Response to reviewers for the paper "Characterization of a real-time tracer for IEPOX-SOA from aerosol mass spectrometer measurements"

By W.W. Hu et al

We appreciate the reviewer's comments and support for publication of this manuscript after minor revisions. Following the reviewer's suggestions, we have carefully revised the manuscript. To facilitate the review process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

Anonymous Referee #1

General Comments

R1.0. In this manuscript, the authors analyze AMS data from multiple sources to determine whether m/z 82 and, more specifically the C5H6O fragment, are robust AMS tracers for SOA formed from isoprene epoxydiols (IEPOX). The main goals of the manuscript are to determine the range of f_{C5H6O} in ambient IEPOX PMF factors, determine the background f_{C5H6O} in different ambient environments, and determine whether SOA generated from monoterpenes (MT) and analyzed with the AMS have significant signal at the C5H6O fragment. The authors quantify the f_{C5H6O} for areas influenced by biomass burning and urban pollution, areas with heavy MT emissions, and areas with strong isoprene emissions. They present a method for estimating the SOA mass formed from IEPOX chemistry from f_{C5H6O} and compare this method to PMF results from the SOAS campaign. They argue that IEPOX SOA mass estimated from f_{C5H6O} should be within a factor of 2 of that determined by a more rigorous PMF analysis.

This manuscript will primarily be of interest to AMS users and less so to general readers of ACP. Nevertheless, the AMS is probably widespread enough to justify publication in ACP rather than a more specialized journal (e.g., AMT). In general, the conclusions are well-supported and the analysis seems to be carefully done and robust. There are however, several things that the authors should do before publication to improve the clarity and readability of the manuscript. First, many of the key figures are essentially illegible because a large amount of data is placed in multi-panel figures that end up being too small to read. Figures 3 and 5 are particularly bad though several others would also benefit from being larger and from multiple datasets being differentiated from one another more clearly. Second, there are several places where the authors could be more clear/specific in their writing. For example, when they refer to IEPOX SOA, it often isn't clear whether they are talking about the PMF factor or the general concept of SOA formed from IEPOX. As another example it isn't clear how exactly all the average f_{C5H6O} values were calculated. There are a relatively large number of typos and grammatical mistakes and, while it was generally clear what the authors meant, it would be good if the authors gave the manuscript a more careful read before final publication. After these corrections are made, the manuscript should be publishable in ACP.

A1.0: All of the items mentioned here are addressed in response to the more specific comments below, in particular R1.1-R1.7, R1.9, R1.13, R2.1, R2.4 and R2.9.

Major Specific Comments

R1.1. P 11227, lines 1-2 and Page 11244 , lines 19-21. Can you be more specific about how you arrive at your conclusion that the IEPOX SOA estimate from f_{C5H6O} will be accurate to within a factor of 2? Have you used your estimation method on more than the SOAS datasets to estimate the accuracy? As you mention, the SOAS data probably represents a best case scenario.

A1.1: The justification on how we obtain the method accuracy to be ~2 may not have been stated clearly enough. We have addressed this topic in detail in 1.2 part of the supporting information of the revised manuscript:

"**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 PMF-resolved IEPOX-SOA (all R>=0.93). When average $f_{C_5H_6O}^{IEPOX-SOA}$=22‰ is used, the slope between estimated IEPOX-SOA vs PMF-resolved IEPOX-SOA 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 PMF-resolved IEPOX-SOA is in a range of 0.7-1.2, i.e. within 30%. "

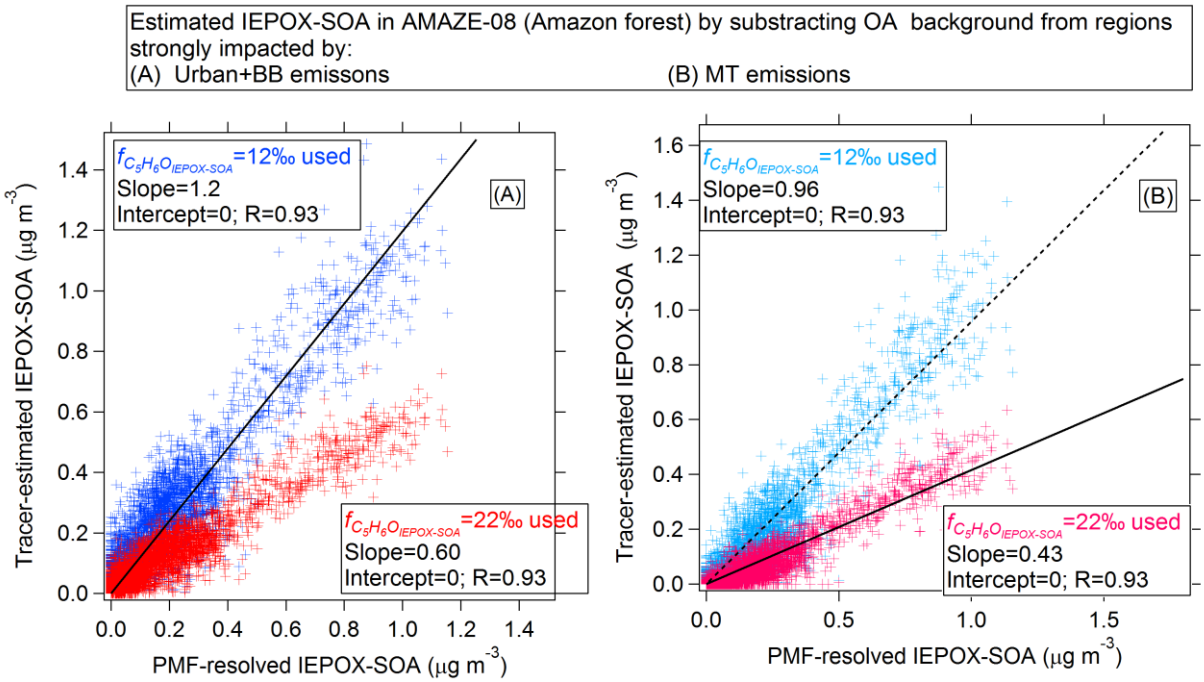


Figure S13. Scatter plot between tracer-estimated IEPOX-SOA and PMF-resolved IEPOX-SOA at a pristine Amazon forest site (AMAZE-08). The tracer-based IEPOX-SOA was estimated using OA background from regions strongly influenced by (A) urban and biomass-burning emissions and (B) monoterpene emissions. In 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‰).

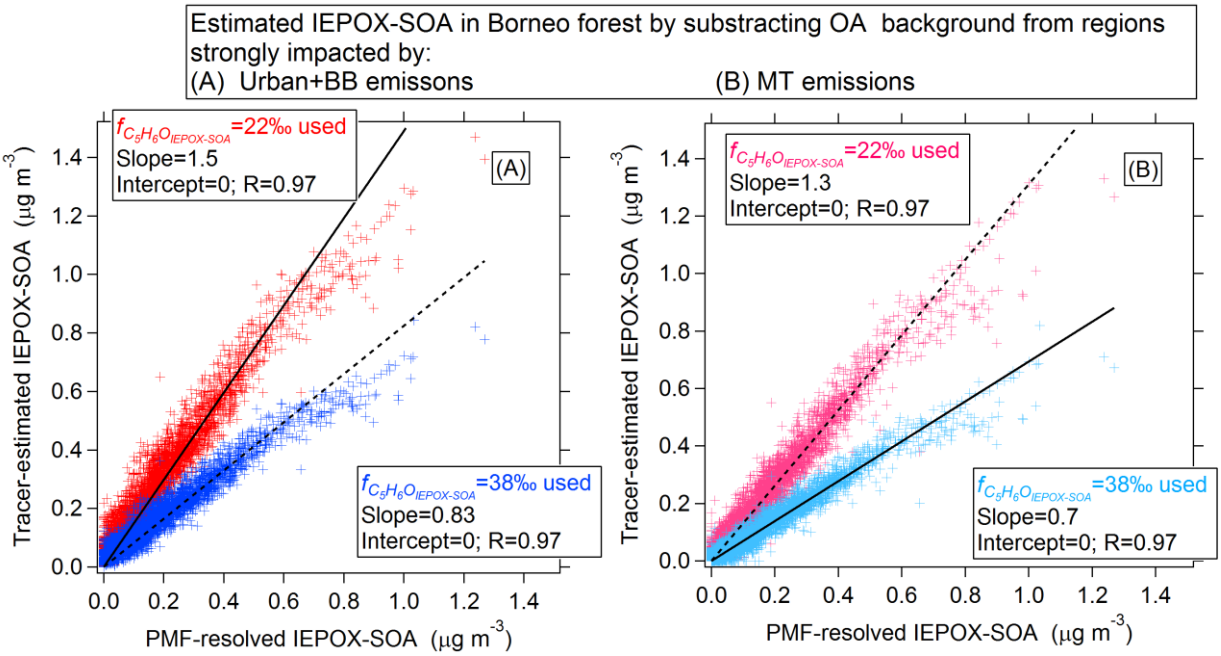


Figure S14 Scatter plot between estimated IEPOX-SOA and PMF-resolved IEPOX-SOA at a Borneo forest site. The tracer-based IEPOX-SOA was estimated using OA background from regions strongly influenced by (A) urban and biomass-burning emissions and (B) monoterpene emissions. In each plot, we used two $f_{C_5H_6O}^{IEPOX-SOA}$,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

R1.2. Can you explain the bounds of when your f_{C5H6O} estimation method can/can't or should/shouldn't be used? Is there a lower limit on f_{C5H6O} (relative to the total organic particle mass) below which the estimation method is no longer accurate? In general it would be a benefit to the AMS community if you can explain the limits and bounds of your estimation method more clearly.

A1.2: Following the reviewer's suggestion, we have addressed this point in the supporting information.

In the main text, we have added a mention of this new information in the last part of section 3.9:

"**Several scenarios based on different $f_{C_5H_6O}^{OA}$ values to use this tracer-based method are addressed in the supporting information. The justification from users on using this method is needed."**

In the supporting information part 1.1 we have added the following text:

"**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 $f^{OA}_{C_5H_6O}$ 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 $f^{OA}_{C_5H_6O}$ and SOA precursors (e.g., isoprene and monoterpene) and 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."

R1.3. Abstract, lines 18-19 and several other places in paper (e.g., p 11243 lines 13-16). Several times in the manuscript, the authors compare f_{C5H6O} of a bulk OA sample (for example, monoterpene SOA) to the f_{C5H6O} found for the PMF factor attributed to IEPOX SOA. They authors do this to illustrate that f_{C5H6O} is enhanced in IEPOX SOA and presumably to imply that the IEPOX f_{C5H6O} signal is enhanced relative to other potential interferences (i.e., monoterpene SOA). However, it isn't really relevant to compare the f_{C5H6O} of a PMF factor that is ~15% of the total OA to the f_{C5H6O} for the entire OA sample. To me this is misleading.

A1.3: We thank the reviewer for pointing out this ambiguity, which appears to have been the largest source of confusion for the ACPD version. To avoid confusion we have changed this notation in the revised paper to always make explicit what we are referring to, as described in the added text below:

"We use a superscript to clarify the type of OA for which $f_{C_5H_6O}$ is being discussed: $f^{OA}_{C_5H_6O}$ refers to $f_{C_5H_6O}$ in total OA, $f^{IEPOX-SOA}_{C_5H_6O}$ to $f_{C_5H_6O}$ in IEPOX-SOA, $f^{MT-SOA}_{C_5H_6O}$ to the $f_{C_5H_6O}$ value in pure MT-SOA and and $f^{OA-Bkg-UB}_{C_5H_6O}$ and $f^{OA-Bkg-MT}_{C_5H_6O}$ refer to background $f^{OA}_{C_5H_6O}$ from areas strongly influenced by urban+biomass-burning emissions and by monoterpene emissions, respectively. If we refer to $f_{C_5H_6O}$ in general, we will still use $f_{C_5H_6O}$."

R1.4. From reading the manuscript, it seems the background f_{C5H6O} is a minimum of 2 per mil and up to 4 per mil for areas of high MT emissions. The f_{C5H6O} for all OA seems to be 5-6 per mil in many areas heavily influenced by isoprene emissions. So the f_{C5H6O} "signal" from IEPOX SOA relative to the background f_{C5H6O} "noise" isn't very elevated in most areas. Borneo (and perhaps the Amazon) seems to be an exception. Can the authors comment more on this issue?

A1.4: We have emphasized the differences of $f_{C_5H_6O}$ between IEPOX-SOA and MT-SOA in the abstract to be clearer:

"**The average laboratory monoterpene SOA value (5.5±2.0‰) is 4 times lower than the average for IEPOX-SOA (22±7‰), which leaves some room to separate both contributions to OA.**"

We have modified the main text and added a new Fig. S8 to more clearly illustrate this difference in the supporting information:

"We note that the average lab-generated MT-SOA value is still 4 times lower than the average for IEPOX-SOA$_{PMF}$ and IEPOX-SOA$_{lab}$ (Fig. S8), and thus there is some room to separate both contributions"

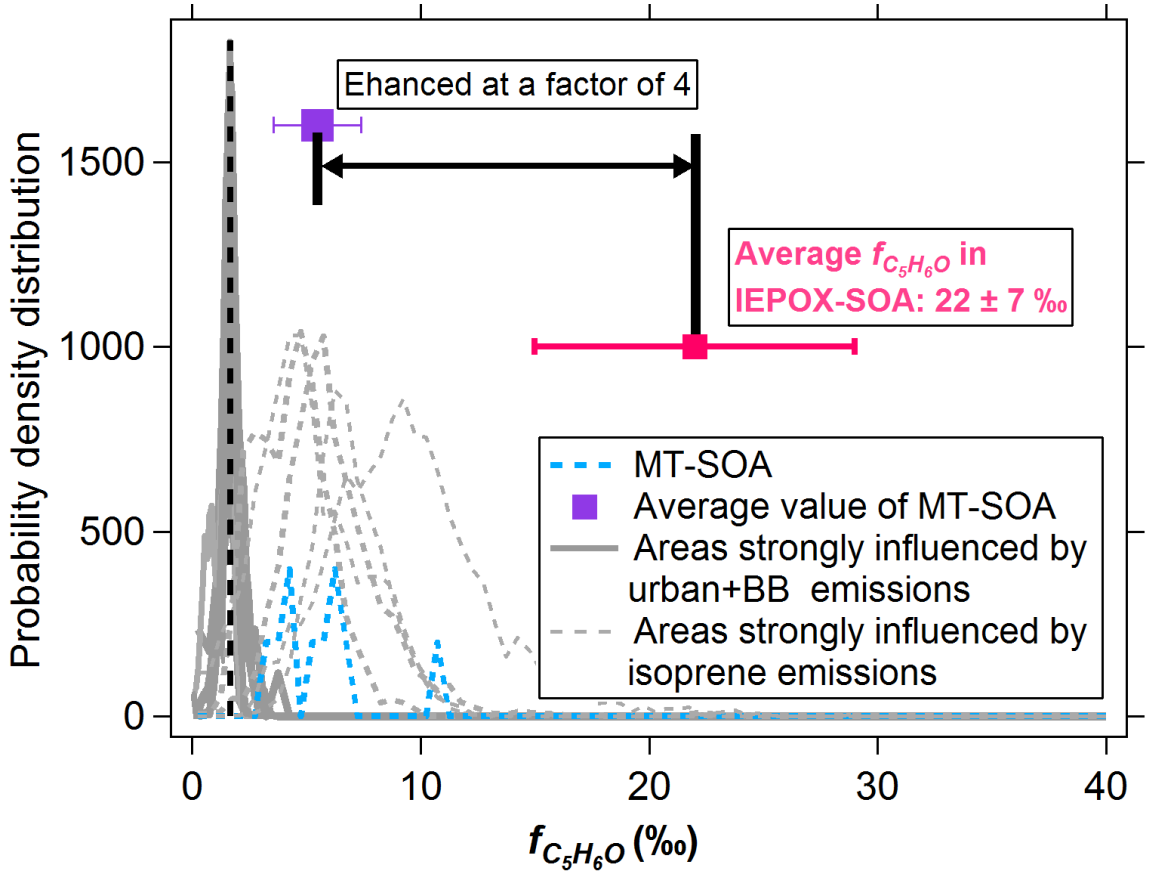


Figure S8 Comparison between $f_{C_5H_6O}^{MT-SOA}$ and $f_{C_5H_6O}^{IEPOX-SOA}$, $f_{C_5H_6O}^{OA}$ from areas strongly influenced by urban + biomass burning and isoprene emissions are also shown.

We also address the reason why smaller differences are observed in $f_{C_5H_6O}^{OA}$ between areas strongly influenced by isoprene emissions and by monoterpene emissions in the last part of section 3.5:

"Note that the difference between $f_{C_5H_6O}^{OA}$ in areas strongly influenced by monoterpene emissions (3.1±0.6‰) and isoprene emissions (6.5±2.2‰) is reduced, compared to a factor of 4 difference between pure MT-SOA (5.5±2.0‰) and IEPOX-SOA (22±7‰). This is likely due to the physical mixing of OA from different sources and in different proportions at each location.

R1.5. Abstract lines 15-20 and through paper. Please explain how you are weighting the average f_{C5H6O} when combining data from many different studies, if at all. I can easily imagine that high frequency data from one study would completely overwhelm the average because of the larger number of points. As an example, aircraft data are recorded generally at 0.1 – 1 Hz, but ground data are typically averaged over significantly longer timescales. How do you treat this?

A1.5: We have added the following text to clarify this issue:

"When we report the average $f_{C_5H_6O}^{OA}$ in each campaign, as shown in the Table 1, we used the average from the time series of $f_{C_5H_6O}^{OA}$ at their raw time resolution (secs to mins). During this process, we exclude points whose OA mass concentrations are below twice the detection limit of OA in AMS (typically 2× 0.26 μg m^{-3}=0.5 μg m^{-3}). When averaging $f_{C_5H_6O}^{OA}$ values across datasets, we counted each dataset as one data point."

R1.6. Related to this point, in the abstract, you list the average f_{C5H6O} for MT influenced airmasses as 3.1 per mil. The Rocky Mountain data average is 3.7 per mil, the DC3 data influenced by MT emissions average 4.1 per mil and the boreal forest data average 2.5 per mil. From these values, it seems like the f_{C5H6O} for MT background should be a little higher than 3.1. How do you calculate the 3.1 number given in the abstract?

A1.6: The 3.1‰ comes from the average value of 2.5‰ in boreal forest and 3.7‰ in Rocky Mountain dataset. We did not include 4.1‰ from DC3 dataset in this calculation, because 4.1‰ is only a single data point that we observed in an aircraft flight, and using that value could bias the average high. When we average all the enhanced $f_{C_5H_6O}^{OA}$ values (from 1.7‰-4.1‰) corresponding to the enhanced monoterpene concentrations for the DC3 flight in the Fig. 6, we obtain a $f_{C_5H_6O}^{OA}$ estimate of 3.0±0.3‰ from this period, which is similar to the average of 3.1‰ averaged from the Rocky mountain site and boreal forest site. We have modified the text in section 3.5 to clarify this point as:

"**The average $f_{C_5H_6O}^{OA}$ in areas strongly influenced by monoterpene emissions is 3.1±0.6‰, obtained by averaging the values from the Rocky mountain forest (3.7‰), European boreal forest (2.5‰), and DC3 flight (3.0‰).**"

R1.7 Through paper: There are a large number of unpublished studies cited in this manuscript. 11 cited referenced are unpublished; 6 are under review (i.e., discussion manuscripts) and 5 are "in preparation". Some of the "in preparation" datasets, primarily from PMF analysis of field data, are used in the manuscript. To me this seems unusual because there has been no peer-

review of this data and insufficient details are provided in the manuscript to assess the data quality. I was unable to find ACP's policy on this, so I leave it to the editor to decide if this is an issue or not. The "in preparation" data are used heavily in the figures and it is difficult to say whether the authors would have come to the same conclusions or whether their conclusions would have been as robust, if this data were to be excluded.

A1.7: We understand the reviewer's concern about citing unpublished studies in our paper. Unfortunately when working on new and very active areas of research, this can sometimes be the case as the other relevant studies are mostly being conducted at the same time. Also importantly our paper should be considered the reference that presents the data for the unpublished studies, and the additional references are provided as a linkage to the literature for readers interested in additional detail on those studies. In addition, excluding the results for which a cited reference is unpublished does not change our conclusions.

In detail, in the ACPD version of our paper, 5 papers were under review but publicly accessible (in ACPD or AMTD) and 5 papers were in preparation. As of the submission of the revised version of our paper, the number of unpublished references has been reduced from 10 to 3. Five papers have been accepted for publication while our paper was under review and revision (an indication of the very active state of this area of research).

One paper is a citation to a referee comment on an ACPD paper that suggested the potential interference of MT-SOA in $f_{C_5H_6O}^{OA}$. We have kept this reference as it was the only mention of this issue that we could find in the literature, and since we only use this reference to suggest a problem that we proceed to explore in detail in our paper. This reference is:

"Anonymous_referee: Interactive comment on "Airborne observations of IEPOX-derived isoprene SOA in the Amazon during SAMBBA" by J. D. Allan et al., Atmos. Chem. Phys. Discuss., 14, C5277–C5279, 2014."

We also cited the overview paper for the SEAC4RS study, which is still in preparation.

"Toon, O. B.: Planning, implementation and scientific goals of the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC4RS) field mission, in prep., 2015".

However, since the SEAC4RS and DC3 datasets used here have been described in another paper, we change this citation to be:

"Liao, J., Froyd, K. D., Murphy, D. M., Keutsch, F. N., Yu, G., Wennberg, P. O., St. Clair, J. M., Crounse, J. D., Wisthaler, A., Mikoviny, T., Jimenez, J. L., Campuzano Jost, P., Day, D. A., Hu, W., Ryerson, T. B., Pollack, I. B., Peischl, J., Anderson, B. E., Ziemba, L. D., Blake, D. R., Meinardi, S., and Diskin, G.: Airborne measurements of organosulfates over the continental US, Journal of Geophysical Research: Atmospheres, 120, 2990-3005, 10.1002/2014jd022378, 2015."

As of the submission of this revised paper, only 1 paper is submitted and 2 papers are in preparation (listed below).

Submitted

Hu, W., Hu, M., Hu, W., Jimenez, J.-L., Yuan, B., Chen, W., Wang, M., Wu, Y., Wang, Z., Chen, C., Peng, J., Shao, M., and Zeng, L.: Chemical composition, sources and aging process of sub-micron aerosols in Beijing: contrast between summer and winter, submitted to JGR, 2015.

In preparation:

Carbone, S., De Brito, J. F., Andreae, M., Pöhlker, C., Chi, X., Saturno, J., Barbosa, H., andArtaxo, P.: Preliminary characterization of submicron secondary aerosol in the amazon forest– ATTO station, in preparation, 2015.

de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Hu, W., Newburn, M. K., Brito, J.,Liu, Y., Isaacman-VanWertz, G., Yee, L. D., Goldstein, A. H., Artaxo, P., Souza, R., Manzi, A.,Jimenez, J. L., Alexander, M. L., and Martin, S. T.: Mass spectral observations of fine aerosol particles and production of SOM at an anthropogenically influenced site during GoAmazon2014wet season, in preparation, 2015.

