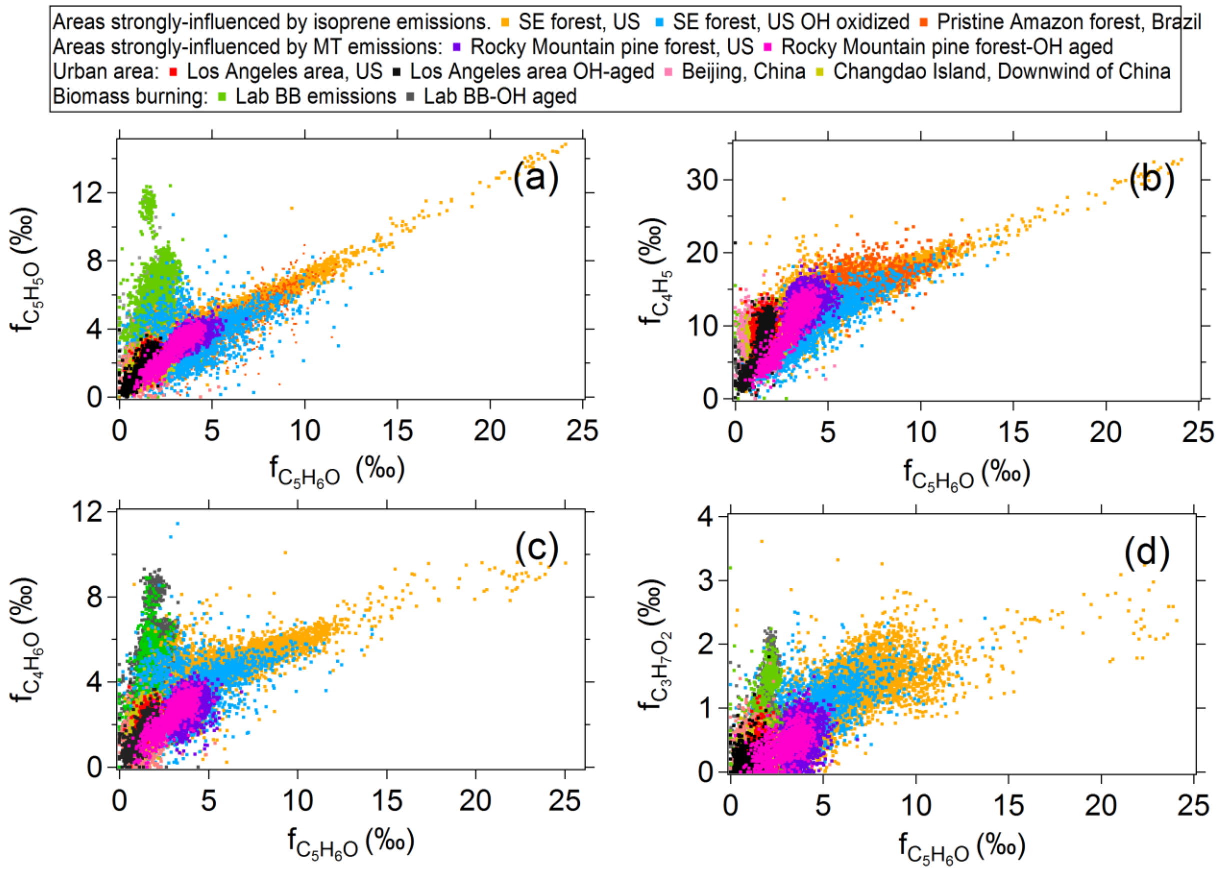

Figure S5. Scatter plots of abundance of ions versus $f^{OA}_{C_5H_6O}$ obtained in different studies: (a) $f^{OA}_{C_5H_5O}$,(b) $f^{OA}_{C_4H_5}$, (c) $f^{OA}_{C_4H_6O}$, and (d) $f^{OA}_{C_3H_7O_2}$. Compared to $f^{OA}_{C_5H_6O}$, $f^{OA}_{C_4H_5}$, $f^{OA}_{C_4H_6O}$, and $f^{OA}_{C_5H_5O}$ have high background levels in urban and biomass-burning emissions. The signal to noise of $f^{OA}_{C_3H_7O_2}$ measured in AMS is very low.

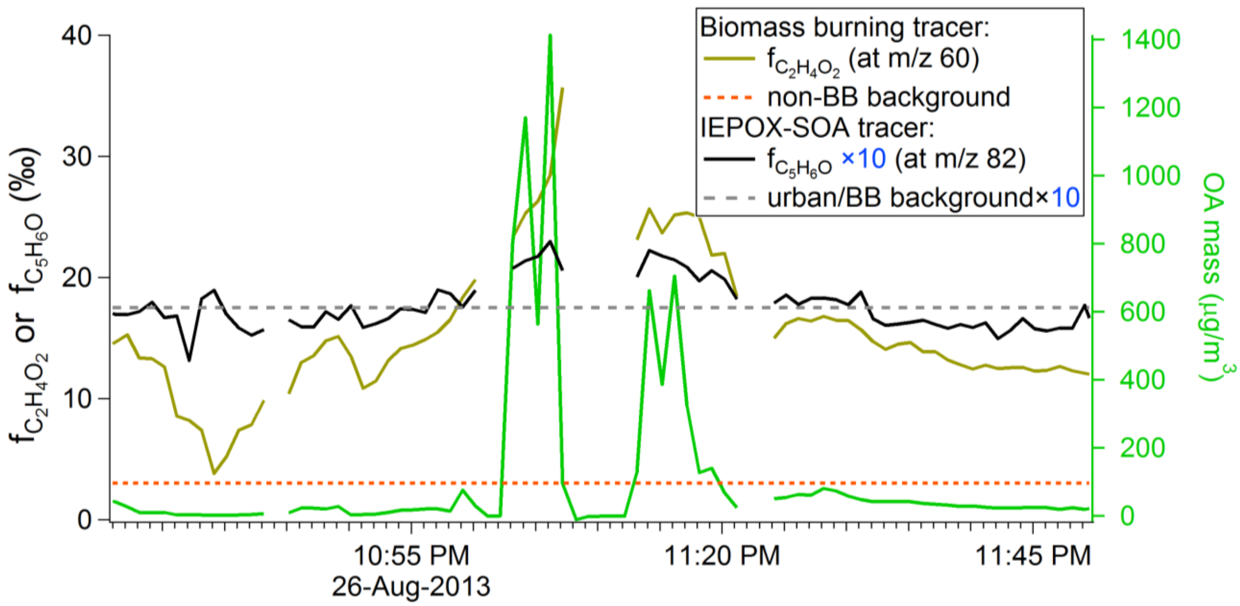

Figure S6. Time series of OA mass concentration, and of tracers for IEPOX-SOA ($f_{C_5H_6O}$) and biomass-burning ($f_{C_2H_4O_2}$, *m/z* 60.0211) compared to their respective backgrounds on the research flight on Aug 26, 2013 during the SEAC4RS campaign. The biomass-burning tracer indicates extensive fire influence during this period, while the IEPOX-SOA tracer stays at background levels across widely varying OA concentrations.