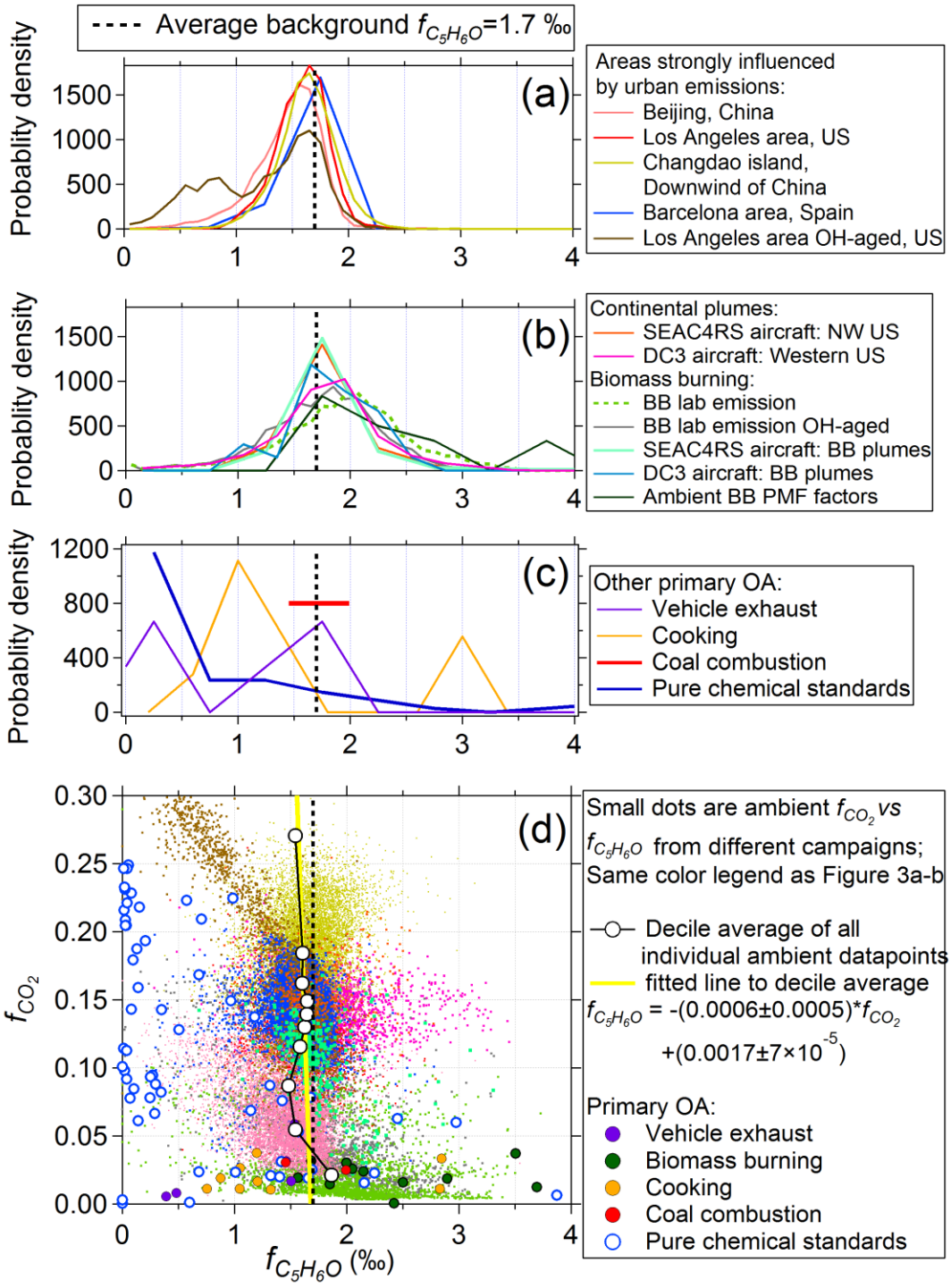
R1.8. Page 11233, line6-8. f_{C5H6O} has a very specific meaning as does f_{82}. They are not the same. I find it highly objectionable that UMR f_{82} data are included in the f_{C5H6O} average and labeled as f_{C5H6O}. Further, it isn't clear which datasets were analyzed for f_{C5H6O} and which for f_{82}. Please either remove the f_{82} from the f_{C5H6O} average or call the average f_{82}.

A1.8: We disagree with the reviewer on this point. We have updated the text to clarify this issue:

"**The average $f_{C_5H_6O}^{IEPOX-SOA}$ value shown here also includes f_{82} data from four UMR IEPOX-SOA$_{PMF}$ spectra. This is justified since $C_5H_6O^+$ accounts for over 95% of *m/z* 82 in IEPOX-SOA based on results from SOAS-CTR and other lab studies (Kuwata et al., 2015). Indeed the average does not change if the UMR studies are removed from the average."**

R1.9 Figure 3: This figure is generally illegible, with the legends particularly so. Please revise. What are the arrows pointing to on the right Y axes?

A1.9: Following the reviewer's suggestion, we have revised our Fig. 3 for clarity as shown below. The arrows have been removed for clarity.



R1.10. Figure 4. It looks like, if a PDF of f_{C5H6O} for monoterpene SOA were placed on this figure, it would be very similar to the PDFs of the isoprene influenced field data. Can you also include the PDF for monoterpene SOA in the figure? Doesn't this argue that there is in fact a

very significant contribution of monoterpene SOA to f_{C5H6O}? It looks like the Borneo data PDF is significantly higher in f_{C5H6O} than the others field data PDFs and the monoterpene lab SOA PDF.

This figure seems to suggest that the "interference" from monoterpene SOA could be worse than the authors argue. If the Borneo data are excluded from the average f_{C5H6O}, does it change significantly?

A1.10: We have updated the two figures below (Fig. 4 and Fig. S8, shown above in response A1.4) by adding the PDF of $f_{C_5H_6O}^{MT-SOA}$ (dashed blue line) from pure MT-SOA (10 data points). A detailed response to this comment can be found in the response to R 1.4.

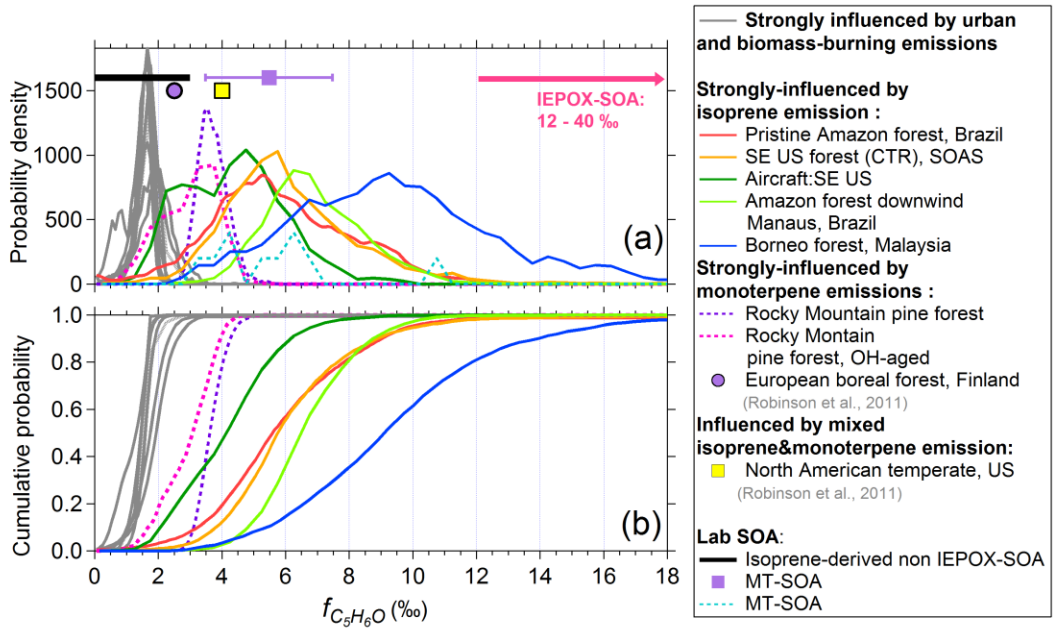


Figure 4. (a) Probability density and (b) cumulative probability distributions of $f_{C_5H_6O}^{OA}$ in studies strongly influenced by isoprene and/or monoterpene emissions. The ranges of $f_{C_5H_6O}$ from other non IEPOX-derived isoprene-SOA and MT-SOA are also shown. The background grey lines are from studies strongly influenced by urban and biomass-burning emissions and are the same data from Fig. 3a − b. The arrow in Fig. 4a indicates the range of $f_{C_5H_6O}^{IEPOX-SOA}$ between 12‰ (start of the arrow) to 40‰ which is beyond the range of x-axis scale.

R1.11. Figure 4: It is very difficult to distinguish the colors of many of the lines from one another because of the color choices and size of the figure. Please revise.

A1.11: The revised figure is shown in response to comment R1.10.

R1.12. It isn't clear what the arrow pointing to the right Y axis is meant to indicate.

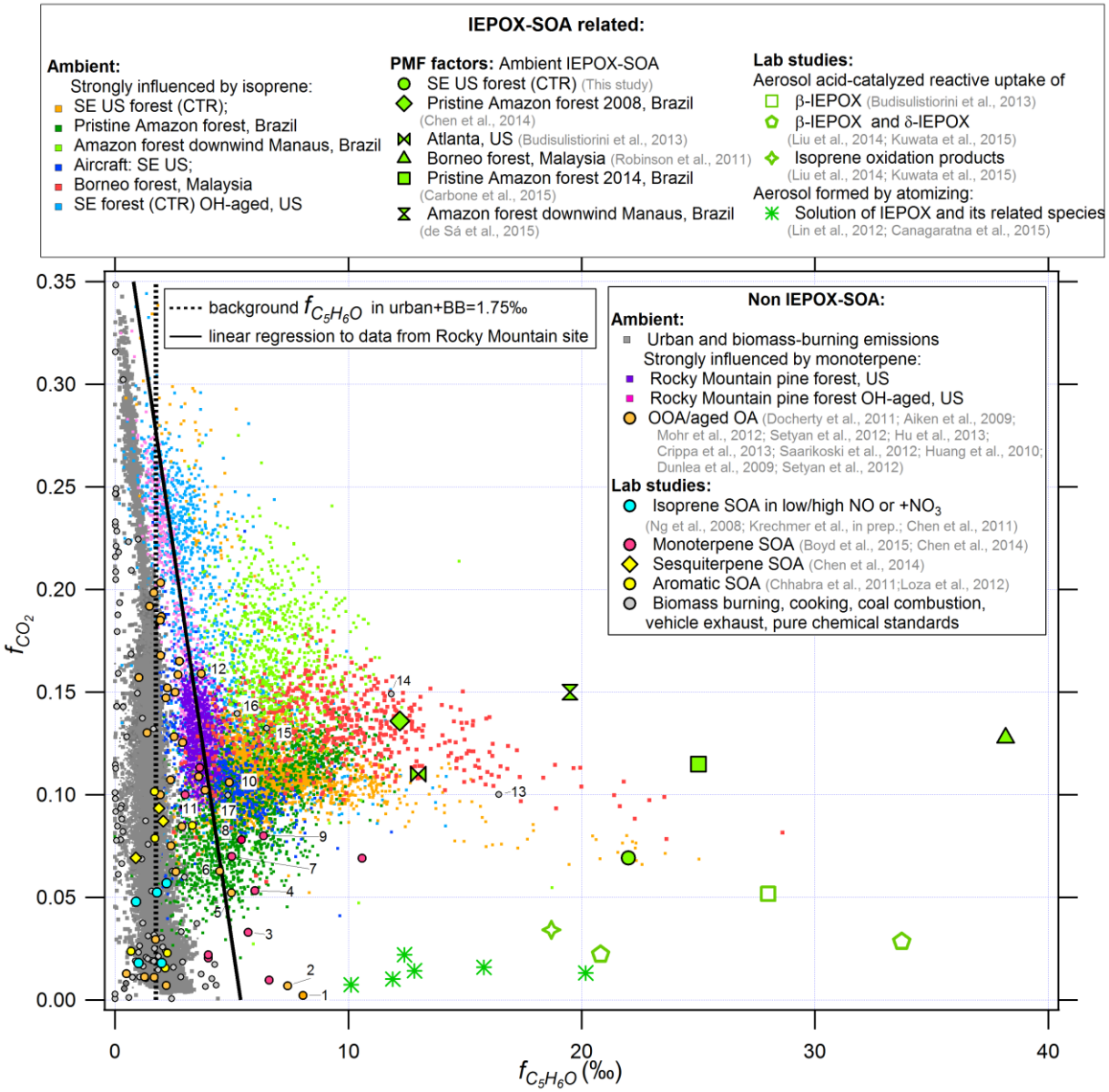
A1.12: We use this arrow to point out the highest $f_{C_5H_6O}^{IEPOX-SOA}$, which is beyond the range of the x-axis in Figure 4. We moved the arrow to the same height as MT-SOA and isoprene-derived

non IEPOX-SOA and added the corresponding explanation in the figure caption (as shown in the response to comment R1.10):

R1.13. Figure 5: The figure is generally illegible due to size and the amount of information on the figure. The symbols are indistinguishable from one another and the legend is impossible to read. I can't make out any of the numbered points aside from 1, 2, and 13. Please revise.

It isn't clear what the pink arrow in the middle of the figure is meant to indicate.

A1.13: Following the reviewer's suggestion, we significantly revised the figure as shown below:



Minor Comments and Technical Corrections

R1.14. Through paper: The authors often use the term average when the text seems to indicate they really mean mode (based on a vertical line drawn to the mode in most figures). Please clarify when/if you mean average and when/if you mean mode. This is relevant because few of the PDFs appear to be normally distributed.

A1.14: We have revised the text as needed to clarify what kind of value (average vs. mode) has used in the paper. Please see the details of the averaging methods used in the response to comment R1.5.

R1.15. Abstract and through paper. It would be helpful to define the per mil symbol the first time in is introduced.

A1.15: Following the reviewer's suggestion, we have defined the per mil in the abstract and main text when it show up in the first time.

In the abstract: **"A background of ~1.7±0.1‰ (‰=parts per thousand) is observed"**

In the main text: "$f_{C_5H_6O}^{IEPOX-SOA}$ **in IEPOX-SOA from SOAS and other field and laboratory studies (Table 1) ranges from 12‰ to 40‰ (‰=parts per thousand)…"**

R1.16. Page 11226, line 4-5. What other low NO oxidation pathways would produce IEPOX-SOA? This is alluded to several times, but never defined. Do you mean IEPOX-SOA the PMF factor or do you mean SOA produced from IEPOX? It is confusing at times to discern whether the authors are talking about SOA formed from IEPOX (a mix of some known and some unknown organics produced by a specific process) or the PMF factor attributed to IEPOX SOA (an output of PMF). This is one clear case.

A1.16: We are referring to the recent finding in Jacobs et al. (2014): IEPOX can be formed in the oxidation of isoprene under high NO, via oxidation the 4-hydroxy-3-nitroxy isoprene (13%). Thus, we revised our sentence in the abstract to be:

"**Total IEPOX-SOA, which may include SOA formed from other parallel isoprene oxidation pathways…**"

We also added corresponding text in the introduction part to clarify:

"Note that some IEPOX can also be formed from isoprene in high NO region via oxidation of the product 4-hydroxy-3-nitroxy isoprene (Jacobs et al., 2014) , however this pathway is thought to be much smaller than the low-NO pathway."

We agree with the reviewer's comment that the specific meaning of the term "IEPOX-SOA" in the paper text can be confusing. Thus, we have added the text below to clarify:

"We denote the IEPOX-SOA factor from PMF as "IEPOX-SOA$_{PMF}$" and IEPOX-SOA from lab studies as "IEPOX-SOA$_{lab}$". If we use "IEPOX-SOA" in the paper, it refers to a broad concept of IEPOX-SOA."

R1.17. Page 11226, line 9-11. Consider revising this sentence for clarity.

A1.17: We revised this sentence as:

"**During the Southern Oxidant and Aerosol Study (SOAS) study, 78% of PMF-resolved IEPOX-SOA is accounted by the measured IEPOX-SOA molecular tracers (methyltetrols, C5-Triols and IEPOX-derived organosulfate), making it the highest level of molecular identification of an ambient SOA component to our knowledge**"

R1.18. Page 11228, lines 22-25. Conversion of IEPOX to IEPOX-SOA requires gas-to-particle partitioning. I think you mean non-reactive partitioning here, but please clarify.

A1.18: Yes, the reviewer is correct. We mean non-reactive partitioning here. We revised the sentence to read:

"…. because gas-phase IEPOX has high volatility, non-reactive gas-to-particle partitioning of IEPOX into OA is negligible under typical ambient concentrations in forest areas"

R1.19. Page 11230, lines 8-9. What is the rationale for including the polluted Amazon site in the

"strongly influenced by isoprene" category as opposed to "strongly influenced by urban emissions" category? To me "polluted" in this context means influenced by Manaus emission. It would be good to clarify why the data were place in one category rather than the other.

A1.19: We added the reason why we classify this site as strongly influenced by isoprene emissions:

"**Two pristine forest site and one forest site partially impacted by urban plumes in the Amazon rain forest (Brazil). The latter site is classified in this category because (i) high isoprene concentrations (e.g. 3 ppb in average peaks in the afternoon) were observed during the study; (ii) the impact of biogenic SOA formed during 1000 km where the air travels over the pristine forest upwind of Manaus; (iii) PMF results indicate an important impact of IEPOX-SOA at this site (de Sá et al., 2015); and (iv) PTRMS results indicate a substantial concentration of the isoprene hydroperoxyde formed by low-NO chemistry."**

R1.20. Page 11230, lines 14-15. Many of campaigns actually haven't been described in the literature and the referenced are listed as "in preparation" (see related comment in major comments section).

A1.20: Please see the response to comment R1.7.

R1.21. Page 11232, lines 26-28. Revise this sentence for clarity.

A1.21: Revised.

Original sentence: "The temporal variation of ion $C_5H_6O^+$ correlates best (R=0.96) with that IEPOX-SOA among all OA ions (Table S1), suggesting that it may be the best tracer among all ions for IEPOX-SOA".

Revised sentence: "**The temporal variation of ion $C_5H_6O^+$ correlates best (R=0.96) with IEPOX-SOA$_{PMF}$ among all measured OA ions (Table S1). This result suggests that $C_5H_6O^+$ ion may be the best ion tracer for IEPOX-SOA among all OA ions.** "

R1.22. Page 11235, line 14. Add "that" between conditions and are.

A1.22: Added.

R1.23. Page 11240, line 4. Revise "Amazon forest down Manaus campaigns".

A1.23: We modified this text to read: "**Amazon forest downwind of Manaus**"

R1.24. Page 11240, line 12. Revise "have low fC5H6O are"

A1.24: We revised the original sentence to be:

"…points with both lower $f_{CO_2}^{OA}$ (<0.08) and low $f_{C_5H_6O}^{OA}$ (< 8‰) values are thought…"

R1.25. Figure5, page 112340, lines 14-19. I'm struggling to see how the points group into a triangle. The points don't seem to group into any shape at all. Please clarify.

A1.25: This trend was perhaps obscured by the complexity of the figure. We have added Figure S10, shown below, to more clearly illustrate the applicability of the "triangle area."

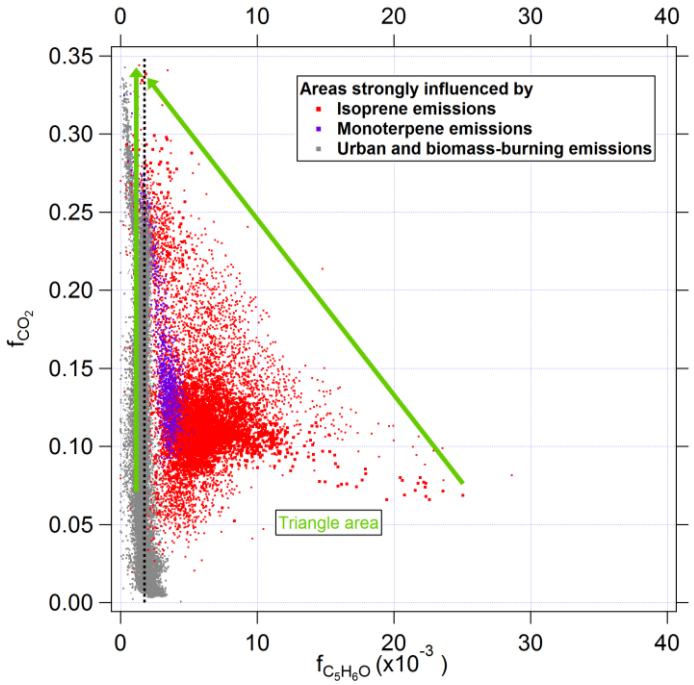


Figure S10. Scatter plot between $f_{CO_2}^{OA}$ and $f_{C_5H_6O}^{OA}$ for all the ambient OA dataset. Green arrows are added to guide the eye.

R1.26 Page 11240, line 16-18. Revise for clarity.

A1.26: Revised.

Original sentence: "This "triangle shape" indicates that in most of campaigns of this study shows the local OA with IEPOX-SOA contributions is influenced by the ambient oxidation processes or mixing with more aged aerosols."

Revised sentence: "This "triangle shape" indicates that as the ambient OA oxidation increases, the IEPOX-SOA signature is reduced, potentially by the ambient oxidation processes or by physical mixing with airmasses containing more aged aerosols."

R1.27 Page 11243, line 13, Revise "An alternative estimate as f_{C5H6O} from area"

A 1.27: We revised the sentence to be:

"**An alternative estimate for background $f^{OA}_{C_5H_6O}$ in areas with strong monoterpene emissions**"

R1.28 Section 3.10 and Figure 8. In the preceding section (3.9), you present two alternative expressions for estimating f_{C5H6O} background for MT influenced areas. Which expression was used in Figure 8?

A1.28: In the Fig. 8, we applied the $f_{C_5H_6O}$ at the Rocky Mountain site estimated by $f_{C_5H_6O} = (0.41 - f_{CO_2}) \times 0.013$ as background $f^{OA}_{C_5H_6O}$ for areas with strong MT-SOA contributions. We added one sentence in the main text to clarify:

"**Finally, we have decided to use $f^{OA}_{C_5H_6O}$ estimated from the Rocky Mountain site as $f^{OA-Bkg-MT}_{C_5H_6O}$ in the following calculation."**

Anonymous Referee #2

General comments

This manuscript presents a relatively comprehensive study using a variety of field and lab results to investigate the strength and limitation of using AMS data to represent ambient SOA formed from IEPOX. This study shows a positive relationship between AMS IEPOX-SOA and GEOSChem modeled gas phase IEPOX at many locations globally w and w/o isoprene emission. This study also estimates the interference in C_5H_6O signal from monoterpene and other sources (e.g urban, biomass burning). The authors found that IEPOX-SOA mass loading derived from AMS data is comparable to the measured molecular tracers concentrations in SOAS. The authors also provide a new method to estimate IEPOX-SOA w/o PMF, which may be useful when PMF is not available. This study brings the aerosol community a better understanding of IEPOX SOA derived from AMS measurements, which have been used in many studies of SOA formed from IEPOX. In general, the authors interpret their data carefully. However, there are a few places not clear in the manuscript. I think this manuscript is suitable for publishing in ACP after the authors address my comments below.

Specific comments

R 2.1. The manuscript uses both PMF IEPOX-SOA factor and f_{C5H6O+} to evaluate if AMS data can well represent SOA from IEPOX. I think the PMF IEPOX-SOA factor is the one that most people in the AMS community use to represent IEPOX SOA mass loadings. The authors checked the background values of f_{C5H6O+} in many non-isoprene dominant environments. Could the authors be clear about how those interferences would be reflected in the IEPOX-SOA factor (ug/m^3) ?

A 2.1: The PMF-resolved IEPOX-SOA factor is indeed the one reported as IEPOX-SOA in most of ambient measurements (Slowik et al., 2010;Robinson et al., 2011;Budisulistiorini et al., 2013;Xu et al., 2014;Budisulistiorini et al., 2015;Chen et al., 2015). One study from Allan et al. (2014) used f_{82} as a tracer for IEPOX-SOA in flight measurements over the Amazon forest. The tracer method was not available until the publication of our paper, and thus it has not been used in past literature.

We believe that the reviewer is asking us to quantify the uncertainty of the IEPOX-SOA mass concentrations reported from PMF. This uncertainty will depend on each specific case. As a representative example, we estimate this uncertainty for the SOAS dataset using the bootstrap method, which provides a quantitative assessment of the uncertainty of the factors (Ulbrich et al., 2009). 100 bootstrapping runs are carried out. The results are shown in the figure below, which was also added to the supporting information (Fig. S1).

The uncertainty (standard deviation) for $C_5H_6O^+$ in IEPOX-SOA is around 3%. The average uncertainty of the IEPOX-SOA mass concentration time series is ~9%.