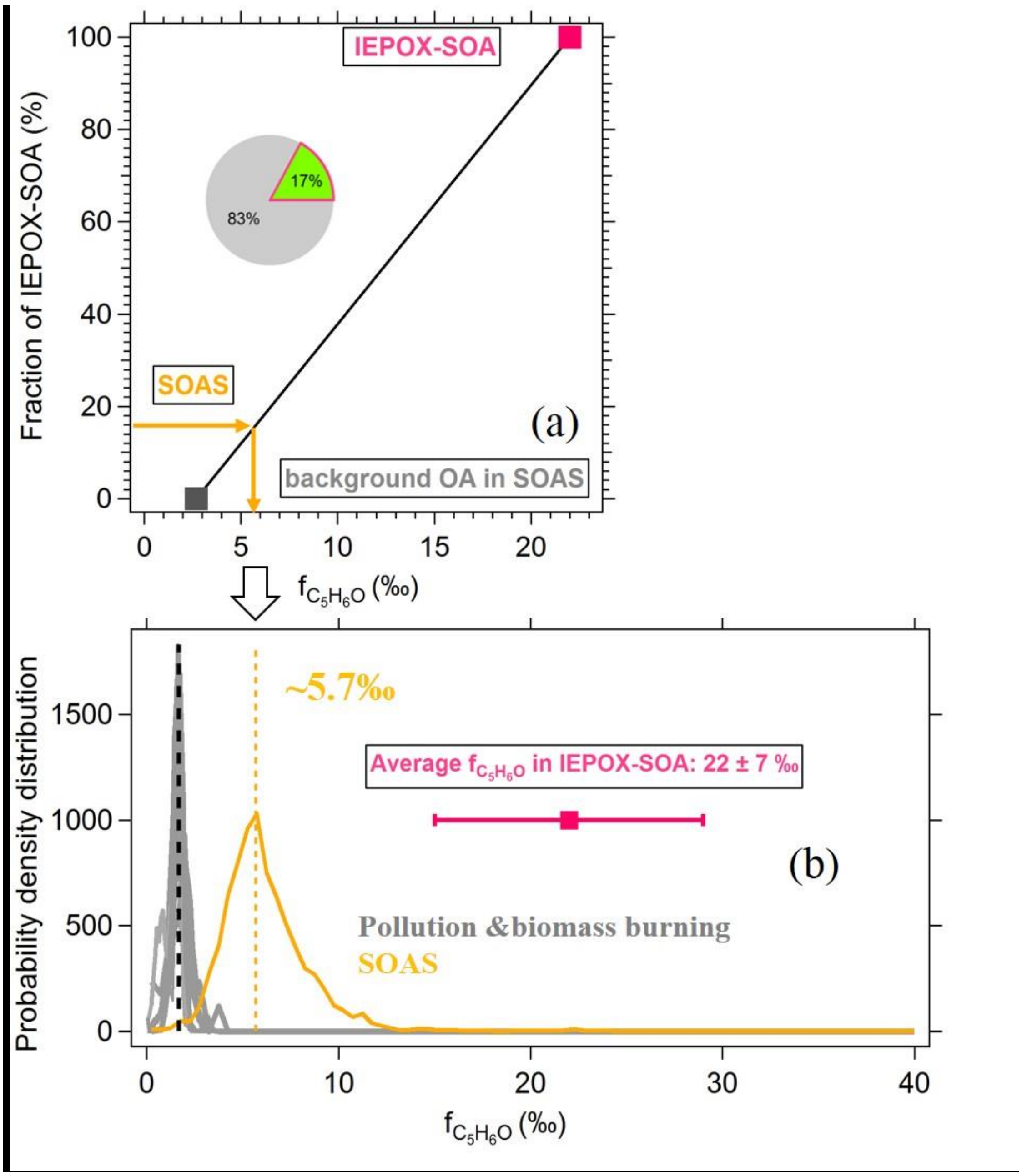

Figure S7. Schematic of the estimation method of IEPOX-SOA based on ambient $f_{C_5H_6O}$. (a) Fraction of IEPOX-SOA in total OA vs ambient $f^{OA}_{C_5H_6O}$ (b) probability distribution of $f^{OA}_{C_5H_6O}$ in SOAS and in background studies. The average background of $f^{OA}_{C_5H_6O}$ from SOAS-CTR 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 $f^{OA}_{C_5H_6O}$ value of 2.7‰ was used here for the background $f^{OA}_{C_5H_6O}$ for SOAS-CTR. $f_{C_5H_6O}$ in IEPOX-SOA$_{PMF}$ 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 $f_{C_5H_6O}^{OA}$ 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 $f_{C_5H_6O}^{OA}$ of ~5.7 ‰, which is consistent with what was observed (Fig. S5b). The peak of the probability distribution of $f_{C_5H_6O}^{OA}$ in SOAS is around 5.7‰.

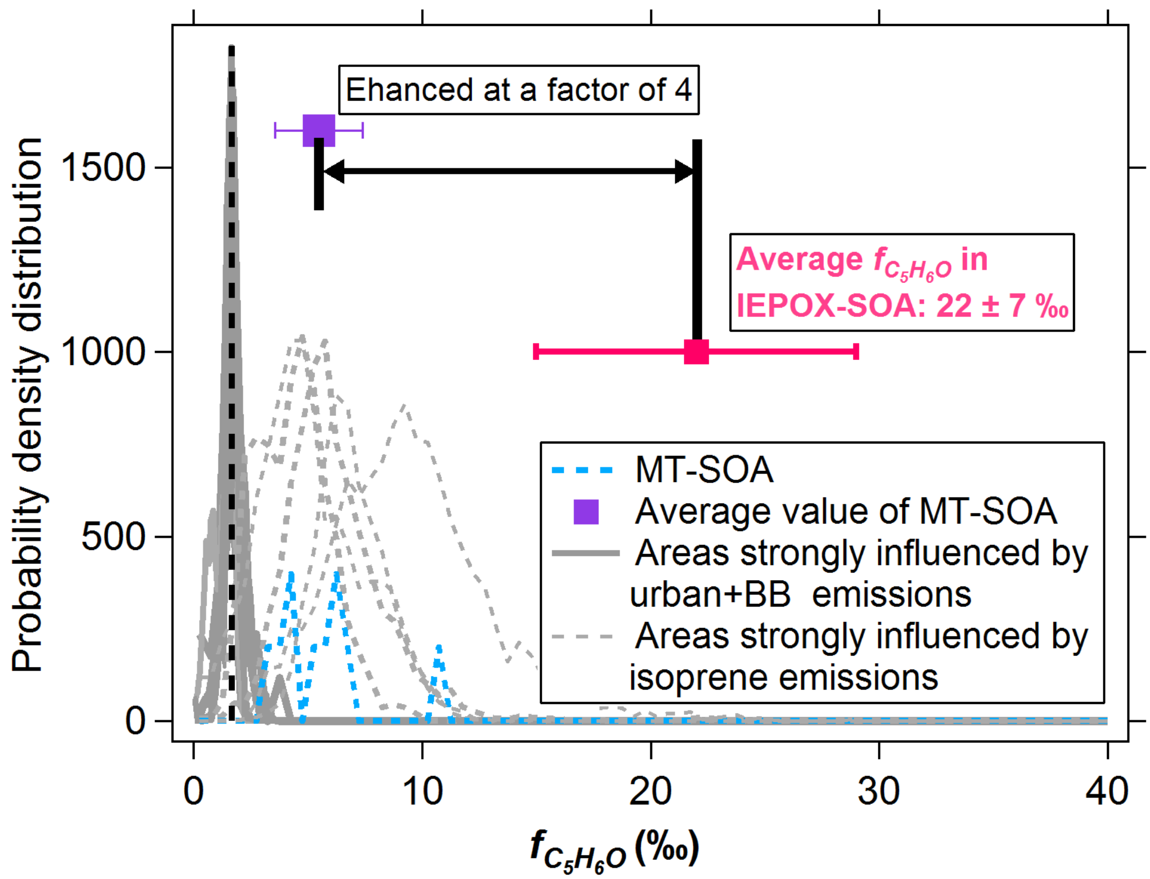

Figure S8 Comparison between $f_{C_5H_6O}^{MT-SOA}$ and $f_{C_5H_6O}^{IEPOX-SOA}$, $f_{C_5H_6O}^{OA}$ from areas strongly influenced by urban + biomass burning and isoprene emissions are also shown.