A summary of this result was added into the paper: **"An uncertainty of IEPOX-SOA$_{PMF}$ mass concentration of ~9% was estimated from 100 bootstrapping runs in PMF analysis (Ulbrich et al., 2009) (Fig. S1). This uncertainty concerns only the PMF separation method. In practice the uncertainty in IEPOX-SOA$_{PMF}$ concentration is dominated by the larger uncertainty on the AMS concentrations arising from the collection efficiency and relative ionization efficiency (Middlebrook et al., 2012).**"

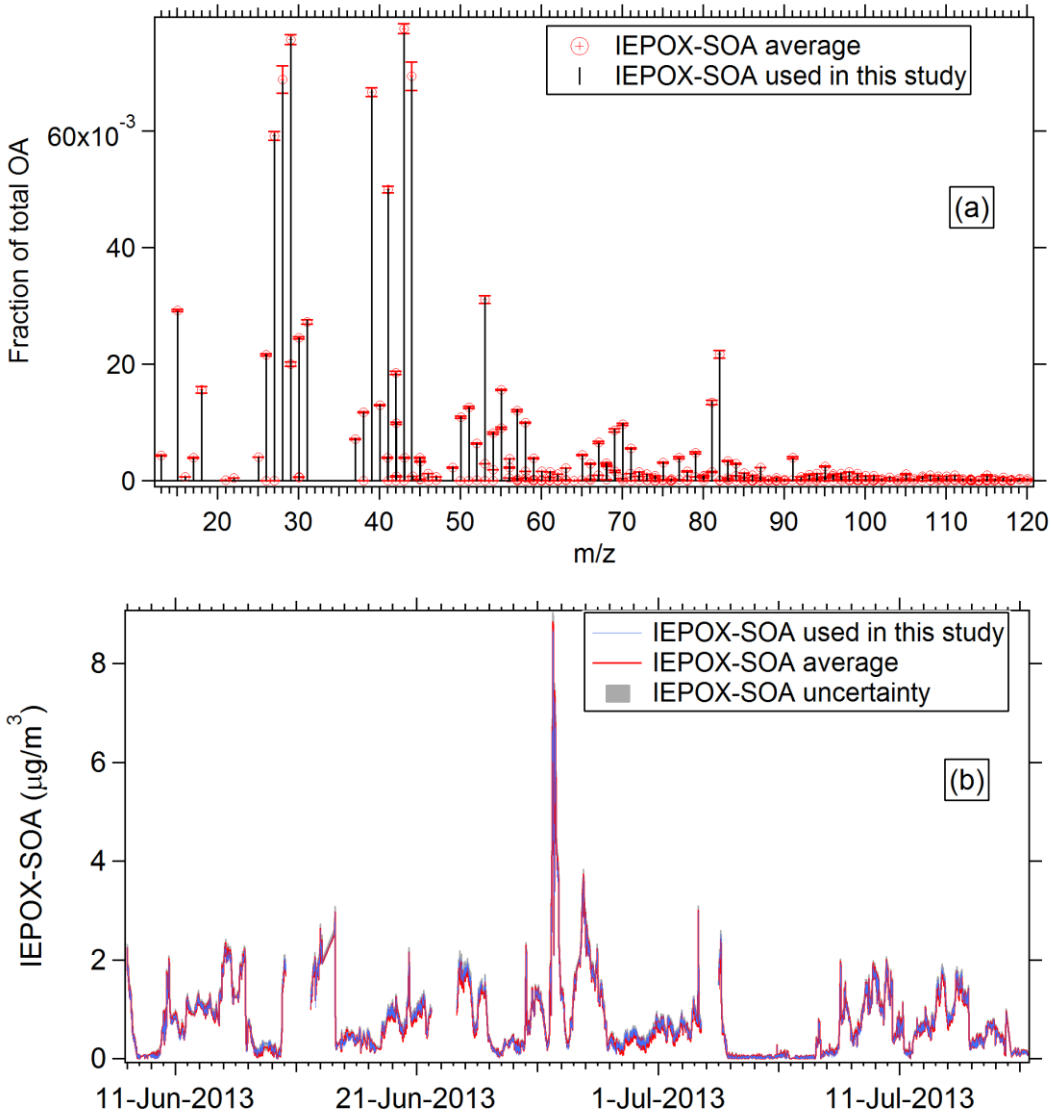


Figure S1. Results from bootstrapping analysis of the 4-factor solution of the SOAS dataset. Average IEPOX-SOA, with standard deviation, are shown for IEPOX-SOA (a) mass spectrum and (b) time series.

R 2.2. Also, it is often not clear when the f_{C5H6O+} values in the manuscript are C5H6O+/OA from IEPOX-SOA factor mass spectra only, from all data or from non-IEPOX-SOA factor data. I

think it is important to keep them consistent. I suggest using "$f_{C5H6O+.all}$" or other symbol to represent from all data and using "$f_{C5H6O+.IEPOX-SOA}$" or other different symbol to represent from IEPOX-SOA factor data only. I was misled at the beginning when I read the manuscript. For example, in the abstract, *f*C5H6O in IEPOX-SOA of (12–40 ‰) looks much higher than that influenced by monoterpene (3.1 ‰). These values are actually apples and oranges.

A2.2: Please see the response to comment R1.3

R2.3. Page 11226 line 24-25: Please state clearly if "the low *f*C5H6O (< 3 ‰) observed in non IEPOX-derived isoprene-SOA" is the result in the lab or in the ambient. Also I think the abstract should be clearer if this result is from part of this study or derived from previous published results.

A2.3: We revised our sentence to clarify this point as:

Original: "The low fC5H6O (< 3 ‰) observed in non IEPOX-derived isoprene-SOA indicates that this tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene**"**

Revised: **"The low $f_{C_5H_6O}$ (<3‰) reported in non IEPOX-derived isoprene-SOA from chamber studies indicates that this tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene"**

R2.4. Figure 2(b) What about the correlation between IEPOX-SOA and C5-alkene triols and IEPOX-derived organosulfates and dimers?

A2.4: We have added the relevant information to the main text (section 3.1) and also Fig. S2 to the supporting information:

"**Other IEPOX-SOA tracers, such as C5-alkene triols, IEPOX-organosulfates, and dimers containing them, can also be measured by offline GC-EI/MS and LC/MS (Lin et al., 2014;Budisulistiorini et al., 2015), and they account for 28% and 24% in total IEPOX-SOA in SOAS (R=0.7), respectively (Fig. S2)**."

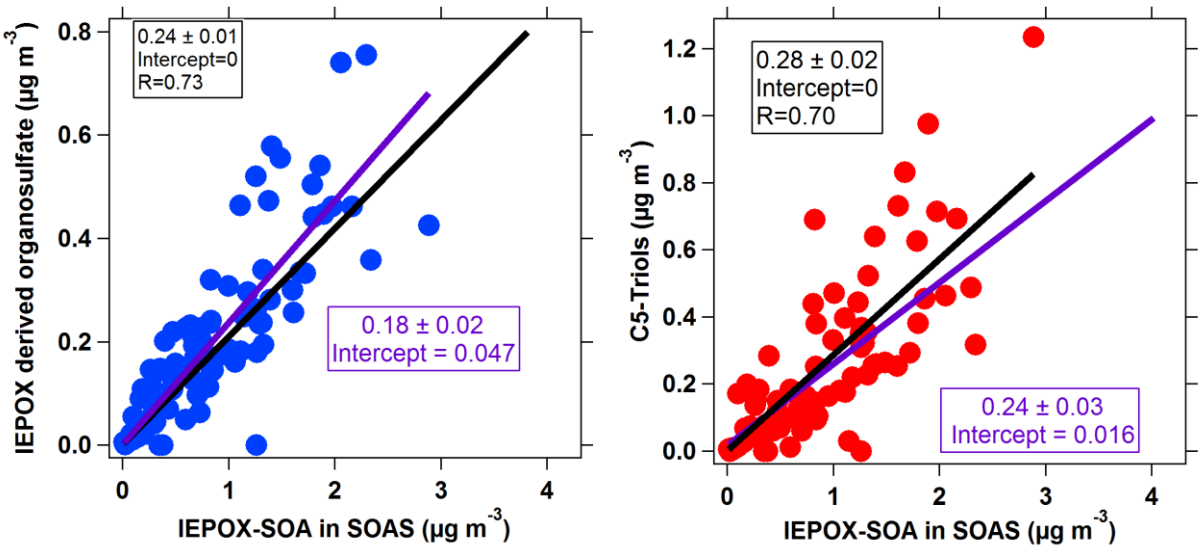


Figure S2. Scatter plots between IEPOX-derived organosulfate and C5-triols vs IEPOX-SOA$_{PMF}$ in the SOAS study. The IEPOX-derived organosulfate and C5-triols were measured in GC/MS and LC/MS analysis of filter extracts (Lin et al., 2014;Budisulistiorini et al., 2015).

R2.5. Page 11232:

"No IEPOX-SOA factor found in areas strongly influenced by urban emissions (e.g. Hayes et al., 2013)" does not give us information whether IEPOX pathway is suppressed by high NO unless you measured high isoprene levels there.

A2.5: We have modified this text to clarify this issue:

"**No IEPOX-SOA$_{PMF}$ factor (i.e. below the PMF detection limit of ~5% of OA, Ulbrich et al., 2009) was found in areas strongly influenced by urban emissions where high NO concentrations suppress the IEPOX pathway, even in the presence of substantial isoprene concentrations (e.g. Hayes et al., 2013).**"

R2.6. Page 11244: "Given the spread of values of *f*C5H6O $_{IEPOX-SOA}$ (12–40 ‰) in different studies, if no additional local IEPOX-SOA spectrum is available for a given site, the estimation from this method should be within a factor of 2 of the actual concentration."

Considering that the interference from monoterpene oxidation is important (e.g. *f*C5H6O in rocky mountain comparable to SE aircraft data: Figure 4) and that estimation from monoterpene interference is derived from only one site (rocky mountain), I think more data are needed to testify the method and the above conclusion is a little bit too strong.

A2.6: Please see response to comment R1.1.

R2.7 Page 11245

Paragraph 2 "Low tracer values (*f*C5H6O < 3 ‰) are observed in non IEPOX-derived isoprene-SOA, indicating that the tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene." Please also state if this is lab or ambient result because the paragraph starts with " In ambient OA …" and this sentence is somehow misleading when I read.

A2.7: This is effectively the same comment as R2.3, but here referring to the text in the conclusions, rather than the main text. Consistent with our response to R2.3, we have revised the next in the conclusions to read:

"**Low tracer values ($f_{C_5H_6O}$<3‰) are observed in non IEPOX-derived isoprene-SOA from laboratory studies, indicating that the tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene**"

R2.8 Figure 2 and Figure 7:

Could the authors give more information about how to get IEPOX-SOA in ug/m^3 ? The mass spectrum of IEPOX-SOA factor in Figure 2 (b) shows many other peaks besides 82 m/z. Is IEPOX-SOA in ug/m^3 a function of f_{C5H6O} in IEPOX-SOA factor and the "weighing" of IEPOX-SOA factor compared to other OA factors? I think this is important to help non AMS people better understand AMS IEPOX-SOA data. The results in Figure 7 and the statement in abstract "During the SOAS study, 78% of IEPOX-SOA is accounted for the measured molecular tracers" rely heavily on this.

A2.8: We addressed this in section 3.1 with the text below, as well as with the description of the tracer-based estimation method in Section 3.9. The uncertainty of IEPOX-SOA$_{PMF}$ is addressed in response to comment R2.1.

"**The IEPOX-SOA$_{PMF}$ mass concentration is the sum of mass concentrations of all the ions in the IEPOX-SOA$_{PMF}$ mass spectra. The "mass concentration" of an ion is used to represent the mass of the species whose detection resulted in the observed ion current of that ion, based on the properties of electron ionization (Jimenez et al., 2003)**",

R2.9 In addition, could the authors provide the uncertainties (or error bars) of the data shown in Figure 7? The statement of "During the SOAS study, 78% of IEPOX-SOA is accounted for the measured molecular tracers, making it the highest level of molecular identification of an ambient SOA component to our knowledge." in the abstract also points to the importance to know the uncertainty.

A2.9: The explanation was added in the main text:

"The uncertainty (standard deviation) of the fraction of IEPOX-SOA molecular tracers in IEPOX-SOA$_{PMF}$ in SOAS study (42%) is estimated by combining the overall uncertainty from IEPOX-SOA molecular tracer measurement (24%), linear regression between tracer vs IEPOX-SOA$_{PMF}$ (17%, see Fig. 2b and Fig. S2), IEPOX-SOA$_{PMF}$ in PMF separation

method (9%) and the quantification of IEPOX-SOA$_{PMF}$ based on AMS calibration (30%) (Middlebrook et al., 2012).”

The uncertainty bar was added to Fig. 7 as well.

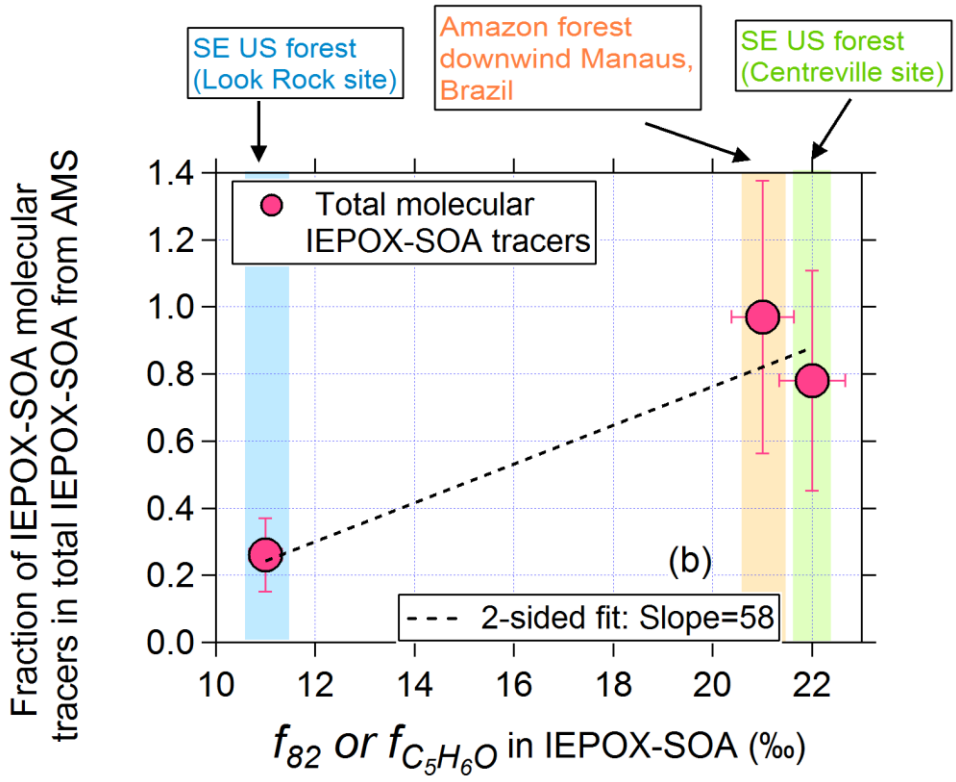


Figure 7. Scatter plot between total IEPOX-SOA molecular tracers (=Methyltetrol + C5-alkene triols +IEPOX-derived organosulfates and dimers) in IEPOX-SOA$_{PMF}$ and $f_{82}^{IEPOX-SOA}$. Besides SOAS, the other two datasets in the graph are from Budisulistiorini et al. (2015) and de Sá et al.(2015). The relative uncertainty value estimated for the SOAS study is applied to the other two datasets.

Technical correction:

R2.10 Page 11226 Line 9: please define “SOAS”

A2.10: Corrected.

We revised the sentence to be: **“During the Southern Oxidant and Aerosol Study (SOAS) study…”**

R2.11 Figure 3: red curves in (a) are hard to distinguish. So are the green ones in (b). Please state clearly what the small dots are in (d).

A2.11: Following the reviewer’s suggestion, we revised our Figure 3. Please see the response to the comment R1.9.

R2.12 Figure 3 and 5: the legends are way too small and won't show up readable in print version.

A2.12: Please see the response to comments R1.9 and R1.13.

R2.13 Check the references to make sure they are recently updated.

A2.13: Thank for reviewer's reminder. We have checked through all the references and made sure they are all updated, and will check again on the ACP proofs after the paper is hopefully accepted. See also our response to comment R1.7.

References:

Allan, J. D., Morgan, W. T., Darbyshire, E., Flynn, M. J., Williams, P. I., Oram, D. E., Artaxo, P., Brito, J., Lee, J. D., and Coe, H.: Airborne observations of IEPOX-derived isoprene SOA in the Amazon during SAMBBA, Atmos. Chem. Phys., 14, 11393-11407, 10.5194/acp-14-11393-2014, 2014.

Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Marth, W. J., Baumann, K., Edgerton, E. S., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Gold, A., and Surratt, J. D.: Real-Time Continuous Characterization of Secondary Organic Aerosol Derived from Isoprene Epoxydiols in Downtown Atlanta, Georgia, Using the Aerodyne Aerosol Chemical Speciation Monitor, Environ Sci Technol, 47, 5686-5694, 10.1021/es400023n, 2013.

Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V. F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A., and Surratt, J. D.: Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee, ground site, Atmos. Chem. Phys. Discuss., 15, 7365-7417, 10.5194/acpd-15-7365-2015, 2015.

Chen, Q., Farmer, D. K., Rizzo, L. V., Pauliquevis, T., Kuwata, M., Karl, T. G., Guenther, A., Allan, J. D., Coe, H., Andreae, M. O., Pöschl, U., Jimenez, J. L., Artaxo, P., and Martin, S. T.: Submicron particle mass concentrations and sources in the Amazonian wet season (AMAZE-08), Atmos. Chem. Phys., 15, 3687-3701, 10.5194/acp-15-3687-2015, 2015.

de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Hu, W., Newburn, M. K., Brito, J., Liu, Y., Isaacman-VanWertz, G., Yee, L. D., Goldstein, A. H., Artaxo, P., Souza, R., Manzi, A., Jimenez, J. L., Alexander, M. L., and Martin, S. T.: Mass spectral observations of fine aerosol particles and production of SOM at an anthropogenically influenced site during GoAmazon2014 wet season, In prep., 2015.

Jacobs, M. I., Burke, W. J., and Elrod, M. J.: Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, Atmos. Chem. Phys., 14, 8933-8946, 10.5194/acp-14-8933-2014, 2014.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X. F., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, J Geophys Res-Atmos, 108, 8425, Doi 10.1029/2001jd001213, 2003.

Kuwata, M., Liu, Y., McKinney, K., and Martin, S. T.: Physical state and acidity of inorganic sulfate can regulate the production of secondary organic material from isoprene photooxidation products, Phys Chem Chem Phys, 17, 5670-5678, 10.1039/c4cp04942j, 2015.

Lin, Y.-H., Budisulistiorini, S. H., Chu, K., Siejack, R. A., Zhang, H., Riva, M., Zhang, Z., Gold, A., Kautzman, K. E., and Surratt, J. D.: Light-Absorbing Oligomer Formation in

Secondary Organic Aerosol from Reactive Uptake of Isoprene Epoxydiols, Environ Sci Technol, 48, 12012-12021, 10.1021/es503142b, 2014.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci Tech, 46, 258-271, 10.1080/02786826.2011.620041, 2012.

Robinson, N. H., Hamilton, J. F., Allan, J. D., Langford, B., Oram, D. E., Chen, Q., Docherty, K., Farmer, D. K., Jimenez, J. L., Ward, M. W., Hewitt, C. N., Barley, M. H., Jenkin, M. E., Rickard, A. R., Martin, S. T., McFiggans, G., and Coe, H.: Evidence for a significant proportion of Secondary Organic Aerosol from isoprene above a maritime tropical forest, Atmos. Chem. Phys., 11, 1039-1050, 10.5194/acp-11-1039-2011, 2011.

Slowik, J. G., Stroud, C., Bottenheim, J. W., Brickell, P. C., Chang, R. Y. W., Liggio, J., Makar, P. A., Martin, R. V., Moran, M. D., Shantz, N. C., Sjostedt, S. J., van Donkelaar, A., Vlasenko, A., Wiebe, H. A., Xia, A. G., Zhang, J., Leaitch, W. R., and Abbatt, J. P. D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, Atmos. Chem. Phys., 10, 2825-2845, 10.5194/acp-10-2825-2010, 2010.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos Chem Phys, 9, 2891-2918, 2009.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proceedings of the National Academy of Sciences, 112, 37-42, 10.1073/pnas.1417609112, 2014.

Characterization of a Real-Time Tracer for Isoprene Epoxydiols-Derived Secondary Organic Aerosol (IEPOX-SOA) from Aerosol Mass Spectrometer Measurements

Weiwei Hu[1,2], Pedro Campuzano-Jost[1,2], Brett B. Palm[1,2], Douglas A. Day[1,2], Amber M. Ortega[1,3], Patrick L. Hayes[1,2*], Jordan E. Krechmer[1,2], Qi Chen[4,5], Mikinori Kuwata[4,6], Yingjun Liu[4], Suzane S. de Sá[4], Karena McKinney[4], Scot T. Martin[4], Min Hu[6], Sri Hapsari Budisulistiorini[7], Matthieu Riva [7], Jason D. Surratt[7], Jason M. St. Clair[8**,***], Gabriel Isaacman-Van Wertz[9], Lindsay D. Yee[9], Allen H. Goldstein[9,10], Samara Carbone[11], Joel F. de Brito[11] Paulo Artaxo[11], Joost de A. Gouw[1,2,12], Abigail Koss[2,12], Armin Wisthaler[13,14], Tomas Mikoviny[13], Thomas Karl[15], Lisa Kaser[16,14], Werner Jud[14], Armin Hansel[14], Kenneth S. Docherty[17], M. Lizabeth Alexander[18], Niall H. Robinson[19****], Hugh. Coe[19], James D. Allan[19,20], Manjula R. Canagaratna[21], Fabien Paulot[22,23], and Jose L. Jimenez[1,2].

1 Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
2 Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
3 Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO, USA
4 School of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA
5 State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China
6 Earth Observatory of Singapore, Nanyang Technological University, Singapore7 Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill, Chapel Hill, NC, USA
8 Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA
9 Department of Environmental Science, Policy, and Management, University of California, Berkeley, CA, USA
10 Department of Civil and Environmental Engineering, University of California, Berkeley, CA, USA
11 Department of Applied Physics, University of Sao Paulo, Sao Paulo, Brazil
12 NOAA Earth System Research Laboratory, Boulder, CO, USA
13 Department of Chemistry, University of Oslo, Oslo, Norway
14 Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria
15 Institute of Atmospheric and Cryospheric Sciences, University of Innsbruck, Innsbruck, Austria
16 Atmospheric Chemistry Division (ACD), National Center for Atmospheric Research, Boulder, CO, USA
17 Alion Science and Technology, Research Triangle Park, NC, USA
18 Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA
19 School of Earth, Atmospheric and Environmental Sciences, University of Manchester, UK
20 National Centre for Atmospheric Science, University of Manchester, UK
21 Aerodyne Research, Inc., Billerica, MA, USA
22 NOAA Geophysical Fluid Dynamics Laboratory, Princeton, NJ, USA
23 Program in Atmospheric and Oceanic Sciences , Princeton University, Princeton, NJ, USA.

*Now at: Department of Chemistry, Université de Montréal, Montréal, QC, Canada
** Now at: Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, USA
*** Now at: Joint Center for Earth Systems Technology, University of Maryland Baltimore County, Baltimore, MD, USA.
**** Now at: Met Office, Exeter, UK

Abstract

Substantial amounts of secondary organic aerosol (SOA) can be formed from isoprene epoxydiols (IEPOX), which are oxidation products of isoprene mainly under low-NO conditions. Total IEPOX-SOA, which may include SOA formed from other parallel isoprene ~~low-NO~~ oxidation pathways, was quantified by applying Positive Matrix Factorization (PMF) to aerosol mass spectrometer (AMS) measurements. The IEPOX-SOA fractions of OA in multiple field studies across several continents are summarized here and show consistent patterns with the concentration of gas-phase IEPOX simulated by the GEOS-Chem chemical transport model. During the Southern Oxidant and Aerosol Study (SOAS) study, 78% of PMF-resolved IEPOX-SOA is accounted by the measured IEPOX-SOA molecular tracers (methyltetrols, C5-Triols and IEPOX-derived organosulfate and its dimers), making it the highest level of molecular identification of an ambient SOA component to our knowledge. Enhanced signal at $C_5H_6O^+$ (*m/z* 82) is found in PMF-resolved IEPOX-SOA spectra. To investigate the suitability of this ion as a tracer for IEPOX-SOA, we examine $f_{C_5H_6O}$ ($f_{C_5H_6O}$= $C_5H_6O^+$/OA) across multiple field, chamber and source datasets. A background of ~1.7±0.1‰ (‰=parts per thousand) is observed in studies strongly influenced by urban, biomass-burning and other anthropogenic primary organic aerosol (POA). Higher background values of 3.1±0.6‰ are found in studies strongly influenced by monoterpene emissions. The average laboratory monoterpene SOA value (5.5±2.0‰) is 4 times lower than the average for IEPOX-SOA (22±7‰), which leaves some room to separate both contributions to OA. Locations strongly influenced by isoprene emissions under low-NO levels had higher $f_{C_5H_6O}$ (~6.5±2.2‰ on average) than other sites, consistent with the expected IEPOX-SOA formation in those studies. $f_{C_5H_6O}$ in IEPOX-SOA is always elevated (12−40‰) but varies substantially between locations, which is shown to reflect large variations in its detailed molecular composition. The low $f_{C_5H_6O}$ (<3‰) reported in non IEPOX-derived isoprene-SOA from chamber studies indicates that this tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene. We introduce a graphical diagnostic to study the presence and aging of IEPOX-SOA as a "triangle plot" of f_{CO_2} vs. $f_{C_5H_6O}$. Finally, we develop a simplified method to estimate ambient IEPOX-SOA mass concentrations, which is shown to perform well compared to the full PMF method. The uncertainty of the tracer method is up to a factor of ~2 if the $f_{C_5H_6O}$ of the local IEPOX-SOA is not available. When only unit mass resolution data is available, as with the aerosol chemical speciation monitor (ACSM), all methods may perform less well because of increased interferences from other ions at *m/z* 82. This study clarifies the strengths and limitations of the different AMS methods for detection of IEPOX-SOA and will enable improved characterization of this OA component.