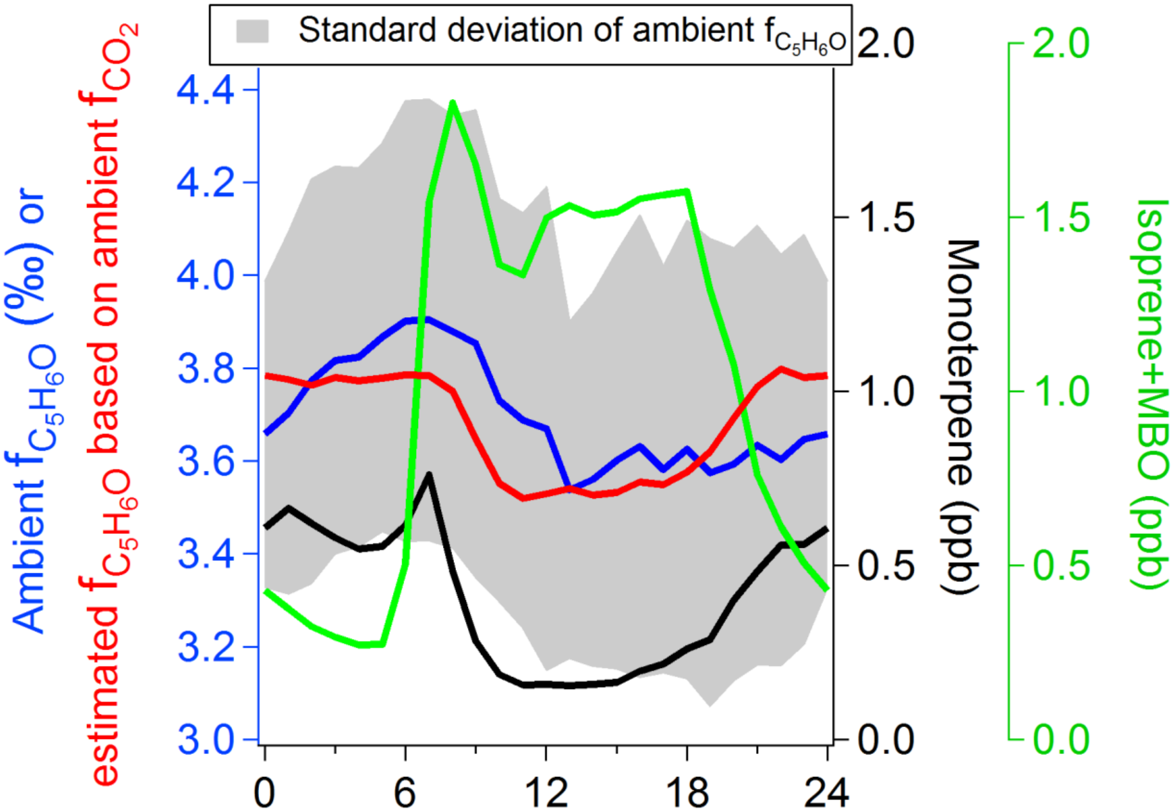

Figure S9. Diurnal variation of ambient $f_{C_5H_6O}^{OA}$ at the Manitou Forest pine forest site in the Rocky Mountains during the BEACHON-RoMBAS 2011 field study, together with diurnal variations of estimated $f_{C_5H_6O}^{OA}$ from $f_{CO_2}^{OA}$ based on regression results between $f_{C_5H_6O}^{OA}$ and $f_{CO_2}^{OA}$ (ambient+Oxidation flow reactor) in this study. The diurnal variation of monoterpene and isoprene+MBO are also shown.

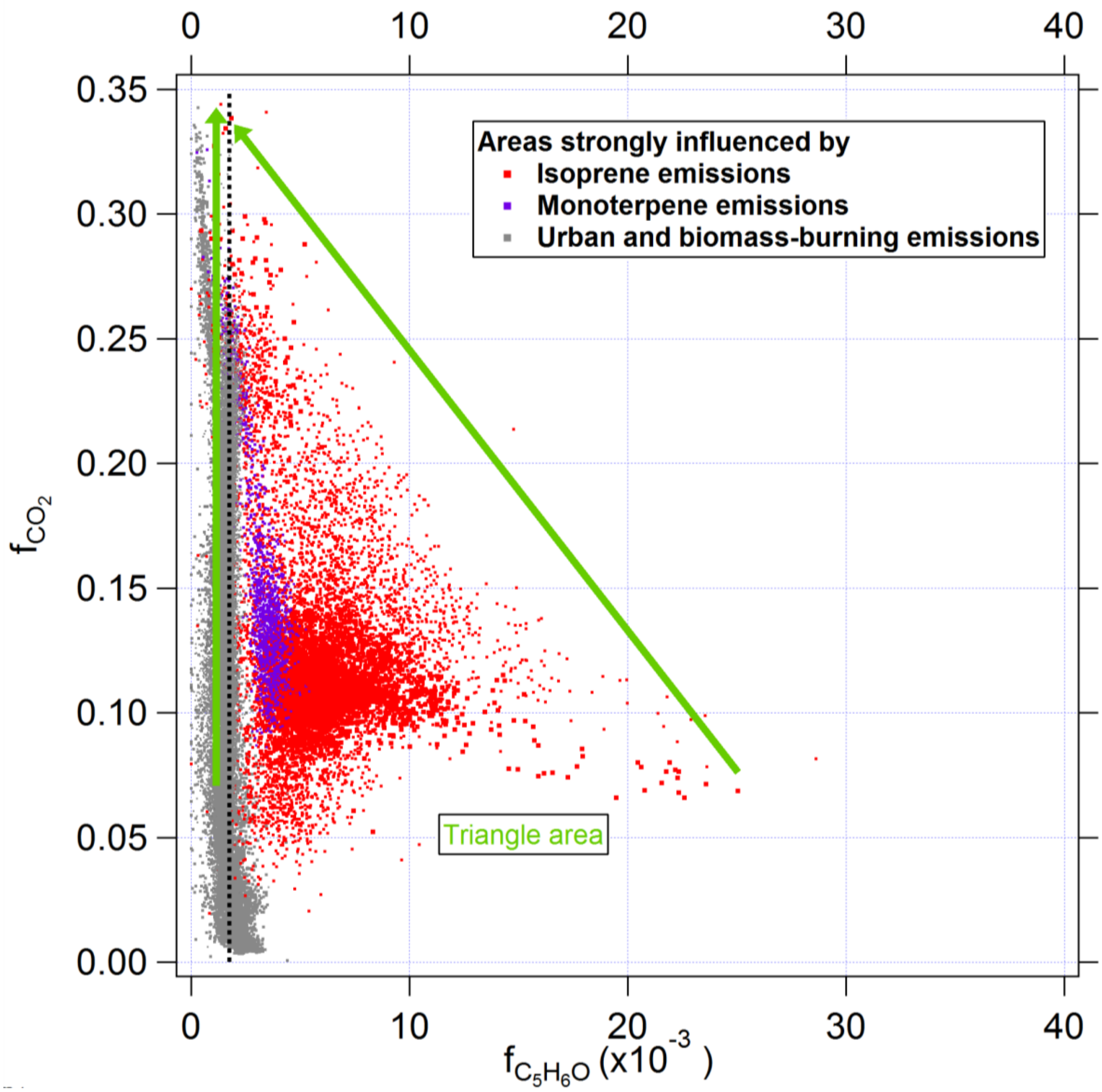

Figure S10. Scatter plot between $f_{CO_2}^{OA}$ and $f_{C_5H_6O}^{OA}$ for all the ambient OA dataset. Green arrows are added to guide the eye.

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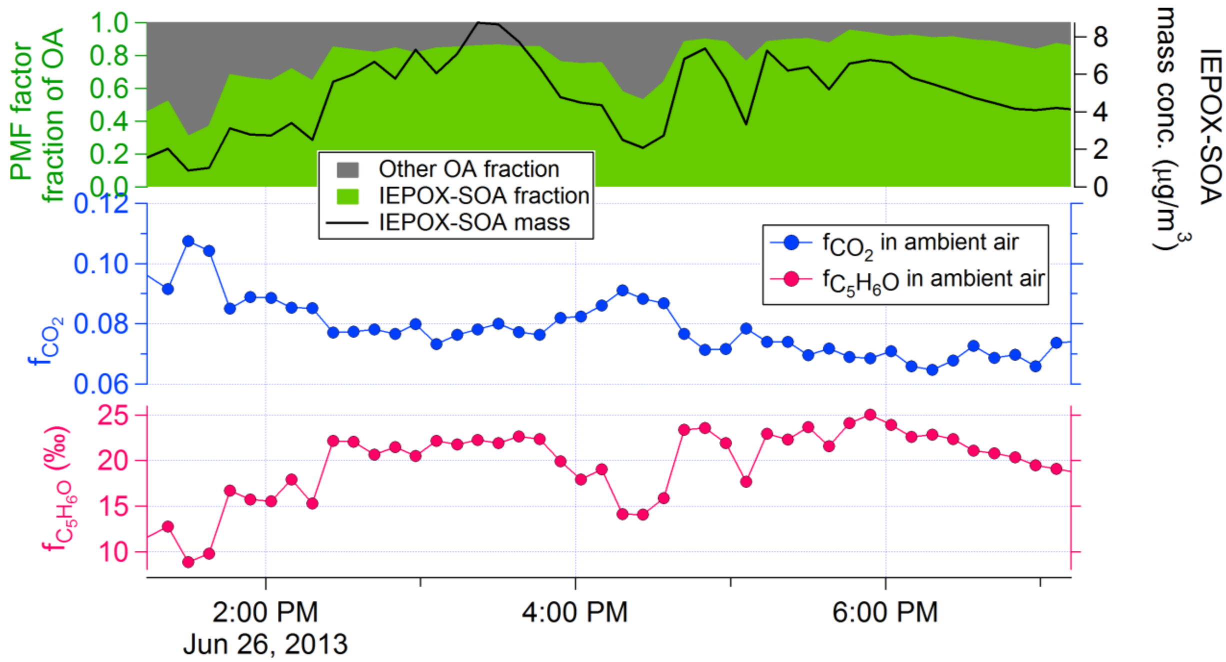

Figure S11. Time series of ambient $f_{C_5H_6O}^{OA}$, $f_{CO_2}^{OA}$, and IEPOX-SOA mass concentrations, together with the IEPOX-SOA fraction of OA during the SOAS-CTR campaign in a SE US forest. During this period, high sulfate and IEPOX-SOA mass concentrations and mass fractions are observed.