1. Introduction

Isoprene (2-methyl-1,3-butadiene, C_5H_8) emitted by vegetation is the most abundant non-methane hydrocarbon emitted to the Earth's atmosphere (~440−600 TgC/year) (Guenther et al., 2012). It is estimated to contribute substantially to the global secondary organic aerosol (SOA) budget (Paulot et al., 2009b;Guenther et al., 2012). Higher SOA yields from isoprene are observed under low-NO_x conditions (Surratt et al., 2010). Under low-NO conditions, i.e. when a substantial fraction of the peroxy radicals do not react with NO, gas-phase isoprene epoxydiols (IEPOX) are produced with high yield through a HO_x-mediated mechanism (Paulot et al., 2009b). Note that some IEPOX can also be formed from isoprene in high NO region via oxidation of the product 4-hydroxy-3-nitroxy isoprene (Jacobs et al., 2014) , however this pathway is thought to be much smaller than the low-NO pathway. Subsequently, IEPOX can be taken up by acidic aerosols (Gaston et al., 2014), where IEPOX-SOA can be formed through acid-catalyzed oxirane ring-opening of IEPOX (Cole-Filipiak et al., 2010;Eddingsaas et al., 2010;Lin et al., 2012;Nguyen et al., 2014), which is thought to be the main pathway to form IEPOX-SOA (Surratt et al., 2010;Pye et al., 2013;Worton et al., 2013). Although the complete molecular composition of IEPOX-SOA has not been elucidated, several molecular species that are part of IEPOX-SOA have been identified through gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS) and particle analysis by laser mass spectrometry (PALMS). They include 2-methyltetrols (and oligomers that contain them) (Surratt et al., 2010;Lin et al., 2014), C_5-alkene triols (Wang et al., 2005), 3-methyltetrahydrofuran-3,4-diols (Lin et al., 2012), and an IEPOX-organosulfate (Froyd et al., 2010;Liao et al., 2014). These molecular species account for a variable fraction of the IEPOX-SOA reported, e.g., 8% in a chamber study (Lin et al., 2012) or 26% in a field study at Look Rock, TN (Budisulistiorini et al., 2015). An estimate of total IEPOX-SOA can also be derived

from an IEPOX-SOA molecular tracer(s) via multiplying the tracer concentration by the total IEPOX-SOA to tracer ratio. However, that method is hindered by the limited information on these molecular tracers and the reported variability of IEPOX-SOA to tracer ratios. IEPOX-SOA may include SOA formed from other parallel isoprene low-NO oxidation pathways (Liu et al., 2014; Krechmer et al. 2015). In addition, the IEPOX-SOA molecular tracers are typically measured with slow time resolution (12/24 h).

Multiple field studies, supported by chamber studies, have shown that the total amount of IEPOX-SOA can be obtained by factor analysis of organic spectra from an aerosol mass spectrometer (AMS) or the aerosol chemical speciation monitor (ACSM) (Robinson et al., 2011;Lin et al., 2012;Budisulistiorini et al., 2013;Nguyen et al., 2014). Robinson et al. (2011) first reported an SOA factor with pronounced f_{82} (= *m/z* 82/OA) in the mass spectra acquired above a forest with high isoprene emissions in Borneo, and hypothesized that the elevated f_{82} may have arisen from methylfuran (C_5H_6O), consistent with $C_5H_6O^+$ being the major ion at *m/z* 82 in isoprene-influenced areas. Lin et al. (2012) demonstrated that the 3-MeTHF-3,4-diols associated with IEPOX-SOA result in enhanced f_{82} in AMS spectra, presumably through the formation methylfuran-like structures during thermal desorption. Electron-impact ionization of aerosols formed by atomizing a solution containing IEPOX ($C_5H_{10}O_3$) can also yield $C_5H_6O^+$ signals in an AMS via two dehydration reactions (Lin et al., 2012). However, because gas-phase IEPOX has high volatility, non-reactive gas-to-particle partitioning of IEPOX into OA is negligible under typical ambient concentrations in forest areas ($1-10$ μg m^{-3}) (Worton et al., 2013).

IEPOX-SOA was estimated to account for 33% of ambient OA in summertime Atlanta from PMF analysis of ACSM spectra. The source apportionment result was supported by the

pronounced f_{82} peak in the factor spectrum and good temporal correlation of the factor with sulfate and 2-methyltetrols (Budisulistiorini et al., 2013). Sulfate is often strongly correlated with the acidity of an aerosol, and might also play a direct role in the chemistry, e.g. via direct reaction or nucleophilic effects (Surratt et al., 2007;Liao et al., 2014;Xu et al., 2014). While discussing the results of a recent aircraft campaign from Brazil, Allan et al. (2014) also used f_{82} as a tracer for IEPOX-SOA.

If f_{82} in AMS spectra (and/or $f_{C_5H_6O}$ in HR-AMS spectra) is dominated by IEPOX-SOA, f_{82} would be a convenient, high-time-resolution, and potentially quantitative tracer for IEPOX-SOA. Thus, it will be very useful for investigating the impacts of SOA formation from isoprene with AMS/ACSM measurements, which have become increasingly common in recent years including some continental-scale continuous networks (Fröhlich et al., 2015). However, no studies to date have systematically examined whether enhanced f_{82} is unique to IEPOX chemistry or whether it could also be enhanced in other sources. Nor has the range of f_{82} been determined for IEPOX-SOA. Questions also have been raised about the uniqueness of this tracer and potential contributions from monoterpene SOA (Anonymous_Referee, 2014).

In this study, the IEPOX-SOA results reported in various field campaigns are summarized and compared to predicted gas-phase IEPOX concentrations from a global model to help confirm the robustness of the AMS identification of this type of SOA. We then investigate the usefulness and limitations of the IEPOX-SOA tracers $f_{C_5H_6O}$ (= $C_5H_6O^+$/OA) and f_{82} by combining AMS data from multiple field and laboratory studies including a new dataset from the 2013 Southern Oxidant and Aerosol Study (SOAS). We compare the tracer levels in different OA sources (urban, biomass burning and biogenic), characterizing the background levels and interferences on this tracer for both high-resolution (HR) and unit mass resolution (UMR) data. We also

provide a simplified method to rapidly estimate IEPOX-SOA from $f_{C_5H_6O}$ and f_{82}. While this method is no substitute for a detailed IEPOX-SOA identification via PMF, it is a simple method to estimate IEPOX-SOA concentrations (or its absence) in real-time from AMS or ACSM measurements or under conditions in real-time, or where PMF analysis is not possible or is difficult to perform.

2 Experimental

We classify the field datasets used in this study into three categories: (1) studies strongly influenced by urban and biomass-burning emissions: Los Angeles area, US and Beijing, China (urban); Changdao island, downwind of China and Barcelona area, Spain (urban downwind); flight data from biomass-burning plumes and continental areas (NW and western, US) in SEAC4RS and DC3 campaigns; and biomass burning lab emissions (FLAME-3 study). (2) Studies strongly influenced by isoprene emissions, including a SE US forest site (SOAS campaign); Two pristine forest site and one forest site partially impacted by urban plumes in the Amazon rain forest (Brazil). The latter site is classified in this category because (i) high isoprene concentrations (e.g. 3 ppb in average peaks in the afternoon) were observed during the study; (ii) the impact of biogenic SOA formed during 1000 km where the air travels over the pristine forest upwind of Manaus; (iii) PMF results indicate an important impact of IEPOX-SOA at this site (de Sá et al., 2015); (iv) PTRMS results indicate a substantial concentration of the isoprene hydroperoxyde formed by low-NO chemistry. Borneo rain forest in Malaysia; and flight data from SE US flights from aircraft campaign (SEAC4RS); (3) Studies strongly influenced by monoterpene emissions in a pine forest in the Rocky Mountains and a European boreal forest. Locations and additional detailed information about these studies can be found in Fig. 1 and Table 1.

With the exception of SOAS, all of the campaigns included in this analysis have been previously described elsewhere (Table 1). The SOAS campaign took place in a forested area of the SE US during June and July, 2013 (Fig. 1) and has several ground sites. The new dataset introduced below was acquired at the SEARCH supersite, Centreville (CTR), AL (32.95° N, 87.13°W). Some results from a different SOAS site (Look Rock, TN) are also discussed later (Budisulistiorini et al., 2015). Relatively high average isoprene and monoterpene concentrations of 3.3±2.4 ppb and 0.7±0.4 ppb, respectively, were observed in SOAS-CTR by on-line GC/MS. Measurements of non-refractory aerosol components of submicron particles (PM_1) were made using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, "AMS" hereafter) (DeCarlo et al., 2006). By applying positive matrix factorization (PMF) to the time series of organic mass spectra (Ulbrich et al., 2009), we separated contributions from IEPOX-SOA and other sources/components of OA. The AMS PMF results used here are very consistent with those from a separate HR-ToF-AMS operated by another group at the same site (Xu et al., 2014). The global gas-phase IEPOX concentrations in 2013 were modeled at as resolution of 2 x 2.5 degrees as described in Nguyen et al. (2015). The gas-phase chemistry of isoprene in GEOS-Chem is based on Paulot et al (2009a;2009b) as described by Mao et al. (2013).

In the following discussion, we denote the IEPOX-SOA factor from PMF as "IEPOX-SOA_{PMF}" and IEPOX-SOA from lab studies as "IEPOX-SOA_{lab}" for clarity. If we use "IEPOX-SOA" in the paper, it refers to a broad concept of IEPOX-SOA. We use a superscript to clarify the type of OA for which $f_{C_5H_6O}$ is being discussed: $f_{C_5H_6O}^{OA}$ refers to $f_{C_5H_6O}$ in total OA, $f_{C_5H_6O}^{IEPOX-SOA}$ to $f_{C_5H_6O}$ in IEPOX-SOA_{PMF} or IEPOX-SOA_{lab}, $f_{C_5H_6O}^{MT-SOA}$ to the $f_{C_5H_6O}$ value in pure MT-SOA and $f_{C_5H_6O}^{OA-Bkg-UB}$ and $f_{C_5H_6O}^{OA-Bkg-MT}$ refer to background $f_{C_5H_6O}^{OA}$ from areas strongly

influenced by urban+biomass-burning emissions and by monoterpene emissions, respectively. If we refer to $f_{C_5H_6O}$ in general, we will still use $f_{C_5H_6O}$. When we report the average $f_{C_5H_6O}^{OA}$ in each campaign, as shown in the Table 1, we used the average from the time series of $f_{C_5H_6O}^{OA}$ at their raw time resolution (secs to mins). During this process, we exclude points whose OA mass concentrations are below twice the detection limit of OA in AMS (typically 2× 0.26 μg m^{-3}=0.5 μg m^{-3}). When averaging $f_{C_5H_6O}^{OA}$ values across datasets, we counted each dataset as one data point.

3 Results and Discussion

3.1 IEPOX-SOA in a SE US forest during SOAS, 2013

We use the SOAS-CTR field study (SE US-CTR) as an example for the determination of IEPOX-SOA from AMS data via PMF analysis. The time series and mass spectrum of this component are shown in Fig. 2. The IEPOX-SOA_{PMF} mass concentration is the sum of mass concentrations of all the ions in the IEPOX-SOA_{PMF} mass spectra. The "mass concentration" of an ion is used to represent the mass of the species whose detection resulted in the observed ion current of that ion, based on the properties of electron ionization (Jimenez et al., 2003). An uncertainty (standard deviation) of IEPOX-SOA_{PMF} mass concentration of ~9% was estimated from 100 bootstrapping runs in PMF analysis (Ulbrich et al., 2009) (Fig. S1). This uncertainty concerns only the PMF separation method. In practice the uncertainty in IEPOX-SOA_{PMF} concentration is dominated by the larger uncertainty on the AMS concentrations arising from the collection efficiency and relative ionization efficiency (Middlebrook et al., 2012).

A strong correlation is found between AMS IEPOX-SOA_{PMF} and 2-methyltetrols (R=0.79) and sulfate (R = 0.75) as expected (Surratt et al., 2010;Lin et al., 2012;Nguyen et al., 2014;Xu et

al., 2014). The diurnal variation of IEPOX-SOA$_{PMF}$ is also similar to gas-phase IEPOX and isoprene measured in SOAS-CTR. 2-Methyltetrols, measured on-line by GC-EI/MS with the SV-TAG instrument (Isaacman et al., 2014), comprise 26% of IEPOX-SOA$_{PMF}$ in SOAS-CTR on average, as shown in Fig. 2b. A similar ratio (29%) is found between 2-methyltetrols measured by offline analysis of filter samples using GC-EI/MS and LC/MS (Lin et al., 2014) and IEPOX-SOA$_{PMF}$. Other IEPOX-SOA tracers, such as C5-alkene triols, IEPOX-organosulfates, and dimers containing them, can also be measured by offline GC-EI/MS and LC/MS (Lin et al., 2014;Budisulistiorini et al., 2015), and they account for 28% and 24% in total IEPOX-SOA$_{PMF}$ in SOAS (R=0.7), respectively (Fig. S2). The total IEPOX-SOA tracers measured in SOAS account for ~78±42% of the total IEPOX-SOA$_{PMF}$ mass concentration. The uncertainty of the fraction of IEPOX-SOA molecular tracers in IEPOX-SOA$_{PMF}$ in SOAS study (42%) is estimated by combining the overall uncertainty from IEPOX-SOA molecular tracer measurement (24%), linear regression between tracer vs IEPOX-SOA$_{PMF}$ (17%, see Fig. 2b and Fig. S2), IEPOX-SOA$_{PMF}$ in PMF separation method (9%) and the quantification of IEPOX-SOA$_{PMF}$ based on AMS calibration (30%) (Middlebrook et al., 2012). This is a remarkably high value compared to the tracer to total SOA ratios for other SOA systems (e.g., SOA from monoterpenes or aromatic hydrocarbons) (Lewandowski et al., 2013) ~~and it is the highest reported in the literature to our knowledge~~. A total tracers to IEPOX-SOA$_{PMF}$ ratio of 26% was reported for the Look Rock site in SOAS (SOAS-LR) (Budisulistiorini et al., 2015). Thus, the measured total molecular tracer fraction in total IEPOX-SOA appears to be quite variable (a factor of 3) even if the same or similar techniques are used. Although the calibration methodology between different campaigns may result in some uncertainties, this value likely changes significantly between different times

and locations, potentially due to changes in particle-phase reaction conditions such as sulfate and water concentrations, acidity, and the identity and concentrations of oligomerization partners.

IEPOX-SOA$_{PMF}$ accounts for 17% of the total OA mass concentration at SOAS-CTR. This is shown in Fig. 1 along with the IEPOX-SOA$_{PMF}$ fraction from several previous studies (Robinson et al., 2011;Slowik et al., 2011;Budisulistiorini et al., 2013;Hayes et al., 2013;Hu et al., 2013;Chen et al., 2014;Hu et al., 2015). Fig. 1 also shows the surface gas-phase IEPOX concentrations for July, 2013 as simulated with GEOS-Chem. At all sites with at least ~30 ppt predicted average IEPOX concentration, IEPOX-SOA$_{PMF}$ is identified in AMS data. IEPOX-SOA$_{PMF}$ accounts for 6% − 36% of total OA in those studies, signifying the importance of IEPOX-SOA for regional and global OA budgets. No IEPOX-SOA$_{PMF}$ factor (i.e. below the PMF detection limit of ~5% of OA, Ulbrich et al., 2009) was found in areas strongly influenced by urban emissions where high NO concentrations suppress the IEPOX pathway, even in the presence of substantial isoprene concentrations (e.g. Hayes et al., 2013). GEOS-Chem indeed predicts negligible modeled gas-phase IEPOX concentrations in those areas, where isoprene peroxy radicals are expected to react primarily with NO. Some IEPOX can also be formed via high NO chemistry (Jacobs et al., 2014) , however this pathway is thought to be much smaller than the low-NO pathway, consistent with the lack of observation of IEPOX-SOA$_{PMF}$ in the polluted studies included here. The fraction of IEPOX-SOA$_{PMF}$ positively correlates with modeled gas-phase IEPOX, as shown in the inset of Fig. 1.

The mass spectrum of IEPOX-SOA during SOAS-CTR is similar to those from other studies as seen in Fig. S3 – S4 (Robinson et al., 2011;Lin et al., 2012;Budisulistiorini et al., 2013;Chen et al., 2014;Nguyen et al., 2014;Xu et al., 2014), and also exhibits a prominent $C_5H_6O^+$ peak at *m/z* 82. We investigated the correlation between the time series of IEPOX-SOA$_{PMF}$ and each ion

in the OA spectra. The temporal variation of ion $C_5H_6O^+$ correlates best (R=0.96) with IEPOX-SOA$_{PMF}$ among all measured OA ions (Table S1). This result suggests that $C_5H_6O^+$ ion may be the best ion tracer for IEPOX-SOA among all OA ions. $C_5H_5O^+$ (*m/z* 81), $C_4H_5^+$ (*m/z* 53), $C_4H_6O^+$ (*m/z* 70) and $C_3H_7O_2^+$ (*m/z* 75) also correlate well with IEPOX-SOA$_{PMF}$ in SOAS-CTR and could be potential tracers for IEPOX-SOA$_{PMF}$. Scatter plots between these four ions and $C_5H_6O^+$ at different campaigns indicate they either have higher background values or lower signal-to-noise compared to $C_5H_6O^+$ (Fig. S5).

$f_{C_5H_6O}^{IEPOX-SOA}$ from SOAS and other field and laboratory studies (Table 1) ranges from 12‰ to 40‰ (‰=parts per thousand) and have an average value of 22±7‰. The average $f_{C_5H_6O}^{IEPOX-SOA}$ value shown here also includes f_{82} data from four UMR IEPOX-SOA$_{PMF}$ spectra. This is justified since $C_5H_6O^+$ accounts for over 95% of *m/z* 82 in IEPOX-SOA based on results from SOAS-CTR and other lab studies (Kuwata et al., 2015). Indeed the average does not change if the UMR studies are removed from the average. These values are substantially higher than those from other types of OA or from locations with little impact from IEPOX-SOA, as discussed below.

3.2 $f_{C_5H_6O}$ in areas with strong influence from urban and biomass burning emissions

We next examine whether POA or SOA from field studies in areas strongly influenced by urban and biomass-burning emissions and without substantial predicted gas-phase IEPOX concentrations or IEPOX-SOA contributions can lead to enhanced $f_{C_5H_6O}^{OA}$. Figure 3a shows the distribution of $f_{C_5H_6O}^{OA}$ in this category of studies peaks at 1.7±0.1‰ (range 0.02 – 3.5‰). Data from continental air masses sampled from aircraft over the western and northwest US (where isoprene emissions are low) are shown in Fig. 3b and show a similar range as the polluted ground sites.

Biomass burning emissions and plumes sampled over multiple studies show a similar range to the pollution studies, with some slightly higher values. The peak of the distribution of $f_{C_5H_6O}^{OA}$ from fresh biomass-burning smoke across many different biomasses during the FLAME-3 study is 2.0‰. During the SEAC4RS aircraft campaign, many biomass burning plumes were sampled, where OA concentrations varied over a wide range (several tens to more than one thousand μg m^{-3}). The average $f_{C_5H_6O}^{OA}$ across these biomass-burning plumes was 1.75‰ with low variability (~20%), see Fig. S6.

We also explore whether other anthropogenic primary OA (POA) emission sources could elevate $f_{C_5H_6O}$ above the observed background levels of ~1.7‰. Figure 3c shows $f_{C_5H_6O}$ for POA spectra from vehicle exhaust, cooking, coal combustion, and multiple pure chemical standards (e.g., some alcohols; di- or poly acids) (Canagaratna et al., 2015). Almost all the values are below 2‰, with exceptions for one type of cooking POA at 3‰, the polyol xylitol (4.2‰), and some acids (5-Oxoazelaic acid= 4.8‰, Gamma ketopimelic acid = 5.2‰, ketopimelic acid = 6.5‰, 3-Hydroxy-3-Methylglutaric acid = 11.8‰, Adipic acid = 16.4‰). All the tracers resulting in elevated $f_{C_5H_6O}$ contain multiple hydroxyl groups, and may result in furan-like structures via facile dehydration reactions (Canagaratna et al., 2015). Xylitol has been proposed as a tracer of toluene SOA (Hu et al., 2008). It has a similar structure to 2-methyltetrols, with 5 -OH groups instead of 4. In the AMS, xylitol may form the methylfuran structure through dehydration reactions like 2-methytetrols. However, $f_{C_5H_6O}$ in other toluene SOA tracers in our dataset show background levels of $f_{C_5H_6O}$ (<2‰). Given the small fraction of xylitol in toluene SOA (Hu et al., 2008), xylitol is unlikely to increase $f_{C_5H_6O}$ in anthropogenic SOA, consistent with our results.

In summary, in the absence of strong impacts from biogenic SOA, the AMS high resolution ion $C_5H_6O^+$ has a clear and stable background, spanning a small range (0.02 – 3.5‰) with an average values around 1.7±0.1‰ ($f_{C_5H_6O}^{OA-Bkg-UB}$), about an order of magnitude lower than the average value (22±7‰) of $f_{C_5H_6O}^{IEPOX-SOA}$.

3.3 Enhancements of $f_{C_5H_6O}$ in areas strongly influenced by isoprene emissions

GEOS-Chem predicts much higher surface gas-phase IEPOX concentrations over the SE US and Amazon rainforest than those in temperate urban areas (Fig. 1). This is expected from high isoprene concentrations (e.g. 3.3 ppb in SOAS-CTR and 4 ppb in the Amazon) under low average NO concentrations (~0.1 ppb) (Karl et al., 2009;Ebben et al., 2011). Probability distributions of $f_{C_5H_6O}^{OA}$ during both campaigns are shown in Fig. 4a, and are very similar with averages of 5 – 6‰ (range 2.5‰ − 11‰). The Amazon forest downwind of Manaus and a Borneo tropical forest study show even higher averages of 7‰ and 10‰, respectively (Robinson et al., 2011;de Sá et al., 2015). During the SEAC4RS aircraft campaign, the average $f_{C_5H_6O}^{OA}$ (4.4±1.6‰) from all SE US flights is also enhanced compared to levels observed in the northwest and western US continental air masses (1.7±0.3‰) where isoprene emissions are much smaller (Guenther et al., 2012). Thus, campaigns in locations strongly influenced by isoprene emissions under lower NO conditions show systematically higher $f_{C_5H_6O}^{OA}$ values (with an average peak of 6.5‰±2.2‰) than background levels found in other locations (1.7‰). The fact that $f_{C_5H_6O}^{OA}$ (6.5±2.2‰) in these studies is lower than the values in IEPOX-SOA (22‰±7‰) is expected, since ambient datasets also include OA from other sources, and confirms that IEPOX-SOA is not an overwhelmingly dominant OA source at most of those locations (See Fig. S7).

3.4 Values of $f_{C_5H_6O}$ in laboratory studies of non IEPOX-derived isoprene SOA

We also investigate $f_{C_5H_6O}$ in laboratory SOA from isoprene in Fig. 4a. For SOA produced by chamber isoprene photooxidation under high NO_x conditions, low $f_{C_5H_6O}$ (<2‰) within the background level is observed (Kroll et al., 2006;Chen et al., 2011). SOA from oxidation of isoprene hydroxyhydroperoxide (ISOPOOH, a product of low-NO oxidation of isoprene) under low-NO conditions, when formed under conditions that are not favorable for the reactive uptake of IEPOX into aerosols also has low $f_{C_5H_6O}$ of 2‰ (Krechmer et al., 2015). Low values of $f_{C_5H_6O}$ (<3‰) are also observed in SOA from isoprene + NO_3 radical reactions without acid seeds (Ng et al., 2008). The low $f_{C_5H_6O}$ (<3‰) observed in non IEPOX-derived isoprene SOA indicate that $f_{C_5H_6O}$ is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene.

3.5 Enhancements of $f_{C_5H_6O}$ in areas strongly influenced by monoterpene emissions

The BEACHON-RoMBAS campaign was carried out in a Rocky Mountain pine forest with high monoterpene emissions that account for 34% in daytime and 66 % at night of the total VOC mixing ratios (on average peaking at 0.15 ppb during day and 0.7 ppb at night) (Fry et al., 2013) but lower isoprene emissions (peaking at 0.35 ppb during daytime) (Kaser et al., 2013;Karl et al., 2014). One-third of the RO_2 radicals react via the low-NO route (i.e. via RO_2 + HO_2) at this site (Fry et al., 2013). The isoprene/monoterpene ratio at the Rocky Mountain site is 0.48, and is ~ 10 − 20 times lower than the value (4.7) in SOAS-CTR and (8.3) in Amazon studies (Chen et al., 2014), suggesting that $f_{C_5H_6O}^{OA}$ may be near background levels because of the very low potential contribution of IEPOX-SOA at the Rocky Mountain site. However, the average $f_{C_5H_6O}^{OA}$ at the Rocky Mountain site is 3.7±0.5‰ (Fig. 4a), which although lower than the average $f_{C_5H_6O}^{OA}$

(6.5‰) found in the SE US-CTR, Amazon and Borneo forests, it is still twice the $f_{C_5H_6O}^{OA-Bkg-UB}$ values of 1.7‰ observed in pollution and smoke-dominated locations.