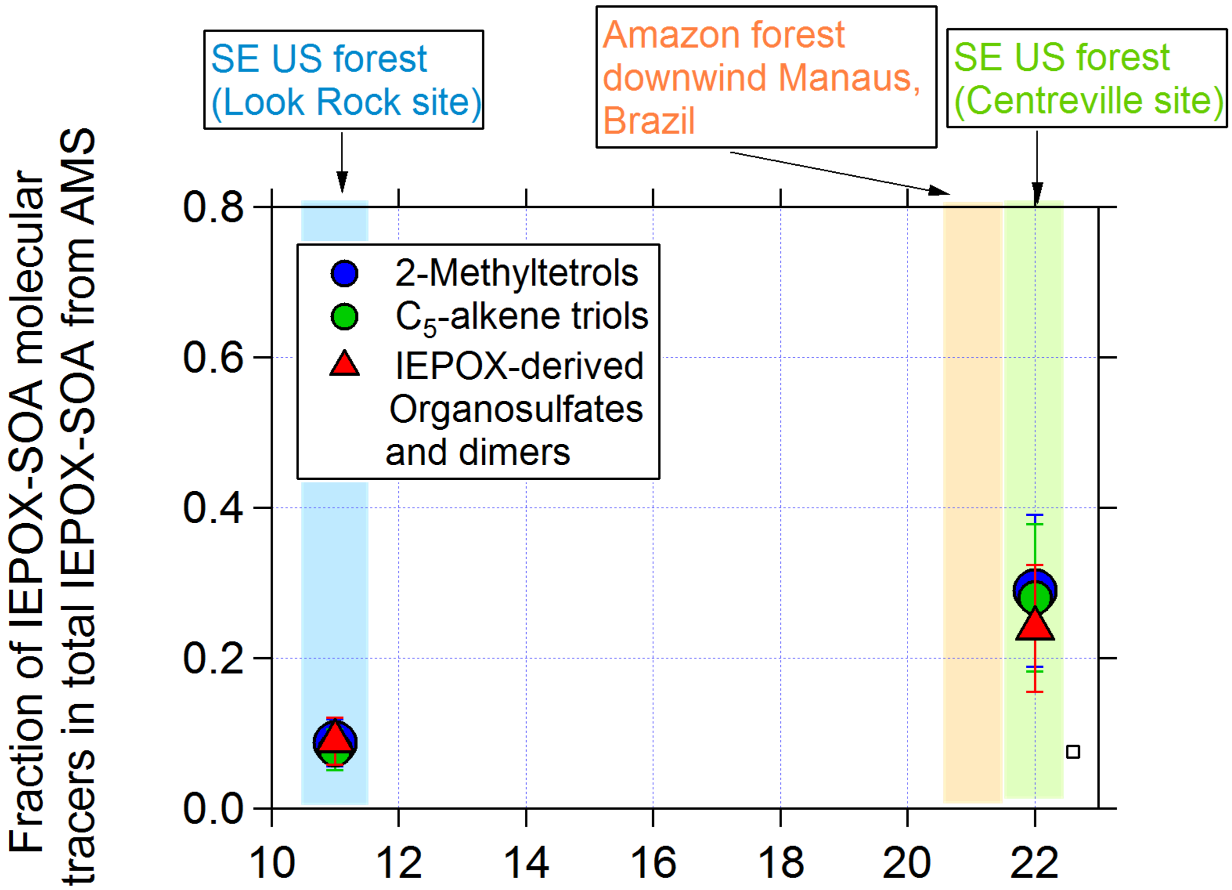

Figure S12 Scatter plot between different IEPOX-SOA molecular tracers (Methyltetrol, C5-alkene triols and IEPOX-derived organosulfates and their dimers) vs IEPOX-SOA$_{PMF}$ and f_{82} in IEPOX-SOA

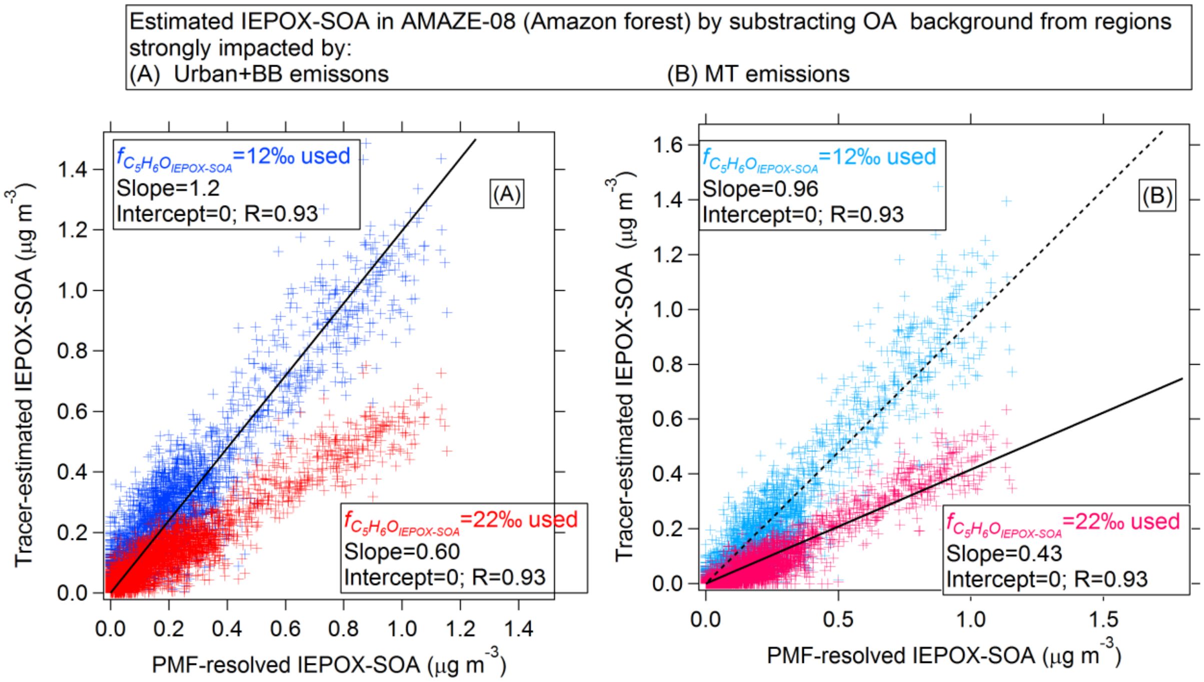

Figure S13. Scatter plot between tracer-estimated IEPOX-SOA and IEPOX-SOA$_{PMF}$ at a pristine Amazon forest site (AMAZE-08). The tracer-based IEPOX-SOA was estimated using OA background from regions strongly influenced by (A) urban and biomass-burning emissions and (B) monoterpene emissions. In each plot, we used two $f_{C_5H_6O}^{IEPOX-SOA}$, from the average IEPOX-SOA$_{PMF}$ ($f_{C_5H_6O}^{IEPOX-SOA}$=22‰) and from the IEPOX-SOA$_{PMF}$ in Amazon forest study ($f_{C_5H_6O}^{IEPOX-SOA}$=12‰).