Three circumstances may lead to such an enhanced $f_{C_5H_6O}^{OA}$ at the Rocky Mountain site, which we examine here. (1) A small amount of IEPOX-SOA may be formed from the limited isoprene present at the Rocky Mountain site and surrounding region. However, the average isoprene concentration in this pine forest area is only 0.2 ppb, which is around 16 times less than that (3.3 ppb) at the SE US site in SOAS. The conditions at the Rocky Mountain site were less favorable for IEPOX-SOA formation due to a higher fraction (70% in daytime) of the RO_2 radicals reacting with NO and less acidic aerosols (Fry et al., 2013;Levin et al., 2014). Thus we can estimate an upper limit contribution of IEPOX-SOA to the $f_{C_5H_6O}^{OA}$ tracer at the Rocky Mountain site assuming the same ratio of IEPOX-SOA to isoprene in both campaigns. In this case, we would expect $f_{C_5H_6O}^{OA}$ at the Rocky Mountain site to be the background level (1.7‰) plus 1/16th of the enhancement above the background observed in SOAS (5‰ − 1.7‰ = 3.3‰) multiplied by the ratio of OA concentrations at both sites (4.8 μg m^{-3} in SE US site vs 1.8 μg m^{-3} in Rocky Mountain site). This calculation results in an expected upper limit $f_{C_5H_6O}^{OA}$ ~ 2.25‰ at the Rocky Mountain site due to the IEPOX-SOA contribution. This estimate is much lower than the observed average 3.7‰. Thus the elevated $f_{C_5H_6O}^{OA}$ in Rocky Mountain pine forest is very unlikely to be due to IEPOX-SOA.

(2) The second explanation of high $f_{C_5H_6O}^{OA}$ observed at Rocky Mountain site is that SOA from monoterpene oxidation (MT-SOA) may have a higher $f_{C_5H_6O}$ than background OA from other sources. Several chamber studies show that MT-SOA, e.g., SOA from ozonolysis (Chhabra et al., 2011;Chen et al., 2014) or photooxidation (Ng et al., 2007) of α-pinene, or NO_3 reaction with α-pinene, or NO_3 reaction with α-pinene, β–pinene and Δ^3–Carene (Fry et al., 2014;Boyd et al.,

2015) can result in higher $f_{C_5H_6O}$ (average 5.5±2.0‰) than background levels of ~1.7‰ (Fig. 4a). We note that the average lab-generated MT-SOA value ($f_{C_5H_6O}^{MT-SOA}$) is still 4 times lower than the average $f_{C_5H_6O}^{IEPOX-SOA}$ for IEPOX-SOA$_{PMF}$ and IEPOX-SOA$_{lab}$ (Fig. S8), and thus there is some room to separate both contributions. Oxidation of monoterpenes can lead to species with multiple –OH groups, which may result in the production of methylfuran (or ions of similar structure) upon AMS analysis. We do not observe enhanced $f_{C_5H_6O}$ in SOA from sesquiterpene oxidation (<2‰) (Chen et al., 2014). The values of $f_{C_5H_6O}^{MT-SOA}$ in chamber studies, together with the finding of a substantial contribution of monoterpenes to SOA at this Rocky Mountain site (Fry et al., 2013) suggest that MT-SOA may explain the values of $f_{C_5H_6O}^{OA}$ observed there.

Two other field studies support the conclusion that ambient MT-SOA may have slightly enhanced $f_{C_5H_6O}$. Fig. 6 shows data from a DC3 aircraft flight in the areas around Missouri and Illinois. Ambient $f_{C_5H_6O}^{OA}$ increases from background levels (~1.7‰) to ~4.1‰ in a highly correlated manner to monoterpene concentration increases (with an average of 3.0‰ during the enhanced period). Meanwhile, isoprene and gas-phase IEPOX stay at low levels similar to the rest of the flight, indicating that enhanced $f_{C_5H_6O}^{OA}$ in the periods with higher MT concentrations should arise from MT-SOA and not IEPOX-SOA. Fig. 4a includes AMS measurements at a MT-emission dominated European boreal forest (Hyytiälä in Finland) (Robinson et al., 2011). Average $f_{C_5H_6O}^{OA}$ is ~2.5‰ at this site, which is again higher than the $f_{C_5H_6O}^{OA-Bkg-UB}$ value of 1.7‰. The slightly lower $f_{C_5H_6O}^{OA}$ in the Boreal forest vs. the Rocky Mountain site may be partially explained by a small contribution from IEPOX-SOA at the latter (estimated above to increase $f_{C_5H_6O}^{OA}$ up to 2.25‰ at the Rocky Mountain site), as well as by differences of the MT-SOA/OA

ratio at both sites (Corrigan et al., 2013) and the relative importance of different MT species and oxidation pathways.

(3) The enhanced $f_{C_5H_6O}^{OA}$ at the Rocky Mountain site may have arisen from oxidation products of 2-methyl-3-buten-2-ol (MBO, $C_5H_{10}O$) emitted from pine trees. MBO, with a daytime average of 2 ppb accounts for ~50% of the total VOC mixing ratio during the day (Karl et al., 2014). MBO has been shown to form aerosol with a 2 – 7 % yield in chamber studies, which is thought to proceed via the uptake of epoxide intermediates ($C_5H_{10}O_2$, vs. IEPOX $C_5H_{10}O_3$) under acidic aerosol conditions (Zhang et al., 2012;Mael et al., 2014;Zhang et al., 2014). Some aerosol species formed by MBO-derived epoxides have similar structures (e.g., $C_5H_{12}O_3$) to the IEPOX oxidation products in SOA and thus they might contribute to $f_{C_5H_6O}^{OA}$. No pure MBO-derived epoxides or their oxidation products in the aerosol phase have been measured by AMS so far, to our knowledge.

To attempt to differentiate whether MT-SOA or MBO-SOA dominate the higher $f_{C_5H_6O}^{OA}$ at the Rocky Mountain site, average diurnal variations of ambient $f_{C_5H_6O}^{OA}$, monoterpene and isoprene+MBO are plotted in Fig. S9. $f_{C_5H_6O}^{OA}$ shows a diurnal pattern that increases at night and peaks in the early morning, similar to the diurnal variation of monoterpenes. Monoterpenes continue to be oxidized during nighttime at this site by NO_3 radical and O_3 with a lifetime of ~30 min (with 5 ppt of NO_3 and 30 ppb of O_3) (Fry et al., 2013). In contrast only a decrease and later a plateau of $f_{C_5H_6O}^{OA}$ are observed during the period with high MBO concentration and higher oxidation rate of MBO due to high OH radical in daytime (as MBO reacts slowly with O_3 and NO_3) (Atkinson and Arey, 2003). While MBO-SOA may or may not have $f_{C_5H_6O}$ above background levels, the diurnal variations point to MT-SOA playing a dominant role in $f_{C_5H_6O}^{OA}$ at this site.

The average $f_{C_5H_6O}^{OA}$ in areas strongly influenced by monoterpene emissions is 3.1±0.6‰, obtained by averaging the values from the Rocky mountain forest (3.7‰), European boreal forest (2.5‰), and DC3 flight (3.0‰). Note that the difference between $f_{C_5H_6O}^{OA}$ in areas strongly influenced by monoterpene emissions (3.1±0.6‰) and isoprene emissions (6.5±2.2‰) is reduced, compared to a factor of 4 differences between pure MT-SOA (5.5±2.0‰) and IEPOX-SOA (22±7‰). This is likely due to the physical mixing of OA from different sources and in different proportions at each location.

3.6 $f_{C_5H_6O}$ vs OA oxidation level (f_{CO_2}) "triangle plot" – background studies

In AMS spectra, the CO_2^+ ion is a marker of aging and oxidation processes (Alfarra et al., 2004;Ng et al., 2011a). To evaluate whether oxidation plays a role on the observed $f_{C_5H_6O}$ for different types of OA, in this section we use plots of f_{CO_2}(= CO_2^+/OA) vs. $f_{C_5H_6O}$ as a graphical diagnostic of this process, similar to graphical diagnostics ("triangle plots") used for other purposes with AMS data (Cubison et al., 2011;Ng et al., 2011a). For studies strongly influenced by urban and biomass-burning emissions in Fig. 3d we observe a wide range of $f_{CO_2}^{OA}$ values from 0.001 to 0.3 (= 30% or 300‰). The wide range of $f_{CO_2}^{OA}$ is due to variable fractions of POA and SOA (mixing effect) and a variable oxidation level of POA and SOA (oxidation effect) in the different studies. In fact, to our knowledge, these studies encompass the values of $f_{CO_2}^{OA}$ observed in all ambient AMS studies to date (Ng et al., 2011a). Several studies when urban and forest air, or biomass burning smoke were aged by intense OH oxidation with an oxidation flow reactor (OFR) (Kang et al., 2007;Li et al., 2013;Ortega et al., 2013) are also included. However, despite the wide range of $f_{CO_2}^{OA}$, $f_{C_5H_6O}^{OA}$ changes little, staying in the range $0.02 - 3.5$‰, and with little apparent dependence on $f_{CO_2}^{OA}$ for the ambient studies. A linear regression to quantiles from this

dataset results in an intercept of 1.7‰ and a very weak decrease with increasing $f_{CO_2}^{OA}$. A stronger decrease is observed when aging urban air (Los Angeles) by intense OH exposure in flow reactor, as shown in Fig. 3d.

Ambient $f_{CO_2}^{OA}$ at the Rocky Mountain forest site shows a moderate oxidation level (0.1 − 0.15), similar to the SE US-CTR (Fig. 5). $f_{C_5H_6O}^{OA}$ in the Rocky mountain site decreases linearly when $f_{CO_2}^{OA}$ increases. During the Rocky Mountain study, the intense OH aging of ambient air in a flow reactor shows a continuation of the trend observed for the ambient data, where $f_{C_5H_6O}^{OA}$ decreases as $f_{CO_2}^{OA}$ increases. A linear regression to the combined ambient and OFR datasets ($f_{C_5H_6O}^{OA}$ = -0.013× $f_{CO_2}^{OA}$+0.0054) will be used below to estimate background $f_{C_5H_6O}^{OA}$ in areas with strong monoterpene and low isoprene emissions.

$f_{C_5H_6O}$ in ambient SOA from other studies catalogued in the HR-AMS spectral database are also shown in Fig. 5. Most urban oxygenated OA (OOA) are within $f_{C_5H_6O}^{OA-Bkg-UB}$ (average 1.7‰; range: 0.02 − 3.5‰), which is consistent with the $f_{C_5H_6O}$ (<3‰) in lab aromatic SOA and other urban OA in Fig. 5. However, some ambient SOA spectra do show higher $f_{C_5H_6O}$ (3 – 10‰) than the $f_{C_5H_6O}^{OA-Bkg-UB}$ (0.02 – 3.5‰), which we will discuss in the next section.

3.7 $f_{C_5H_6O}$ vs. OA oxidation level (f_{CO_2}) – IEPOX-SOA influenced Studies

$f_{CO_2}^{OA}$ vs. $f_{C_5H_6O}^{OA}$ in studies impacted by IEPOX-SOA are shown in Fig. 5. Consistent with the distributions discussed above, the bulk of points from these areas all show distinctively enhanced $f_{C_5H_6O}^{OA}$ when compared to background $f_{C_5H_6O}^{OA}$ points of similarly moderate or higher oxidation levels. The $f_{C_5H_6O}^{OA}$ measurements with lower $f_{CO_2}^{OA}$ values are more broadly distributed than the $f_{C_5H_6O}^{OA}$ points with higher $f_{CO_2}^{OA}$ values in SE US-CTR, SEAC4RS, Borneo forest and Amazon

forest downwind of Manaus. However, increased $f_{C_5H_6O}^{OA}$ with higher $f_{CO_2}^{OA}$ was observed in the Amazon. Both oxidation and mixing of airmasses with different OA can influence these observations. $f_{C_5H_6O}^{IEPOX-SOA}$ in IEPOX-SOA usually will decrease with oxidative aging. E.g., $f_{C_5H_6O}^{OA}$ from the SOAS oxidation flow reactor decreases continuously as OA becomes more oxidized than ambient OA in SOAS-CTR ($f_{CO_2}^{OA}$ increases from 0.15 to 0.3). Airmass mixing effects are more complex. Depending on the $f_{CO_2}^{OA}$ in the airmasses mixed with, $f_{C_5H_6O}^{OA}$ in IEPOX-SOA-rich air can show positive, neutral or negative trends with increasing $f_{CO_2}^{OA}$. E.g., in pristine Amazon forest, points with both lower $f_{CO_2}^{OA}$ (<0.08) and $f_{C_5H_6O}^{OA}$ (< 8‰) values are thought to be mainly caused by advection of POA from occasional local pollution.

The overall trend for the ambient measurements in studies strongly influenced by isoprene emissions (Fig. 5) is that those points cluster in a triangle shape and $f_{C_5H_6O}^{OA}$ decreases as $f_{CO_2}^{OA}$ increases, as illustrated in Fig. S10. This "triangle shape" indicates that as the ambient OA oxidation increases, the IEPOX-SOA signature is reduced, potentially by the ambient oxidation processes or by physical mixing with airmasses containing more aged aerosols.

Finally, points with higher $f_{C_5H_6O}$ in OOA/aged OA are labeled with numbers in Fig. 5. The sources of those labeled points are summarized in Table S2. OA from those studies are all partially influenced by biogenic emissions. For example, during measurements of ambient OA in the Central Valley of California (number 2), high isoprene emissions and acidic particles were observed (Dunlea et al., 2009), suggesting that potential IEPOX-SOA formed in this area may explain the higher $f_{C_5H_6O}^{OA}$ there.

3.8 Best estimate of $f_{C_5H_6O}$ in IEPOX-SOA

IEPOX-SOA from different field campaigns and chamber studies lay towards the right and on the bottom half of Fig. 5. IEPOX-SOA from chamber studies show systematically lower $f_{CO_2}^{IEPOX-SOA}$ than ambient studies. This is likely explained by the lack of additional aging in the laboratory studies, because all the lab IEPOX-SOA were measured directly after uptake gas-phase IEPOX onto acidic aerosol without undergoing substantial additional oxidation.

A wide range (12 – 40‰) of $f_{C_5H_6O}^{IEPOX-SOA}$ is observed with an average of 22‰±7‰ in ambient and lab IEPOX-SOA. $f_{C_5H_6O}^{IEPOX-SOA}$ did not show a trend vs. $f_{CO_2}^{IEPOX-SOA}$. The IEPOX-SOA molecular tracer 3-MeTHF-3,4-diols has been shown to enhance the $f_{C_5H_6O}$ in OA (Fig. 5) (Lin et al., 2012;Canagaratna et al., 2015). Except 3-MeTHF-3,4-diols none of the other pure IEPOX-derived polyols standards have been atomized and injected into the AMS system so far, to our knowledge. We suspect other polyols such as 2-methyltetrols may also lead to such an enhancement through dehydration reactions in the AMS vaporizer leading to methylfuran-type structures. The diversity of $f_{C_5H_6O}^{IEPOX-SOA}$ in different studies is related with the variable content of specific IEPOX-SOA molecular species that enhance $f_{C_5H_6O}^{IEPOX-SOA}$ differently. The fractions of molecular IEPOX-SOA species in total IEPOX-SOA$_{PMF}$ is plotted vs $f_{C_5H_6O}$ in IEPOX-SOA in three different studies in Fig. 7, which show a strong correlation between each other. The strong simultaneous variation of both quantities indicates that the diversity of $f_{C_5H_6O}^{IEPOX-SOA}$ is very likely explained by the variability of the molecules comprising IEPOX-SOA among different studies.

During one day in SOAS (June 26th, 2013), IEPOX-SOA$_{PMF}$ comprised 80 − 90% of total OA (Fig. S11), possibly due to high sulfate concentrations favoring IEPOX-SOA formation. $f_{C_5H_6O}^{OA}$ reached 25‰, which is similar to the 22‰ for the IEPOX-SOA$_{PMF}$ from this study, and consistent with a slightly lower value for the average vs. freshest ambient IEPOX-SOA. Among the chamber studies, the study of reactive uptake of isoprene-oxidation products into an acidic

seed is most similar to the full chemistry in real ambient environments (Liu et al., 2014), and reports similar $f_{C_5H_6O}^{IEPOX-SOA}$ values (19‰). Hence, we propose an average $f_{C_5H_6O}^{IEPOX-SOA}$ (22‰) from both studies as the typical value of fresh IEPOX-SOA.

3.9 Proposed Method for Real-Time Estimation of IEPOX-SOA

So far, PMF of AMS spectra is the only demonstrated method for quantifying total IEPOX-SOA concentrations. However, the PMF method is labor-intensive and requires significant expertise, and may fail to resolve a certain factor when present in lower mass fractions (<5%). A simpler, real-time method to estimate IEPOX-SOA would be useful in many studies, including ground-based and aircraft campaigns.

We propose an estimation method for IEPOX-SOA based on the mass concentration of its tracer ion $C_5H_6O^+$. To do this, we express the mass concentration of $C_5H_6O^+$ as

$$C_5H_6O^+_{total} = C_5H_6O^+_{IEPOX-SOA,ambient} + C_5H_6O^+_{background}. \quad (1)$$

Where, $C_5H_6O^+_{total}$ is measured total $C_5H_6O^+$ signal in AMS; $C_5H_6O_{IEPOX-SOA,ambient}$ and $C_5H_6O^+_{background}$ are the $C_5H_6O^+$ signals contributed by IEPOX-SOA in ambient OA and other background OA (non IEPOX-SOA).

Then, $C_5H_6O_{IEPOX-SOA,ambient}$ and $C_5H_6O^+_{background}$ can be calculated as:

$$C_5H_6O^+_{IEPOX-SOA,ambient} = IEPOX\text{-}SOA \times f_{C_5H_6O}^{IEPOX-OA}. \quad (2)$$

$$C_5H_6O^+_{background} = (OA_{mass} - IEPOX\text{-}SOA) \times f_{C_5H_6O}^{OA-Bkg}. \quad (3)$$

Where, $f_{C_5H_6O}^{IEPOX-OA}$ is the fractional contribution of $C_5H_6O^+$ to the total ion signal in the spectra of IEPOX-SOA from IEPOX-SOA$_{lab}$ or IEPOX-SOA$_{PMF}$ factors. $f_{C_5H_6O}^{OA-Bkg}$ is the background $f_{C_5H_6O}$ in other non-IEPOX-SOA, e.g., values from OA strongly influenced by urban and biomass-burning emissions ($f_{C_5H_6O}^{OA-Bkg-UB}$).

Then, by combining Eq. (1) − (3), we can express $C_5H_6O^+_{total}$ as:

$$C_5H_6O^+_{total} = IEPOX\text{-}SOA \times f^{IEPOX-OA}_{C_5H_6O} + (OA - IEPOX\text{-}SOA) \times f^{OA-Bkg}_{C_5H_6O}. \quad (4)$$

Finally, IEPOX-SOA can be estimated as:

$$IEPOX\text{-}SOA = \frac{C_5H_6O^+_{total} - OA \times f^{OA-Bkg}_{C_5H_6O}}{f^{IEPOX-OA}_{C_5H_6O} - f^{OA-Bkg}_{C_5H_6O}}. \quad (5)$$

In Eq. (5), $C_5H_6O^+_{total}$ and OA mass are measured directly by AMS. $f^{OA-Bkg}_{C_5H_6O}$ and $f^{IEPOX-OA}_{C_5H_6O}$ are two parameters that must be determined by other means.

As discussed above, the background value in the absence of a substantial impact of MT-SOA is ~1.7‰. In studies influenced by monoterpene emissions, the background value may be elevated by MT-SOA. $f^{OA}_{C_5H_6O}$ at the Rocky Mountain site estimated by $f^{OA}_{C_5H_6O} = (0.41 - f^{OA}_{CO_2}) \times 0.013$ (Fig. 5) can be used as $f^{OA-Bkg}_{C_5H_6O}$ for areas with strong MT-SOA contributions ($f^{OA-Bkg-MT}_{C_5H_6O}$). There is some uncertainty in this value, due to possible contributions of a small amount of IEPOX-SOA, MBO-SOA, and other OA sources at this site. An alternative estimate for $f^{OA-Bkg-MT}_{C_5H_6O}$ would be ~ 1.7‰ + 3×MT_{avg} (ppb), which is also approximately consistent with our ambient data, but may have higher uncertainty. Further characterization of the background $f_{C_5H_6O}$ in areas with MT-SOA impact is of interest for future studies. Finally, we have decided to use $f^{OA}_{C_5H_6O}$ estimated from the Rocky Mountain site as $f^{OA-Bkg-MT}_{C_5H_6O}$ in the following calculation. As discussed above, we use average $f^{IEPOX-OA}_{C_5H_6O}$ = 22‰ in Eq. (3) as a representative value of ambient IEPOX-SOA. Several scenarios based on different $f^{OA}_{C_5H_6O}$ values to use this tracer-based method are addressed in the supporting information. The justification from users on using this method is needed.

3.10 Application of the Real-Time Estimation Method of IEPOX-SOA

To test the proposed estimation method, we use SE US forest (SOAS) data as an example in Fig. 8, applying both background estimates (urban & biomass burning, and monoterpene emissions). Since there are high monoterpene concentrations (~1 ppb during the night) in SOAS, we expect the MT-influenced background to be more accurate. The IEPOX-SOA estimated by subtracting the MT-SOA background (IEPOX-SOA_{MT}) is indeed better correlated with IEPOX-SOA_{PMF} ($R=0.99$) than that ($R = 0.96$) when the urban & biomass-burning background is applied (IEPOX-$SOA_{urb\&bb}$). The intercept of regression line between IEPOX-SOA_{MT} and IEPOX-SOA_{PMF} is zero, indicating the background of IEPOX-SOA contributed by MT-SOA is clearly deducted.

The regression slope between IEPOX-SOA_{MT} and IEPOX-SOA_{PMF} is 0.95, suggesting that $C_5H_6O^+$ in SE US CTR site (SOAS) may be slightly overcorrected by minimizing $C_5H_6O^+$ from monoterpene emissions. This underestimation may be associated with higher MT-SOA contribution to $C_5H_6O^+$ in Rocky Mountain pine forest site than SE US forest site, or interference from IEPOX-SOA/MBO-SOA at the Rocky Mountain site. IEPOX-$SOA_{urb\&bb}$ is 1.26 times higher than IEPOX-SOA_{PMF}. Thus, as expected IEPOX-SOA_{MT} and IEPOX-$SOA_{urb\&bb}$ provide lower and upper limits of estimated IEPOX-SOA.

Among all the datasets introduced in this study, the SOAS-CTR dataset should be the best case scenario since $f_{C_5H_6O}^{IEPOX-OA}$= 22‰ is coincidently the same value in the spectrum of IEPOX-SOA_{PMF} in SOAS-CTR and a large fraction (17%) of IEPOX-SOA existed in SOAS-CTR as well. Given the spread of values of $f_{C_5H_6O}^{IEPOX-OA}$ (12 − 40‰) in different studies, if no additional local IEPOX-SOA spectrum is available for a given site, the estimation from this method should

be within a factor of ~2 of the actual concentration, as illustrated in Fig. S13-S14. Further information concerning the estimation method using unit mass resolution *m/z* 82 (or f_{82}) can be found in the Appendix.

4. Conclusions

To investigate if the ion $C_5H_6O^+$ (at *m/z* 82) in AMS spectra is a good tracer for IEPOX-SOA, tens of field and lab studies are combined and compared, including the SOAS 2013 campaign in the SE US. The results show that $f_{C_5H_6O}^{OA}$ is clearly elevated when IEPOX-SOA is present, and thus has potential usefulness as a tracer of this aerosol type. The average $f_{C_5H_6O}^{IEPOX-OA}$ in chamber and ambient studies is 22±7‰ (range 12‰ − 40‰). No dependence of $f_{C_5H_6O}^{IEPOX-OA}$ on oxidation level ($f_{CO_2}^{IEPOX-SOA}$) was found. Background $f_{C_5H_6O}$ in OA strongly influenced by urban or biomass-burning emissions or pure anthropogenic POAs averages 1.7±0.1‰ (range 0.02 − 3.5‰).

In ambient OA that is strongly influenced by isoprene emissions under lower NO, we observe systematically higher $f_{C_5H_6O}^{OA}$ (with an average of ~6.5±2.2‰), consistent with presence of IEPOX-SOA. Low tracer values ($f_{C_5H_6O}$<3‰) are observed in non IEPOX-derived isoprene-SOA from laboratory studies, indicating that the tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene.

Higher background values of $f_{C_5H_6O}^{OA}$ (3.1±0.6‰ in average) were found in area strongly impacted by monoterpene emissions. $f_{CO_2}^{MT-SOA}$ is 5.5±2.0‰, which are substantially lower than for IEPOX-SOA (22±7‰), and thus they leave some room to separate both contributions. A

$f_{C_5H_6O}^{OA-Bkg-MT}$ as a function of $f_{CO_2}^{OA}$ in monoterpene emissions is determined by linear regressing the $f_{C_5H_6O}^{OA}$ and $f_{CO_2}^{OA}$ at a Rocky Mountain pine forest site.

A simplified method to estimate IEPOX-SOA based on measured ambient $C_5H_6O^+$, CO_2^+ and OA in AMS is proposed. Good correlations (R>0.96) between estimated IEPOX-SOA and IEPOX-SOA$_{PMF}$ are obtained for SOAS, confirming the potential usefulness of this estimation method. Given the observed variability in IEPOX-SOA composition, the method is expected to be within a factor of ~2 of the true concentration if no additional information about the local IEPOX-SOA is available for a given study. When only unit mass resolution data is available as in ACSM data, all methods may perform less well because of increased interferences from other ions at *m/z* 82.

ACKNOWLEDGMENT

This study was partially supported by NSF AGS-1243354 and AGS-1360834, NASA NNX12AC03G, DOE (BER/ASR) DE-SC0011105, and NOAA NA13OAR4310063. B. Palm and J. Krechmer are grateful for fellowships from EPA STAR (FP-91761701-0 and FP-91770901-0) and CIRES. A. Ortega is grateful for a CU-Boulder Chancellor's and DOE SCGF (ORAU/ORISE) fellowship. A. Wisthaler and T. Mikoviny were supported by the Austrian Federal Ministry for Transport, Innovation and Technology (BMVIT) through the Austrian Space Applications Programme (ASAP) of the Austrian Research Promotion Agency (FFG), and the Visiting Scientist Program at the National Institute of Aerospace (NIA). G. Isaacman-VanWertz is grateful for an NSF Fellowship (DGE-1106400). UC Berkeley was supported by NSF AGS-1250569. We acknowledge the logistical support from the LBA Central O_ce at INPA (Instituto Nacional de Pesquisas da Amazonia). P. Artaxo acknowledges support from FAPESP grants 2013/05014-0 and 2014/05238-8 and CNPq support from grants 457843/2013-6 and 307160/2014-9. We acknowledges this work was funded by the U.S. Environmental Protection Agency (EPA) through grant number 835404. The contents of this publication are solely the responsibility of the authors and do not necessarily represent the o_cial views of the U.S. EPA. Further, the U.S. EPA does not endorse the purchase of any commercial products or services mentioned in the publication. The U.S. EPA through its O_ce of Research and Development collaborated in the research described here. It has been subjected to Agency review and approved for publication, but may not necessarily reflect ocial Agency policy. The authors would also like to thank the Electric Power Research Institute (EPRI) for their support. M. Riva and J. D. Surratt wish to thank the Camille and Henry Dreyfus Postdoctoral Fellowship Program in Environmental Chemistry for their financial support. We thank J. Crounse and P. Wennberg from Caltech for gas-phase IEPOX data in SOAS-CTR and DC3, under support from NASA NNX12AC06G. We thank Lu Xu and Nga Lee Ng from Georgia Tech for providing data from their studies. We acknowledge funding from the UK Natural Environment Research Council through the OP3 and SAMBBA projects (Grant refs. NE/D002117/1 and NE/J010073/1).

APPENDIX

In addition to the preceding high resolution $C_5H_6O^+$ data analysis, we also investigated unit mass resolution (UMR) *m/z* 82 as a tracer of IEPOX-SOA. In addition to $C_5H_6O^+$ (*m/z* 82.0419), the reduced ion $C_6H_{10}^+$ and oxygenated ion $C_4H_2O_2^+$ often contribute signal to UMR *m/z* 82. The average background level of f_{82}^{OA} (= *m/z* 82/OA) is from 4.3±0.9‰ (0.01 to 10‰) in studies strongly influenced by urban, biomass-burning and other anthropogenic POA, as shown in Fig. A1a – c. This value is higher than the high-resolution $f_{C_5H_6O}^{OA-Bkg-UB}$ (1.7‰) in the same studies. Background f_{82}^{OA} increases when OA is fresher (lower f_{44}, f_{44}^{OA}=*m/z* 44/OA) as shown in Fig A1d, and can be estimated as $f_{82}^{OA}=5.5\times10^{-3}-8.2\times10^{-3}\times f_{44}^{OA}$ in areas strongly impacted by urban and biomass-burning emissions. The uncertainty of calculated f_{82} can be as high as 30% in the lower fresh OA plumes by considering the uncertainties from quantile average and linear regression. There are also some pure chemical species that exhibit high f_{82} values, as shown in Fig. A1c. These species include docosanol, eicosanol and oleic acid. However, none of these pure chemical species alone contributes substantially to ambient aerosol.

The probability density distributions of f_{82}^{OA} in studies strongly influenced by isoprene emissions are shown in Fig. A2a. The peaks (~8.7±2.5‰) are similar in SE US, pristine, polluted Amazon forest, Borneo forest to high resolution $f_{C_5H_6O}^{OA}$ (~6.5±2.2‰), indicating $C_5H_6O^+$ is the dominant ion at UMR *m/z* 82 in these studies. Compared to the studies with strong urban and biomass-burning emissions, clear enhancements of f_{82}^{OA} in studies strongly influenced by isoprene emissions are still observed, but with less contrast than for in high resolution datasets (Fig. A2 – A3).

Figure 2Aa also shows the probability density distributions of f_{82}^{OA} at Rocky Mountain and European boreal forests (strongly influenced by monoterpene emissions). Those distributions

peak at ~5‰, which are within the range (0.01 − 10‰) of f_{82}^{OA} in aerosols strongly influenced by urban and biomass-burning emissions. In the lab studies, most of f_{82}^{MT-SOA} (average 6.7±2.2‰; range 4 − 11‰) observed in the spectra of MT-SOA are also comparable to background f_{82}^{OA} levels (average 4.3±0.9‰; range 0.01−10‰), and tend to be in the higher f_{82}^{OA} region from urban and biomass-burning emissions. A linear regression line of f_{44}^{OA} vs f_{82}^{OA} for the Rocky Mountain site (f_{82}^{OA}=7.7×10^{-3} $^{-}$*0.019*× f_{44}^{OA}) is used to estimate the background f_{82}^{OA} from areas strongly influenced by monoterpene emissions.

In summary, elevated f_{82}^{OA} in studies with high isoprene-emissions is observed. Pronounced $f_{82}^{IEPOX-SOA}$ should be a key feature of IEPOX-SOA spectra. Thus IEPOX-SOA can be estimated as Eq. (6) here:

$$\text{IEPOX-SOA} = \frac{m82_{total} - m82_{background}}{f_{82}^{IEPOX-SOA} - f_{82}^{OA-Bkg}} = \frac{m82_{total} - OA_{\,mass} \times f_{82}^{OA-Bkg}}{f_{82}^{IEPOX-SOA} - f_{82}^{OA-Bkg}}, \quad (6)$$

where $f_{82}^{IEPOX-SOA}$ is 22‰ as obtained average (Fig. A3). In Eq. (4), f_{82}^{OA-Bkg} can be calculated as a function of f_{44}^{OA} in studies strongly influenced by urban and biomass-burning emissions (f_{82}^{OA}=5.5×10^{-3} − 8.2×10^{-3} × f_{44}^{OA}) or monoterpene emissions (f_{82}^{OA}=7.7×10^{-3} $^{-}$*0.019*× f_{44}^{OA}), as discussed earlier. $m82_{total}$ and $OA_{\,mass}$ are the measured ambient *m/z* 82 and OA mass concentrations by AMS. Because f_{82} in MT-SOA and OA from urban and biomass-burning emissions cannot be separated, only one background value of f_{82}^{OA-Bkg} will be used in the UMR method.

To test this UMR empirical method, we apply Eq. (6) to SOAS-CTR dataset, see Fig. A4. The estimated IEPOX-SOA in SOAS-CTR from both background corrections (urban+biomass burning vs monoterpene) both correlates well with IEPOX-SOA$_{PMF}$ with R=0.97 and R=0.98,

respectively. The regression slopes between estimated fresh IEPOX-SOA vs IEPOX-SOA$_{PMF}$ are 1.11 and 0.94, which are within 15% of 1:1 line. The deviation of estimated IEPOX-SOA from UMR by subtracting the background of MT-SOA influences is similar to that from HR in the SOAS dataset, indicating the UMR-based IEPOX-SOA estimation may perform as well as HR in areas with high IEPOX-SOA fractions. For areas with small IEPOX-SOA fractions, more uncertainties may exist in UMR calculation, e.g., there are wider variations of f_{82}^{OA-Bkg} from urban and biomass-burning emissions with oxidation level, whereas a smaller and less variable $f_{C_5H_6O}^{OA-Bkg}$ is found in HR. Overall, *m/z* 82 in unit mass resolution data is also useful to estimate IEPOX-SOA. The different methods to estimate IEPOX-SOA may perform less well because of increased interferences from other ions at *m/z* 82, however at locations with very high fractions of IEPOX-SOA such as SOAS-CTR, the UMR-based method performs well.

References

Aiken, A. C., Salcedo, D., Cubison, M. J., Huffman, J. A., DeCarlo, P. F., Ulbrich, I. M., Docherty, K. S., Sueper, D., Kimmel, J. R., Worsnop, D. R., Trimborn, A., Northway, M., Stone, E. A., Schauer, J. J., Volkamer, R. M., Fortner, E., de Foy, B., Wang, J., Laskin, A., Shutthanandan, V., Zheng, J., Zhang, R., Gaffney, J., Marley, N. A., Paredes-Miranda, G., Arnott, W. P., Molina, L. T., Sosa, G., and Jimenez, J. L.: Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) - Part 1: Fine particle composition and organic source apportionment, Atmos Chem Phys, 9, 6633-6653, 2009.

Alfarra, M.: Insights Into Atmospheric Organic Aerosols Using An Aerosol Mass Spectrometer, Doctor, Institute of Science and Technology, University of Manchester, Manchester, 2004.

Alfarra, M. R., Coe, H., Allan, J. D., Bower, K. N., Boudries, H., Canagaratna, M. R., Jimenez, J. L., Jayne, J. T., Garforth, A. A., Li, S. M., and Worsnop, D. R.: Characterization of urban and rural organic particulate in the lower Fraser valley using two aerodyne aerosol mass spectrometers, Atmos Environ, 38, 5745-5758, DOI 10.1016/j.atmosenv.2004.01.054, 2004.

Allan, J. D., Morgan, W. T., Darbyshire, E., Flynn, M. J., Williams, P. I., Oram, D. E., Artaxo, P., Brito, J., Lee, J. D., and Coe, H.: Airborne observations of IEPOX-derived isoprene SOA in the Amazon during SAMBBA, Atmos. Chem. Phys., 14, 11393-11407, 10.5194/acp-14-11393-2014, 2014.

Anonymous_Referee: Interactive comment on "Airborne observations of IEPOX-derived isoprene SOA in the Amazon during SAMBBA" by J. D. Allan et al., Atmos. Chem. Phys. Discuss, 14,, C5277–C5279, 2014.

Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chem Rev, 103, 4605−4638, 10.1002/chin.200410285, 2003.

Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H., Worsnop, D. R., and Jimenez, J. L.: Measurements of secondary organic aerosol from oxidation of cycloalkenes, terpenes, and m-xylene using an Aerodyne aerosol mass spectrometer, Environ Sci Technol, 39, 5674-5688, Doi 10.1021/Es048061a, 2005.

Barth, M. C., Cantrell, C. A., Brune, W. H., Rutledge, S. A., Crawford, J. H., Huntrieser, H., Carey, L. D., MacGorman, D., Weisman, M., Pickering, K. E., Bruning, E., Anderson, B., Apel, E., Biggerstaff, M., Campos, T., Campuzano-Jost, P., Cohen, R., Crounse, J., Day, D. A., Diskin, G., Flocke, F., Fried, A., Garland, C., Heikes, B., Honomichl, S., Hornbrook, R., Huey, L. G., Jimenez, J. L., Lang, T., Lichtenstern, M., Mikoviny, T., Nault, B., O'Sullivan, D., Pan, L. L., Peischl, J., Pollack, I., Richter, D., Riemer, D., Ryerson, T., Schlager, H., Clair, J. S., Walega, J., Weibring, P., Weinheimer, A., Wennberg, P., Wisthaler, A., Wooldridge, P. J., and Ziegler, C.: The Deep Convective Clouds and Chemistry (DC3) Field Campaign, B. Am. Meteorol. Soc., published online first, doi:10.1175/bams-d-13-00290.1, 2014.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.

Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Marth, W. J., Baumann, K., Edgerton, E. S., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Gold, A., and Surratt, J. D.: Real-Time Continuous Characterization of Secondary Organic Aerosol Derived from Isoprene Epoxydiols in Downtown Atlanta, Georgia, Using the Aerodyne Aerosol Chemical Speciation Monitor, Environ Sci Technol, 47, 5686-5694, 10.1021/es400023n, 2013.

Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V. F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A., and Surratt, J. D.: Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee ground site, Atmos. Chem. Phys., 15, 8871-8888, 10.5194/acp-15-8871-2015, 2015.

738 Canagaratna, M. R., Jayne, J. T., Ghertner, D. A., Herndon, S., Shi, Q., Jimenez, J. L., Silva, P. J.,
739 Williams, P., Lanni, T., Drewnick, F., Demerjian, K. L., Kolb, C. E., and Worsnop, D. R.: Chase
740 studies of particulate emissions from in-use New York City vehicles, Aerosol Sci Tech, 38, 555-
741 573, Doi 10.1080/02786820490465504, 2004.
742 Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz,
743 L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and
744 Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass
745 spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15,
746 253-272, 10.5194/acp-15-253-2015, 2015.
747 Carbone, S., De Brito, J. F., Andreae, M., Pöhlker, C., Chi, X., Saturno, J., Barbosa, H., and Artaxo, P.:
748 Preliminary characterization of submicron secondary aerosol in the amazon forest – ATTO
749 station, In prep., 2015.
750 Chang, R. Y. W., Leck, C., Graus, M., Müller, M., Paatero, J., Burkhart, J. F., Stohl, A., Orr, L. H.,
751 Hayden, K., Li, S. M., Hansel, A., Tjernström, M., Leaitch, W. R., and Abbatt, J. P. D.: Aerosol
752 composition and sources in the central Arctic Ocean during ASCOS, Atmos. Chem. Phys., 11,
753 10619-10636, 10.5194/acp-11-10619-2011, 2011.
754 Chen, Q., Liu, Y., Donahue, N. M., Shilling, J. E., and Martin, S. T.: Particle-Phase Chemistry of
755 Secondary Organic Material: Modeled Compared to Measured O:C and H:C Elemental Ratios
756 Provide Constraints, Environ Sci Technol, 45, 4763-4770, 10.1021/es104398s, 2011.
757 Chen, Q., Farmer, D. K., Rizzo, L. V., Pauliquevis, T., Kuwata, M., Karl, T. G., Guenther, A., Allan, J.
758 D., Coe, H., Andreae, M. O., Pöschl, U., Jimenez, J. L., Artaxo, P., and Martin, S. T.: Fine-mode
759 organic mass concentrations and sources in the Amazonian wet season (AMAZE-08), Atmos.
760 Chem. Phys. Discuss., 14, 16151-16186, 10.5194/acpd-14-16151-2014, 2014.
761 Chhabra, P. S., Ng, N. L., Canagaratna, M. R., Corrigan, A. L., Russell, L. M., Worsnop, D. R., Flagan,
762 R. C., and Seinfeld, J. H.: Elemental composition and oxidation of chamber organic aerosol,
763 Atmos. Chem. Phys., 11, 8827-8845, 10.5194/acp-11-8827-2011, 2011.
764 Coggon, M. M., Sorooshian, A., Wang, Z., Metcalf, A. R., Frossard, A. A., Lin, J. J., Craven, J. S.,
765 Nenes, A., Jonsson, H. H., Russell, L. M., Flagan, R. C., and Seinfeld, J. H.: Ship impacts on the
766 marine atmosphere: insights into the contribution of shipping emissions to the properties of
767 marine aerosol and clouds, Atmos. Chem. Phys., 12, 8439–8458, doi:10.5194/acp-12-8439-2012,
768 2012.
769 Cole-Filipiak, N. C., O'Connor, A. E., and Elrod, M. J.: Kinetics of the Hydrolysis of Atmospherically
770 Relevant Isoprene-Derived Hydroxy Epoxides, Environ Sci Technol, 44, 6718-6723,
771 10.1021/es1019228, 2010.
772 Corrigan, A. L., Russell, L. M., Takahama, S., Äijälä, M., Ehn, M., Junninen, H., Rinne, J., Petäjä, T.,
773 Kulmala, M., Vogel, A. L., Hoffmann, T., Ebben, C. J., Geiger, F. M., Chhabra, P., Seinfeld, J.
774 H., Worsnop, D. R., Song, W., Auld, J., and Williams, J.: Biogenic and biomass burning organic
775 aerosol in a boreal forest at Hyytiälä, Finland, during HUMPPA-COPEC 2010, Atmos. Chem.
776 Phys., 13, 12233-12256, 10.5194/acp-13-12233-2013, 2013.
777 Crippa, M., El Haddad, I., Slowik, J. G., DeCarlo, P. F., Mohr, C., Heringa, M. F., Chirico, R., Marchand,
778 N., Sciare, J., Baltensperger, U., and Prévôt, A. S. H.: Identification of marine and continental
779 aerosol sources in Paris using high resolution aerosol mass spectrometry, J.Geophys. Res.-
780 Atmos., 118, 1950–1963, doi:10.1002/jgrd.50151, 2013.
781 Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel,
782 E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T.,
783 Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A., and
784 Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft
785 and laboratory studies, Atmos. Chem. Phys., 11, 12049-12064, 10.5194/acp-11-12049-2011,
786 2011.

de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Hu, W., Newburn, M. K., Brito, J., Liu, Y., Isaacman-VanWertz, G., Yee, L. D., Goldstein, A. H., Artaxo, P., Souza, R., Manzi, A., Jimenez, J. L., Alexander, M. L., and Martin, S. T., In prep., 2015.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal Chem, 78, 8281-8289, Doi 10.1021/Ac061249n, 2006.

Docherty, K. S., Aiken, A. C., Huffman, J. A., Ulbrich, I. M., DeCarlo, P. F., Sueper, D., Worsnop, D. R., Snyder, D. C., Peltier, R. E., Weber, R. J., Grover, B. D., Eatough, D. J., Williams, B. J., Goldstein, A. H., Ziemann, P. J., and Jimenez, J. L.: The 2005 Study of Organic Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition, Atmos. Chem. Phys., 11, 12387-12420, 10.5194/acp-11-12387-2011, 2011.

Dunlea, E. J., DeCarlo, P. F., Aiken, A. C., Kimmel, J. R., Peltier, R. E., Weber, R. J., Tomlinson, J., Collins, D. R., Shinozuka, Y., McNaughton, C. S., Howell, S. G., Clarke, A. D., Emmons, L. K., Apel, E. C., Pfister, G. G., van Donkelaar, A., Martin, R. V., Millet, D. B., Heald, C. L., and Jimenez, J. L.: Evolution of Asian aerosols during transpacific transport in INTEX-B, Atmos Chem Phys, 9, 7257-7287, 2009.

Dzepina, K., Arey, J., Marr, L. C., Worsnop, D. R., Salcedo, D., Zhang, Q., Onasch, T. B., Molina, L. T., Molina, M. J., and Jimenez, J. L.: Detection of particle-phase polycyclic aromatic hydrocarbons in Mexico City using an aerosol mass spectrometer, Int J Mass Spectrom, 263, 152-170, DOI 10.1016/j.ijms.2007.01.010, 2007.

Ebben, C. J., Martinez, I. S., Shrestha, M., Buchbinder, A. M., Corrigan, A. L., Guenther, A., Karl, T., Petäjä, T., Song, W. W., Zorn, S. R., Artaxo, P., Kulmala, M., Martin, S. T., Russell, L. M., Williams, J., and Geiger, F. M.: Contrasting organic aerosol particles from boreal and tropical forests during HUMPPA-COPEC-2010 and AMAZE-08 using coherent vibrational spectroscopy, Atmos. Chem. Phys., 11, 10317-10329, 10.5194/acp-11-10317-2011, 2011.

Eddingsaas, N. C., VanderVelde, D. G., and Wennberg, P. O.: Kinetics and Products of the Acid-Catalyzed Ring-Opening of Atmospherically Relevant Butyl Epoxy Alcohols, The Journal of Physical Chemistry A, 114, 8106-8113, 10.1021/jp103907c, 2010.

Fröhlich, R., Crenn, V., Setyan, A., Belis, C. A., Canonaco, F., Favez, O., Riffault, V., Slowik, J. G., Aas, W., Aijälä, M., Alastuey, A., Artiñano, B., Bonnaire, N., Bozzetti, C., Bressi, M., Carbone, C., Coz, E., Croteau, P. L., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Jayne, J. T., Lunder, C. R., Minguillón, M. C., Močnik, G., O'Dowd, C. D., Ovadnevaite, J., Petralia, E., Poulain, L., Priestman, M., Ripoll, A., Sarda-Estève, R., Wiedensohler, A., Baltensperger, U., Sciare, J., and Prévôt, A. S. H.: ACTRIS ACSM intercomparison – Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers, Atmos. Meas. Tech., 8, 2555-2576, 10.5194/amt-8-2555-2015, 2015.

Froyd, K. D., Murphy, S. M., Murphy, D. M., de Gouw, J. A., Eddingsaas, N. C., and Wennberg, P. O.: Contribution of isoprene-derived organosulfates to free tropospheric aerosol mass, P. Natl. Acad. Sci. USA, 107, 21360–21365, doi:10.1073/pnas.1012561107, 2010.

Fry, J. L., Draper, D. C., Zarzana, K. J., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Brown, S. S., Cohen, R. C., Kaser, L., Hansel, A., Cappellin, L., Karl, T., Hodzic Roux, A., Turnipseed, A., Cantrell, C., Lefer, B. L., and Grossberg, N.: Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011, Atmos. Chem. Phys., 13, 8585-8605, 10.5194/acp-13-8585-2013, 2013.

Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkler, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L.: Secondary Organic Aerosol Formation and Organic Nitrate Yield from NO3 Oxidation of Biogenic Hydrocarbons, Environ. Sci. Technol, 48, 11944–11953, doi:10.1021/es502204x, 2014.

Gaston, C. J., Riedel, T. P., Zhang, Z., Gold, A., Surratt, J. D., and Thornton, J. A.: Reactive Uptake of an Isoprene-Derived Epoxydiol to Submicron Aerosol Particles, Environ. Sci. Technol., 48, 11178–11186, doi:10.1021/es5034266, 2014.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.

Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., Hu, W. W., Toohey, D. W., Flynn, J. H., Lefer, B. L., Grossberg, N., Alvarez, S., Rappenglück, B., Taylor, J. W., Allan, J. D., Holloway, J. S., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Massoli, P., Zhang, X., Liu, J., Weber, R. J., Corrigan, A. L., Russell, L. M., Isaacman, G., Worton, D. R., Kreisberg, N. M., Goldstein, A. H., Thalman, R., Waxman, E. M., Volkamer, R., Lin, Y. H., Surratt, J. D., Kleindienst, T. E., Offenberg, J. H., Dusanter, S., Griffith, S., Stevens, P. S., Brioude, J., Angevine, W. M., and Jimenez, J. L.: Organic aerosol composition and sources in Pasadena, California, during the 2010 CalNex campaign, Journal of Geophysical Research: Atmospheres, 118, 9233-9257, 10.1002/jgrd.50530, 2013.

He, L. Y., Lin, Y., Huang, X. F., Guo, S., Xue, L., Su, Q., Hu, M., Luan, S. J., and Zhang, Y. H.: Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning, Atmos. Chem. Phys., 10, 11535-11543, 10.5194/acp-10-11535-2010, 2010.

Hersey, S. P., Craven, J. S., Schilling, K. A., Metcalf, A. R., Sorooshian, A., Chan, M. N., Flagan, R. C., and Seinfeld, J. H.: The Pasadena Aerosol Characterization Observatory (PACO): chemical and physical analysis of the Western Los Angeles basin aerosol, Atmos. Chem. Phys., 11, 7417-7443, 10.5194/acp-11-7417-2011, 2011.