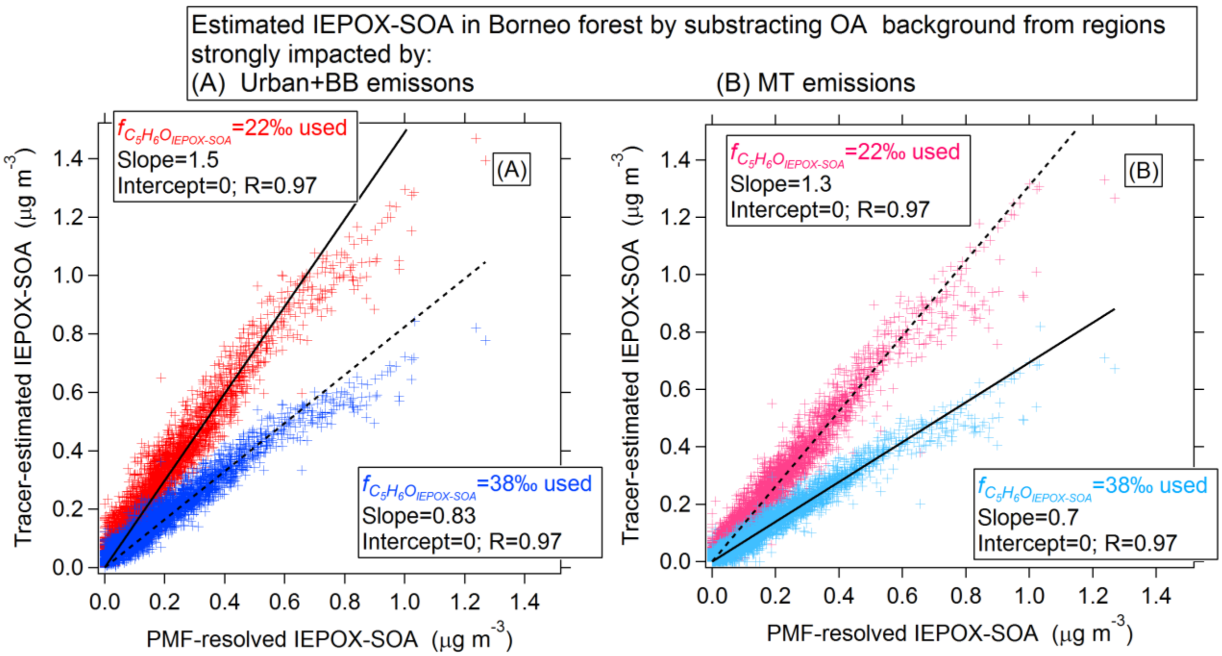

Figure S14 Scatter plot between estimated IEPOX-SOA and IEPOX-SOA$_{PMF}$ at a Borneo forest site. The tracer-based IEPOX-SOA was estimated using OA background from regions strongly influenced by (A) urban and biomass-burning emissions and (B) monoterpene emissions. In each plot, we used two $f_{C_5H_6O}^{IEPOX-SOA}$, from the average IEPOX-SOA$_{PMF}$ ($f_{C_5H_6O}^{IEPOX-SOA}$=22‰) and from the IEPOX-SOA$_{PMF}$ in Borneo forest study ($f_{C_5H_6O}^{IEPOX-SOA}$=38‰).

1.1 Bounds for using the IEPOX-SOA estimation method

In theory, our method can easily produce an estimate of "IEPOX-SOA" from an AMS dataset, but the errors could be substantial in some cases. The guidelines below are meant to limit the errors when applying this method:

1) We first recommend making the scatter plot of $f_{CO_2}^{OA}$ and $f_{C_5H_6O}^{OA}$ and then compare it to Fig. 5 in this study to help evaluate the possible presence of IEPOX-SOA.
2) For datasets where an important influence of MT-SOA is suspected: if all the $f_{C_5H_6O}^{OA}$ in total OA are ~3.1‰ or lower within measurement noise, the estimated IEPOX-SOA will show negative and positive values scattered around zero, indicating negligible IEPOX-SOA in the dataset. A similar conclusion can be reached for urban or BB-dominated locations when $f_{C_5H_6O}^{OA}$~1.7‰ or lower for most data points.
3) When the scatter plot between $f_{CO_2}^{OA}$ and $f_{C_5H_6O}^{OA}$ shows obvious enhanced $f_{C_5H_6O}^{OA}$ above the most-relevant background value, users can easily use the tracer-based method to estimate the IEPOX-SOA mass concentration. If the source of the background OA is not known, we suggest using both background corrections and reporting the range of results.
4) Cases intermediate between No. 2 and 3 above, i.e. when $f_{C_5H_6O}^{OA}$ is only slightly above the relevant background level will have the largest relative uncertainty. In this case we recommend applying the method and evaluating the results carefully, as exemplified for the Rocky Mountain dataset in this paper (section 3.5). E.g. diurnal variations of $f_{C_5H_6O}^{OA}$ and SOA precursors (e.g., isoprene and monoterpene), together with diurnal variation of estimated IEPOX-SOA, provide useful indicators about whether the results are meaningful. For cases in which the fraction of IEPOX-SOA in total OA is relatively low (e.g., <5%) and the fraction of MT-SOA in total OA is high (e.g., >50%), the uncertainty of the IEPOX-SOA estimate will be very high. For this type of situation the full PMF method may be required.

Besides ease of use, another advantage of the tracer-based estimation method is that it can be used to quantify IEPOX-SOA based on brief periods of elevated concentrations, e.g. as often encountered in aircraft studies. In those cases it may be difficult for PMF to resolve an IEPOX-SOA factor, but no such limitation applies to this estimation method.

1.2 Uncertainties of IEPOX-SOA estimation method.

To estimate the accuracy of our IEPOX-SOA tracer-based estimation method, we used this method to estimate IEPOX-SOA from another two ambient datasets with the lowest and highest $f_{C_5H_6O}^{IEPOX-SOA}$ in PMF-resolved IEPOX-SOA (IEPOX-SOA$_{PMF}$) among all the studies in this paper. The lowest value is from a dataset in the pristine Amazon forest (AMAZE-08) where $f_{C_5H_6O}^{IEPOX-SOA}$= 12‰ (Chen et al., 2015) and the highest value from a dataset in a Borneo forest with $f_{C_5H_6O}^{IEPOX-SOA}$= 38‰ (Robinson et al., 2011). Since the $f_{C_5H_6O}^{IEPOX-SOA}$ values in these two datasets are the two farthest from the average $f_{C_5H_6O}^{IEPOX-SOA}$ (22±7‰), the estimation method results from these two datasets represent the worst case scenarios for all datasets published so far.

The estimation results from both datasets are shown in Fig. S13 and Fig. S14. Both of the background OA corrections for areas strongly influenced by urban+BB emissions and by monoterpene emissions are used.

Overall, all variants of the estimated IEPOX-SOA correlate well with IEPOX-SOA_{PMF} (all R>=0.93). When average $f_{C_5H_6O}^{IEPOX-SOA}$=22‰ is used, the slope between estimated IEPOX-SOA vs IEPOX-SOA_{PMF} is between 0.43-1.5, i.e. within a factor of 2.2. When the actual $f_{C_5H_6O}^{IEPOX-SOA}$in each dataset is used, the slope between estimated IEPOX-SOA vs IEPOX-SOA_{PMF} is in a range of 0.7-1.2, i.e. within 30%.

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