Hu, D., Bian, Q., Li, T. W. Y., Lau, A. K. H., and Yu, J. Z.: Contributions of isoprene, monoterpenes, β-caryophyllene, and toluene to secondary organic aerosols in Hong Kong during the summer of 2006, Journal of Geophysical Research: Atmospheres, 113, D22206, 10.1029/2008jd010437, 2008.

Hu, W., Hu, M., Hu, W., Jimenez, J.-L., Yuan, B., Chen, W., Wang, M., Wu, Y., Wang, Z., Chen, C., Peng, J., Shao, M., and Zeng, L.: Chemical composition, sources and aging process of sub-micron aerosols in Beijing: contrast between summer and winter, submitted, 2015.

Hu, W. W., Hu, M., Yuan, B., Jimenez, J. L., Tang, Q., Peng, J. F., Hu, W., Shao, M., Wang, M., Zeng, L. M., Wu, Y. S., Gong, Z. H., Huang, X. F., and He, L. Y.: Insights on organic aerosol aging and the influence of coal combustion at a regional receptor site of central eastern China, Atmos. Chem. Phys., 13, 10095-10112, 10.5194/acp-13-10095-2013, 2013.

Huang, X. F., He, L. Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L. W., Liu, X. G., Zhang, Y. H., Jayne, J. T., Ng, N. L., and Worsnop, D. R.: Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos Chem Phys, 10, 8933-8945, DOI 10.5194/acp-10-8933-2010, 2010.

Isaacman, G., Kreisberg, N. M., Yee, L. D., Worton, D. R., Chan, A. W. H., Moss, J. A., Hering, S. V., and Goldstein, A. H.: Online derivatization for hourly measurements of gas- and particle-phase semi-volatile oxygenated organic compounds by thermal desorption aerosol gas chromatography (SV-TAG), Atmos. Meas. Tech., 7, 4417-4429, 10.5194/amt-7-4417-2014, 2014.

Jacobs, M. I., Burke, W. J., and Elrod, M. J.: Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, Atmos. Chem. Phys., 14, 8933-8946, 10.5194/acp-14-8933-2014, 2014.

Jimenez-Group: Aerosol Mass Spectrometer Web Mass Spectral Database, High-Resolution AMS Spectra, available at: http://cires.colorado.edu/jimenez-group/HRAMSsd/ (last access: 15 December 2014); unit mass resolution spectra, available at: http://cires.colorado.edu/jimenez-group/AMSsd/ (last access: 15 December 2014), University of Colorado, Boulder,

2015.
Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X. F., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, J. Geophys. Res.-Atmos., 108, 8425, doi:10.1029/2001jd001213, 2003.
Kang, E., Root, M. J., Toohey, D. W., and Brune, W. H.: Introducing the concept of Potential Aerosol Mass (PAM), Atmos. Chem. Phys., 7, 5727-5744, 10.5194/acp-7-5727-2007, 2007.
Karl, T., Guenther, A., Turnipseed, A., Tyndall, G., Artaxo, P., and Martin, S.: Rapid formation of isoprene photo-oxidation products observed in Amazonia, Atmos. Chem. Phys., 9, 7753-7767, 10.5194/acp-9-7753-2009, 2009.
Karl, T., Kaser, L., and Turnipseed, A.: Eddy covariance measurements of isoprene and 232-MBO based on NO+ time-of-flight mass spectrometry, Int J Mass Spectrom, 365–366, 15-19, 2014.
Kaser, L., Karl, T., Schnitzhofer, R., Graus, M., Herdlinger-Blatt, I. S., DiGangi, J. P., Sive, B., Turnipseed, A., Hornbrook, R. S., Zheng, W., Flocke, F. M., Guenther, A., Keutsch, F. N., Apel, E., and Hansel, A.: Comparison of different real time VOC measurement techniques in a ponderosa pine forest, Atmos. Chem. Phys., 13, 2893-2906, 10.5194/acp-13-2893-2013, 2013.
Katrib, Y., Martin, S. T., Hung, H.-M., Rudich, Y., Zhang, H., Slowik, J. G., Davidovits, P., Jayne, J. T., and Worsnop, D. R.: Products and Mechanisms of Ozone Reactions with Oleic Acid for Aerosol Particles Having Core−Shell Morphologies, The Journal of Physical Chemistry A, 108, 6686-6695, 10.1021/jp049759d, 2004.
Krechmer, J. E., Coggon, M. M., Massoli, P., Nguyen, T. B., Crounse, J. D., Hu, W., Day, D. A., Tyndall, G. S., Henze, D. K., Rivera-Rios, J. C., Nowak, J. B., Kimmel, J. R., Mauldin, R. L., Stark, H., Jayne, J. T., Sipilä, M., Junninen, H., St. Clair, J. M., Zhang, X., Feiner, P. A., Zhang, L., Miller, D. O., Brune, W. H., Keutsch, F. N., Wennberg, P. O., Seinfeld, J. H., Worsnop, D. R., Jimenez, J. L., and Canagaratna, M. R.: Formation of Low Volatility Organic Compounds and Secondary Organic Aerosol from Isoprene Hydroxyhydroperoxide Low-NO Oxidation, Environ Sci Technol, 10.1021/acs.est.5b02031, 2015.
Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, Environ Sci Technol, 40, 1869-1877, Doi 10.1021/Es0524301, 2006.
Kuwata, M., Liu, Y., McKinney, K., and Martin, S. T.: Physical state and acidity of inorganic sulfate can regulate the production of secondary organic material from isoprene photooxidation products, Phys Chem Chem Phys, 17, 5670-5678, 10.1039/c4cp04942j, 2015.
Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prevot, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, Atmos Chem Phys, 7, 1503-1522, 2007.
Levin, E. J. T., Prenni, A. J., Palm, B. B., Day, D. A., Campuzano-Jost, P., Winkler, P. M., Kreidenweis, S. M., DeMott, P. J., Jimenez, J. L., and Smith, J. N.: Size-resolved aerosol composition and its link to hygroscopicity at a forested site in Colorado, Atmos. Chem. Phys., 14, 2657-2667, 10.5194/acp-14-2657-2014, 2014.
Lewandowski, M., Piletic, I. R., Kleindienst, T. E., Offenberg, J. H., Beaver, M. R., Jaoui, M., Docherty, K. S., and Edney, E. O.: Secondary organic aerosol characterisation at field sites across the United States during the spring–summer period, International Journal of Environmental Analytical Chemistry, 93, 1084-1103, 10.1080/03067319.2013.803545, 2013.
Li, R., Palm, B. B., Borbon, A., Graus, M., Warneke, C., Ortega, A. M., Day, D. A., Brune, W. H., Jimenez, J. L., and de Gouw, J. A.: Laboratory Studies on Secondary Organic Aerosol Formation from Crude Oil Vapors, Environ Sci Technol, 47, 12566-12574, 10.1021/es402265y, 2013.
Li, Y. J., Yeung, J. W. T., Leung, T. P. I., Lau, A. P. S., and Chan, C. K.: Characterization of Organic Particles from Incense Burning Using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer, Aerosol Sci Tech, 46, 654-665, 10.1080/02786826.2011.653017, 2011.

938 Liao, J., Froyd, K. D., Murphy, D. M., Keutsch, F. N., Yu, G., Wennberg, P. O., Clair, J. S., Crounse, J.
939 D., Wisthaler, A., Mikoviny, T., Ryerson, T. B., Pollack, I. B., Peischl, J. L., Collett, J., Jimenez,
940 J. L., Campuzano-Jost, P., Day, D. A., Hu, W. W., Anderson, B. E., Ziemba, L. D., Blake, D. R.,
941 Meinardi, S., and Diskin.G.: Airborne organosulfates measurements over the continental US, J
942 Geophys Res-Atmos, 120, 2990-3005, 2014.
943 Liggio, J., Li, S. M., and Mclaren, R.: Reactive uptake of glyoxal by particulate matter, J Geophys Res-
944 Atmos, 110, D10304, doi:10.1029/2004jd005113, 2005.
945 Lin, Y.-H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L.,
946 Knipping, E. M., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene
947 Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed Reactive
948 Uptake Studies with Authentic Compounds, Environ Sci Technol, 46, 250-258,
949 10.1021/es202554c, 2012.
950 Lin, Y.-H., Budisulistiorini, S. H., Chu, K., Siejack, R. A., Zhang, H., Riva, M., Zhang, Z., Gold, A.,
951 Kautzman, K. E., and Surratt, J. D.: Light-Absorbing Oligomer Formation in Secondary Organic
952 Aerosol from Reactive Uptake of Isoprene Epoxydiols, Environ Sci Technol, 48, 12012-12021,
953 10.1021/es503142b, 2014.
954 Liu, Y., Kuwata, M., Strick, B. F., Thomson, R. J., Geiger, F. M., McKinney, K., and Martin, S. T.:
955 Uptake of Epoxydiol Isomers Accounts for Half of the Particle-Phase Material Produced from
956 Isoprene Photooxidation via the HO2 pathway, Environ Sci Technol, 49, 250-258,
957 10.1021/es5034298, 2014.
958 Loza, C. L., Chhabra, P. S., Yee, L. D., Craven, J. S., Flagan, R. C., and Seinfeld, J. H.: Chemical aging
959 of m-xylene secondary organic aerosol: laboratory chamber study, Atmos. Chem. Phys., 12, 151-
960 167, 10.5194/acp-12-151-2012, 2012.
961 Mael, L. E., Jacobs, M. I., and Elrod, M. J.: Organosulfate and Nitrate Formation and Reactivity from
962 Epoxides Derived from 2-Methyl-3-buten-2-ol, The Journal of Physical Chemistry A,
963 10.1021/jp510033s, 2014.
964 Mao, J., Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., Keller, C. A., Hudman,
965 R. C., Barkley, M. P., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United
966 States: Sensitivity to isoprene chemistry, Journal of Geophysical Research: Atmospheres, 118,
967 2013JD020231, 10.1002/jgrd.50817, 2013.
968 Minguillón, M. C., Perron, N., Querol, X., Szidat, S., Fahrni, S. M., Alastuey, A., Jimenez, J. L., Mohr,
969 C., Ortega, A. M., Day, D. A., Lanz, V. A., Wacker, L., Reche, C., Cusack, M., Amato, F., Kiss,
970 G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco, R., Peñuelas, J., Metzger,
971 A., Schallhart, S., Müller, M., Hansel, A., Burkhart, J. F., Baltensperger, U., and Prévôt, A. S. H.:
972 Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter
973 during the DAURE campaign in Northeast Spain, Atmos. Chem. Phys., 11, 12067-12084,
974 10.5194/acp-11-12067-2011, 2011.
975 Mohr, C., Huffman, J. A., Cubison, M. J., Aiken, A. C., Docherty, K. S., Kimmel, J. R., Ulbricht, I. M.,
976 Hannigan, M., and Jimenez, J. L.: Characterization of Primary Organic Aerosol Emissions from
977 Meat Cooking, Trash Burning, and Motor Vehicles with High-Resolution Aerosol Mass
978 Spectrometry and Comparison with Ambient and Chamber Observations, Environ Sci Technol,
979 43, 2443-2449, Doi 10.1021/Es8011518, 2009.
980 Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A.,
981 Querol, X., Seco, R., Peñuelas, J., Jiménez, J. L., Crippa, M., Zimmermann, R., Baltensperger,
982 U., and Prévôt, A. S. H.: Identification and quantification of organic aerosol from cooking and
983 other sources in Barcelona using aerosol mass spectrometer data, Atmos. Chem. Phys., 12, 1649-
984 1665, 10.5194/acp-12-1649-2012, 2012.
985 Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C.,
986 Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and Seinfeld, J.

H.: Effect of NOx level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, Atmos Chem Phys, 7, 5159-5174, 2007.
Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO3), Atmos. Chem. Phys., 8, 4117-4140, 10.5194/acp-8-4117-2008, 2008.
Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, Atmos. Chem. Phys., 11, 6465-6474, 10.5194/acp-11-6465-2011, 2011a.
Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M., and Worsnop, D. R.: Real-Time Methods for Estimating Organic Component Mass Concentrations from Aerosol Mass Spectrometer Data, Environ Sci Technol, 45, 910-916, 10.1021/es102951k, 2011b.
Nguyen, T. B., Coggon, M. M., Bates, K. H., Zhang, X., Schwantes, R. H., Schilling, K. A., Loza, C. L., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds, Atmos. Chem. Phys., 14, 3497-3510, 10.5194/acp-14-3497-2014, 2014.
Nguyen, T. B., Crounse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, Proceedings of the National Academy of Sciences, 112, E392-E401, 10.1073/pnas.1418702112, 2015.
Ortega, A. M., Day, D. A., Cubison, M. J., Brune, W. H., Bon, D., de Gouw, J. A., and Jimenez, J. L.: Secondary organic aerosol formation and primary organic aerosol oxidation from biomass-burning smoke in a flow reactor during FLAME-3, Atmos. Chem. Phys., 13, 11551-11571, 10.5194/acp-13-11551-2013, 2013.
Ortega, J., Turnipseed, A., Guenther, A. B., Karl, T. G., Day, D. A., Gochis, D., Huffman, J. A., Prenni, A. J., Levin, E. J. T., Kreidenweis, S. M., DeMott, P. J., Tobo, Y., Patton, E. G., Hodzic, A., Cui, Y. Y., Harley, P. C., Hornbrook, R. S., Apel, E. C., Monson, R. K., Eller, A. S. D., Greenberg, J. P., Barth, M. C., Campuzano-Jost, P., Palm, B. B., Jimenez, J. L., Aiken, A. C., Dubey, M. K., Geron, C., Offenberg, J., Ryan, M. G., Fornwalt, P. J., Pryor, S. C., Keutsch, F. N., DiGangi, J. P., Chan, A. W. H., Goldstein, A. H., Wolfe, G. M., Kim, S., Kaser, L., Schnitzhofer, R., Hansel, A., Cantrell, C. A., Mauldin, R. L., and Smith, J. N.: Overview of the Manitou Experimental Forest Observatory: site description and selected science results from 2008 to 2013, Atmos. Chem. Phys., 14, 6345-6367, 10.5194/acp-14-6345-2014, 2014.
Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, Atmos. Chem. Phys., 9, 1479-1501, 10.5194/acp-9-1479-2009, 2009a.
Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., St. Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, Science, 325, 730-733, 10.1126/science.1172910, 2009b.
Phinney, L., Leaitch, W. R., Lohmann, U., Boudries, H., Worsnop, D. R., Jayne, J. T., Toom-Sauntry, D., Wadleigh, M., Sharma, S., and Shantz, N.: Characterization of the aerosol over the sub-arctic north east Pacific Ocean, Deep-Sea Res Pt Ii, 53, 2410-2433, DOI 10.1016/j.dsr2.2006.05.044, 2006.
Pye, H. O. T., Pinder, R. W., Piletic, I. R., Xie, Y., Capps, S. L., Lin, Y.-H., Surratt, J. D., Zhang, Z., Gold, A., Luecken, D. J., Hutzell, W. T., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Lewandowski, M., and Edney, E. O.: Epoxide Pathways Improve Model Predictions of Isoprene Markers and Reveal Key Role of Acidity in Aerosol Formation, Environ Sci Technol, 47, 11056-11064, 10.1021/es402106h, 2013.
Robinson, N. H., Hamilton, J. F., Allan, J. D., Langford, B., Oram, D. E., Chen, Q., Docherty, K., Farmer, D. K., Jimenez, J. L., Ward, M. W., Hewitt, C. N., Barley, M. H., Jenkin, M. E., Rickard, A. R., Martin, S. T., McFiggans, G., and Coe, H.: Evidence for a significant proportion of Secondary

1037 Organic Aerosol from isoprene above a maritime tropical forest, Atmos. Chem. Phys., 11, 1039-
1038 1050, 10.5194/acp-11-1039-2011, 2011.
1039 Saarikoski, S., Carbone, S., Decesari, S., Giulianelli, L., Angelini, F., Canagaratna, M., Ng, N. L.,
1040 Trimborn, A., Facchini, M. C., Fuzzi, S., Hillamo, R., and Worsnop, D.: Chemical
1041 characterization of springtime submicrometer aerosol in Po Valley, Italy, Atmos. Chem. Phys.,
1042 12, 8401–8421, doi:10.5194/acp-12-8401-2012, 2012.
1043 Sage, A. M., Weitkamp, E. A., Robinson, A. L., and Donahue, N. M.: Evolving mass spectra of the
1044 oxidized component of organic aerosol: results from aerosol mass spectrometer analyses of aged
1045 diesel emissions, Atmos. Chem. Phys., 8, 1139-1152, 10.5194/acp-8-1139-2008, 2008.
1046 Schneider, J., Weimer, S., Drewnick, F., Borrmann, S., Helas, G., Gwaze, P., Schmid, O., Andreae, M.
1047 O., and Kirchner, U.: Mass spectrometric analysis and aerodynamic properties of various types of
1048 combustion-related aerosol particles, Int J Mass Spectrom, 258, 37-49, DOI
1049 10.1016/j.ijms.2006.07.008, 2006.
1050 Schneider, J., Freutel, F., Zorn, S. R., Chen, Q., Farmer, D. K., Jimenez, J. L., Martin, S. T.,
1051 Artaxo, P., Wiedensohler, A., and Borrmann, S.: Mass-spectrometric identification of pri15
1052 mary biological particle markers and application to pristine submicron aerosol measurements
1053 in Amazonia, Atmos. Chem. Phys., 11, 11415–11429, doi:10.5194/acp-11-11415-
1054 2011, 2011.
1055 Setyan, A., Zhang, Q., Merkel, M., Knighton, W. B., Sun, Y., Song, C., Shilling, J. E., Onasch, T. B.,
1056 Herndon, S. C., Worsnop, D. R., Fast, J. D., Zaveri, R. A., Berg, L. K., Wiedensohler, A.,
1057 Flowers, B. A., Dubey, M. K., and Subramanian, R.: Characterization of submicron particles
1058 influenced by mixed biogenic and anthropogenic emissions using high-resolution aerosol mass
1059 spectrometry: results from CARES, Atmos. Chem. Phys., 12, 8131-8156, 10.5194/acp-12-8131-
1060 2012, 2012.
1061 Slowik, J. G., Brook, J., Chang, R. Y. W., Evans, G. J., Hayden, K., Jeong, C. H., Li, S. M., Liggio, J.,
1062 Liu, P. S. K., McGuire, M., Mihele, C., Sjostedt, S., Vlasenko, A., and Abbatt, J. P. D.:
1063 Photochemical processing of organic aerosol at nearby continental sites: contrast between urban
1064 plumes and regional aerosol, Atmos. Chem. Phys., 11, 2991-3006, 10.5194/acp-11-2991-2011,
1065 2011.
1066 Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L.,
1067 Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for
1068 organosulfates in secondary organic aerosol, Environ Sci Technol, 41, 517-527, Doi
1069 10.1021/Es062081q, 2007.
1070 Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P.,
1071 Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary
1072 organic aerosol formation from isoprene, Proceedings of the National Academy of Sciences, 107,
1073 6640-6645, 10.1073/pnas.0911114107, 2010.
1074 Takegawa, N., Miyakawa, T., Kawamura, K., and Kondo, Y.: Contribution of selected dicarboxylic and
1075 omega-oxocarboxylic acids in ambient aerosol to the m/z 44 signal of an aerodyne aerosol mass
1076 spectrometer, Aerosol Sci Tech, 41, 418-437, Doi 10.1080/02786820701203215, 2007.
1077 Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of
1078 organic components from Positive Matrix Factorization of aerosol mass spectrometric data,
1079 Atmos Chem Phys, 9, 2891-2918, 2009.
1080 Wang, W., Kourtchev, I., Graham, B., Cafmeyer, J., Maenhaut, W., and Claeys, M.: Characterization of
1081 oxygenated derivatives of isoprene related to 2-methyltetrols in Amazonian aerosols using
1082 trimethylsilylation and gas chromatography/ion trap mass spectrometry, Rapid Commun Mass
1083 Sp, 19, 1343-1351, 10.1002/rcm.1940, 2005.
1084 Weimer, S., Alfarra, M. R., Schreiber, D., Mohr, M., Prévôt, A. S. H., and Baltensperger, U.: Organic
1085 aerosol mass spectral signatures from wood-burning emissions: Influence of burning conditions
1086 and wood type, J. Geophys. Res., 113, D10304, doi:10.1029/2007jd009309, 2008.

Worton, D. R., Surratt, J. D., LaFranchi, B. W., Chan, A. W. H., Zhao, Y., Weber, R. J., Park, J.-H., Gilman, J. B., de Gouw, J., Park, C., Schade, G., Beaver, M., Clair, J. M. S., Crounse, J., Wennberg, P., Wolfe, G. M., Harrold, S., Thornton, J. A., Farmer, D. K., Docherty, K. S., Cubison, M. J., Jimenez, J.-L., Frossard, A. A., Russell, L. M., Kristensen, K., Glasius, M., Mao, J., Ren, X., Brune, W., Browne, E. C., Pusede, S. E., Cohen, R. C., Seinfeld, J. H., and Goldstein, A. H.: Observational Insights into Aerosol Formation from Isoprene, Environ Sci Technol, 47, 11403-11413, 10.1021/es4011064, 2013.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proceedings of the National Academy of Sciences, 112, 37-42, 10.1073/pnas.1417609112, 2014.

Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, Atmos. Chem. Phys., 15, 7307-7336, 10.5194/acp-15-7307-2015, 2015.

Zhang, H., Worton, D. R., Lewandowski, M., Ortega, J., Rubitschun, C. L., Park, J.-H., Kristensen, K., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Gilman, J., Kuster, W. C., de Gouw, J., Park, C., Schade, G. W., Frossard, A. A., Russell, L., Kaser, L., Jud, W., Hansel, A., Cappellin, L., Karl, T., Glasius, M., Guenther, A., Goldstein, A. H., Seinfeld, J. H., Gold, A., Kamens, R. M., and Surratt, J. D.: Organosulfates as Tracers for Secondary Organic Aerosol (SOA) Formation from 2-Methyl-3-Buten-2-ol (MBO) in the Atmosphere, Environ Sci Technol, 46, 9437-9446, 10.1021/es301648z, 2012.

Zhang, H., Zhang, Z., Cui, T., Lin, Y.-H., Bhathela, N. A., Ortega, J., Worton, D. R., Goldstein, A. H., Guenther, A., Jimenez, J. L., Gold, A., and Surratt, J. D.: Secondary Organic Aerosol Formation via 2-Methyl-3-buten-2-ol Photooxidation: Evidence of Acid-Catalyzed Reactive Uptake of Epoxides, Environmental Science & Technology Letters, 1, 242-247, 10.1021/ez500055f, 2014.

Table 1. Datasets used in this study[a]. Ranges or average plus standard deviation of $f_{C_5H_6O}$ (high resolution) and f_{82} (unit mass resolution) in different studies are also included.

Name of datasets	Time Period	Site locations and descriptions	Campaign name	Ranges or average±std.dev. $f_{C_5H_6O}$ (‰)	Ranges or average±std.dev. f_{82} (‰)	References
Studies strongly-influenced by isoprene emissions under lower NO						
SE US forest-CTR site	Jun-Jul, 2013	Centreville, AL,	SOAS	6.2±2.4	7.6±2.2	(1)
Pristine Amazon forest 2008, Brazil	Feb-Mar, 2008	Pristine rain forest site, TT34,	AMAZE-08	5.0±2.3	7.9±1.7	(2)
Amazon forest downwind Manaus, Brazil	Feb-Mar, 2014	T3 site, near Manacapuru	GoAmazon2014/5	6.9±1.6	7.1±1.0	(3)
Pristine Amazon forest 2014, Brazil	Aug-Dec,2014	T0 site, ~150 km northeast of Manaus	GoAmazon2014/5	N/A	5.6±1.7	(4)
SE US	Aug-Sep, 2013	Aircraft measurement:	SEAC4RS	4.3±1.6	N/A	(5)
Borneo forest, Malaysia	Jun-Jul, 2008	Rain forest GAW station, Sabah, Malaysia	OP3	10±0.3	12.4±0.4	(6)
Atlanta, US	Aug-Sep, 2011	Urban JST site, Atlanta, Georgia, US	N/A	N/A	3.7±1.9	(7)
Atlanta (JST), US	May, 2012	Urban JST site, Atlanta, Georgia, US	N/A	3.3±0.9	N/A	(8)
Atlanta (GT), US	Aug, 2012	Urban Georgia Tech site, Georgia, US	N/A	5.4±1.9	N/A	(8)
Yorkville, US	July, 2012	Rural sites, 80km northwest of JST site, Georgia, US	N/A	7.7±2.2	N/A	(8)
Harrow, Canada	Jun-Jul, 2007	Harrow site, rural sites surrounded by farmland, Canada	BAQSMET	N/A	N/A	(9)
Bear Creek, Canada	Jun-Jul, 2007	Bear Creek site, wetlands area surrounded by farmland, Canada	BAQSMET	N/A	N/A	(9)
Studies strongly-influenced by monoterpene emissions						

Rocky mountain pine forest, CO, USA	Jul-Aug, 2011	Manitou Experimental Forest Observatory, CO,	BEACHON-RoMBAS	3.7±0.5	5.1±0.5	(10)
European Boreal forest, Finland	2008-2009	Hyytiala site in Pine forest, Finland	EUCAARI campaign	2.5±0.1 [b]	4.8±0.1 [b]	(11)
Studies mixed-influenced by isoprene and monoterpene emissions						
North American temperate, US	Aug-Sep, 2007	Blodgett Forest Ameriflux Site, CA, US	BEARPEX	4.0±<0.1 [b]	4.0±<0.1 [b]	(11)
Studies strongly-influenced by urban emissions						
Los Angeles area , CA, USA	May-Jun, 2010	Pasadena, US	CalNex	1.6±0.2	3.6±0.5	(12)
Beijing, China	Nov-Dec, 2010	Peking University, in NW of Beijing city, China	N/A	1.5±0.3	4.6±0.7	(13)
Changdao island, Downwind of China	Mar-Apr, 2011	Changdao island, China	CAPTAIN	1.6±0.2	3.8±0.5	(14)
Barcelona area, Spain	Feb-Mar, 2009	Montseny, Spain	DAURE	1.6±0.2	4.8±0.9	(15)
Studies of biomass-burning smokes						
BB Chamber study	Sep–Oct, 2009	Missoula, MO, USA	FLAME-3	1.9±0.6	5.9±1.4	(16)
Biomass burning plumes	Aug-Sep, 2013	All over US, aircraft measurement	SEAC4RS	1.8±0.5	N/A	(6)
Biomass burning plumes	May-Jun, 2011	All over US, aircraft measurement	DC-3	1.8±0.4	N/A	(17)
Continental plumes						
NW US	Aug-Sep, 2013	Aircraft measurement	SEAC4RS	1.7±0.3	N/A	(16)
Western US	May-Jun, 2011	Aircraft measurement	DC-3	1.9±0.6	N/A	(17)
OA from specific sources						
IEPOX-SOA from ambient PMF factors and chamber studies.				22±7	22±7	(18)
Isoprene derived non-IEPOX SOA (reaction with OH under conditions of high NO or low NO without seed not favorable for the reactive-uptake of IEPOX, reaction with NO3 without seed)				<3	<3	(19)

Monoterpene-derived SOA	5.5±2.0	6.7±2.0	(20)
Other SOA (not from isoprene and mononterpene)	2.2±0.9	6.1±2.1	(21)
Cooking	1.5±0.8	8.2±1.1	(22)
Coal combustion	1.4-2.0	N/A	(23)
Vehicle emission	1.1±0.6	5.1±1.1	(24)
Biomass burning	2.3±0.7	4.3±1.5	(25)
Pure chemical species	0.7±1.0	4.0±5.5	(26)

a- HR-ToF-AMS was used for all the campaigns except the Atlanta, US and Pristine Amazon forest 2014, Brazil using ACSM.

b- Standard error

(1) This study; (2) (Chen et al., 2014); (3) (de Sá et al., 2015); (4) (Carbone et al., 2015); (5)(Liao et al., 2014) ; (6) (Robinson et al., 2011); (7) (Budisulistiorini et al., 2013); (8) (Xu et al., 2014;Xu et al., 2015) (~~8~~9) (Slowik et al., 2011); (~~9~~10) (Ortega et al., 2014); (1~~0~~1) (Robinson et al., 2011); (~~11~~12) (Hayes et al., 2013); (~~12~~13) (Hu et al., 2015); (~~13~~13) (Hu et al., 2013); (~~14~~15) (Minguillón et al., 2011); (~~15~~16) (Ortega et al., 2013); (~~16~~17) (Barth et al., 2014); (~~17~~18) (Chhabra et al., 2011;Robinson et al., 2011;Budisulistiorini et al., 2013;Chen et al., 2014;Liu et al., 2014;Kuwata et al., 2015); (~~18~~19) (Kroll et al., 2006;Ng et al., 2008;Krechmer et al., 2015); (~~19~~20) (Bahreini et al., 2005;Chen et al., 2014;Boyd et al., 2015); (~~20~~21) (Bahreini et al., 2005;Liggio et al., 2005;Chhabra et al., 2011;Loza et al., 2012); (~~21~~22) (Lanz et al., 2007;Mohr et al., 2009;He et al., 2010;Huang et al., 2010;Mohr et al., 2012;Crippa et al., 2013;Hu et al., 2015); (~~22~~23) (Hu et al., 2013;Hu et al., 2015); (~~23~~24) (Canagaratna et al., 2004;Lanz et al., 2007;Sage et al., 2008;Aiken et al., 2009;Mohr et al., 2009;Chang et al., 2011;Docherty et al., 2011;Hersey et al., 2011;Ng et al., 2011b;Coggon et al., 2012;Mohr et al., 2012;Saarikoski et al., 2012;Setyan et al., 2012;Crippa et al., 2013); (~~24~~25) (Schneider et al., 2006;Weimer et al., 2008;Aiken et al., 2009;He et al., 2010;Ng et al., 2011b;Schneider et al., 2011;Mohr et al., 2012;Saarikoski et al., 2012;Crippa et al., 2013;Hu et al., 2013;Hu et al., 2015); (~~25~~26) (Alfarra, 2004;Katrib et al., 2004;Phinney et al., 2006;Dzepina et al., 2007;Takegawa et al., 2007;Aiken et al., 2009;Li et al., 2011;Schneider et al., 2011)

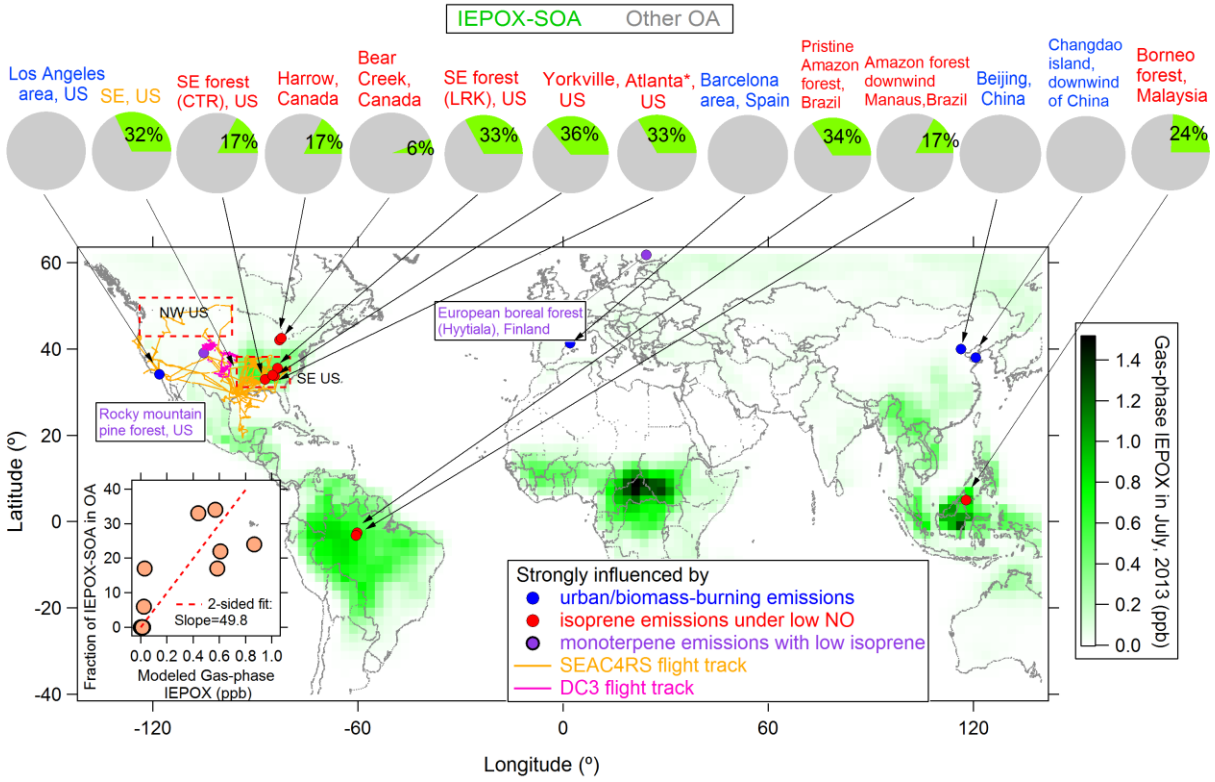


Figure 1. Locations of field campaigns used in this study. The IEPOX-SOA fractions of OA in different studies are shown in the pie charts on the top of graph. Site names are color-coded with site types. Detailed information these studies can be found in Table 1. Note that the Atlanta pie chart was averaged by three urban datasets in Budisulistiorini et al. (2013) and Xu et al. (2015). The green background is color coded with modeled global gas-phase IEPOX concentrations for July, 2013 from the GEOS-Chem model. The insert shows as scatter plot of observed average fraction of IEPOX-SOA in OA vs. GEOS-Chem modeled gas-phase IEPOX in various field campaigns.

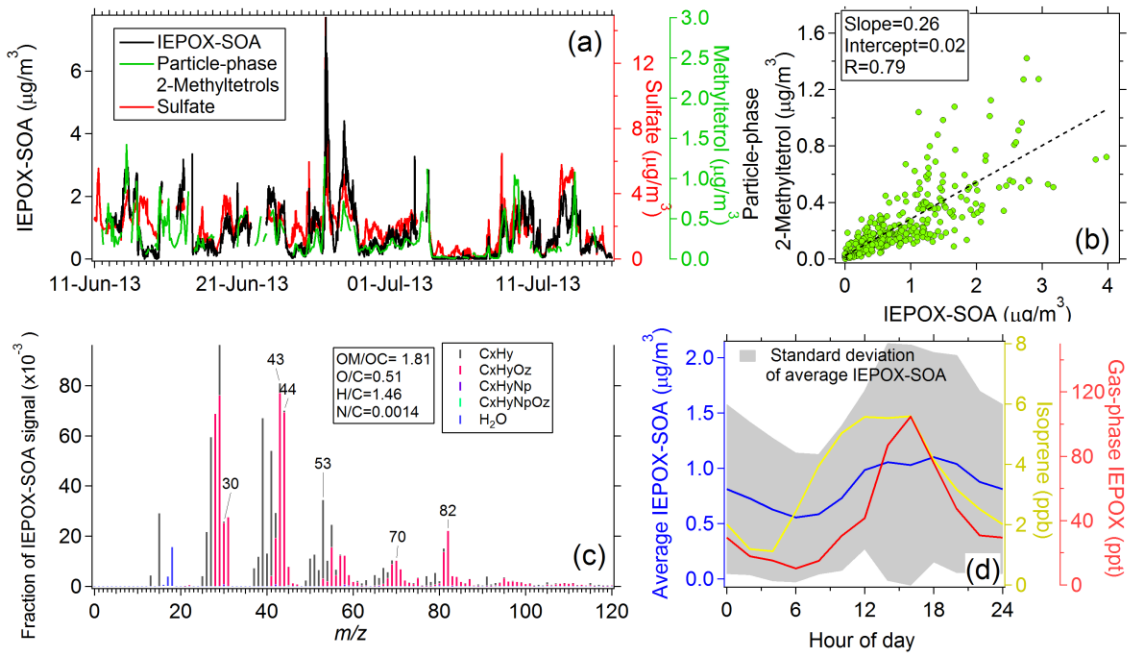


Figure 2. Results from the SOAS campaign in a SE US forested site. (a) Time series of IEPOX-SOA$_{PMF}$, sulfate and particle-phase 2-methylterols (a key IEPOX uptake product) from on-line GC/MS; (b) Scatter plot between particle-phase 2-methylterols and IEPOX-SOA. (c) Mass spectrum of IEPOX-SOA; (d) Diurnal cycle of IEPOX-SOA, isoprene and gas-phase IEPOX (the latter measured by CF_3O^- CIMS).

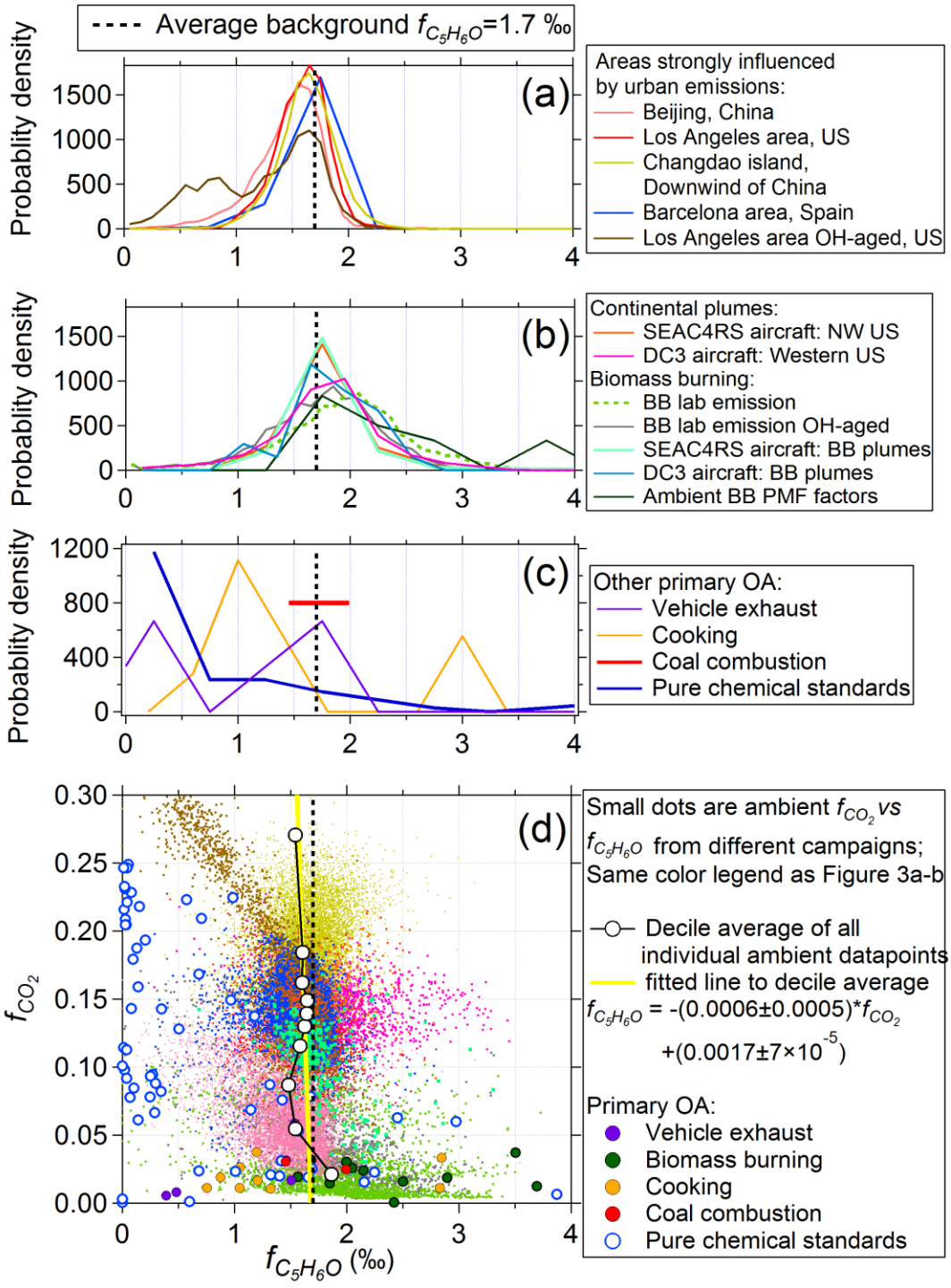


Figure 3. Probability density distributions of $f_{C_5H_6O}$ in studies (a) strongly influenced by urban emissions; (b) continental air masses sampled from aircraft and biomass-burning emissions; (c) other anthropogenic primary OA sources and pure chemical standards. The dashed line (1.7‰) is the average $f_{C_5H_6O}$ in studies shown in panels (a) − (b). (d) Scatter plot of f_{CO_2} (f_{CO_2}=CO_2^+/OA)

vs. $f_{C_5H_6O}$ for all studies shown in panels (a) − (c), using the same color scheme. Quantile averages of $f_{C_5H_6O}$ across all studies sorted by f_{CO_2} are also shown, as is a linear regression line to the quantile points.

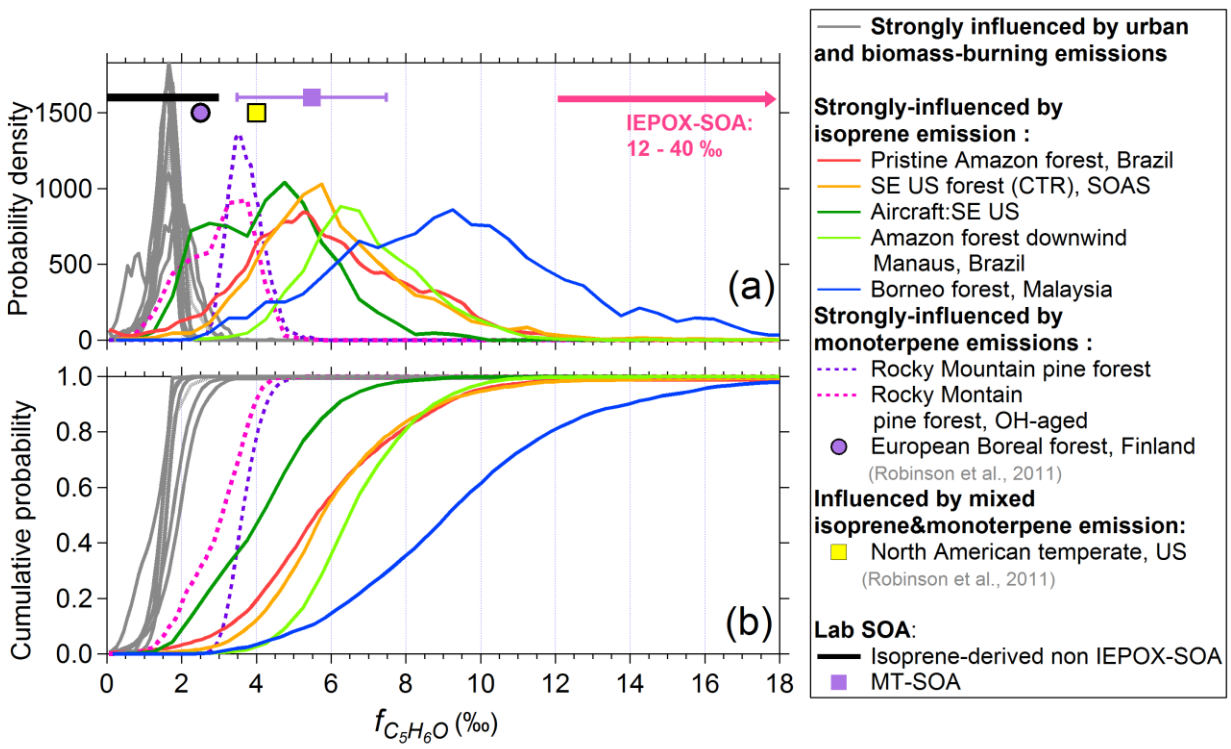


Figure 4. (a) Probability density and (b) cumulative probability distributions of $f_{C_5H_6O}^{OA}$ in studies strongly influenced by isoprene and/or monoterpene emissions. The ranges of $f_{C_5H_6O}$ from other non IEPOX-derived isoprene-SOA and MT-SOA are also shown. The background grey lines are from studies strongly influenced by urban and biomass-burning emissions and are the same data from Fig. 3a − b. The arrow in Fig. 4a indicates the range of $f_{C_5H_6O}^{IEPOX-SOA}$ between 12‰ (start of the arrow) to 40‰ which is beyond the range of x-axis scale.

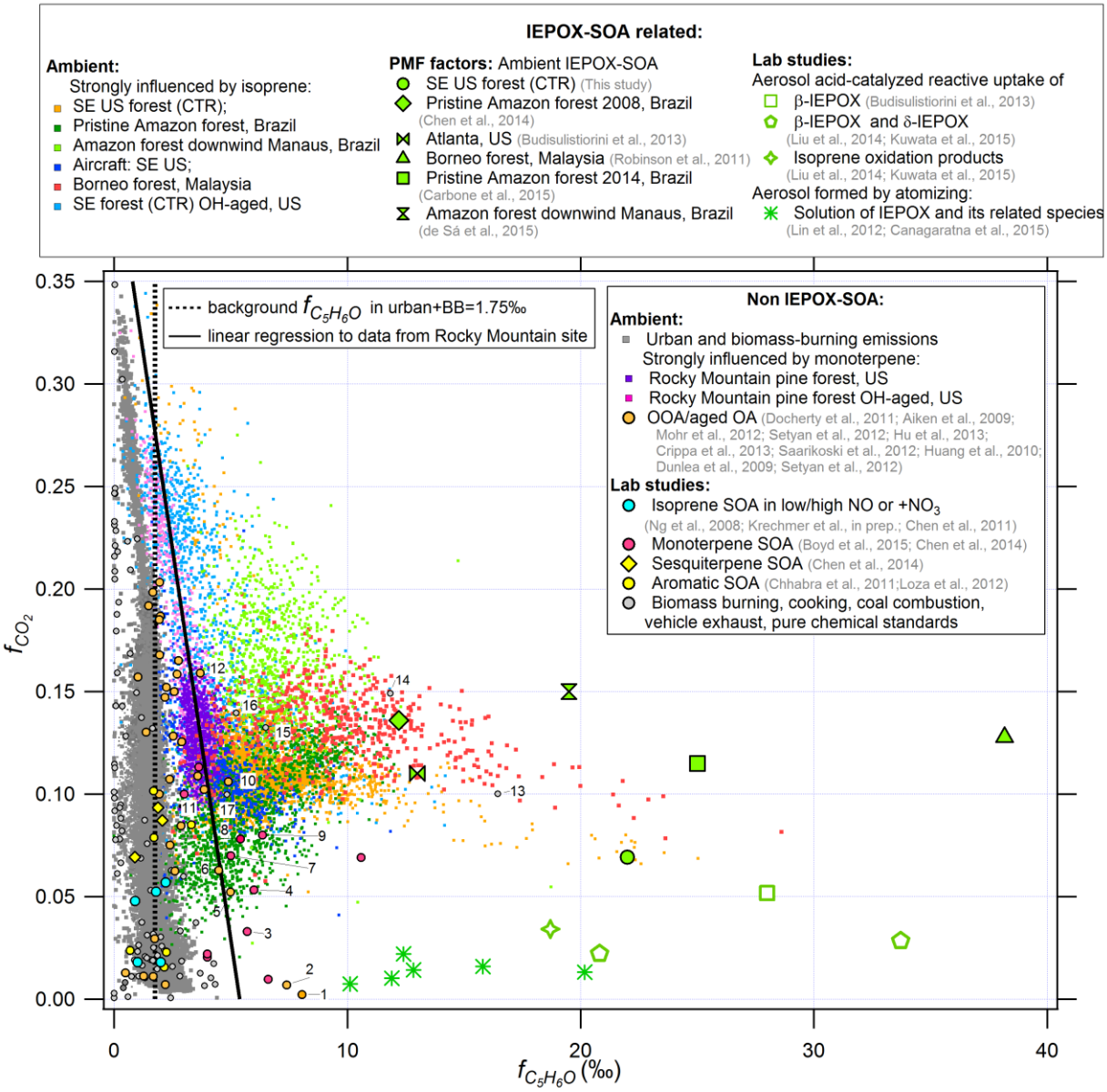


Figure 5. Scatter plot of f_{CO_2} and $f_{C_5H_6O}$ in studies strongly by isoprene and monoterpene emissions, as well as other OA sources. The grey dots represent background levels from studies strongly influenced by urban and biomass-burning emissions in Fig. 3d. f_{CO_2} and $f_{C_5H_6O}$ values from multiple sources of OA are also shown, together with IEPOX-SOA from different ambient PMF factors and chamber studies. A linear regression line of f_{CO_2} and $f_{C_5H_6O}$ calculated from Rocky Mountain pine forest is also displayed. We labeled some symbols with high $f_{C_5H_6O}$ in numbers. From number 1 − 12 are all OAs with biogenic influences. Number 13 − 17 are some

pure chemical standards (acids) as discussed above. For detailed information on the meaning of the numbered symbols see supporting information Table S2.

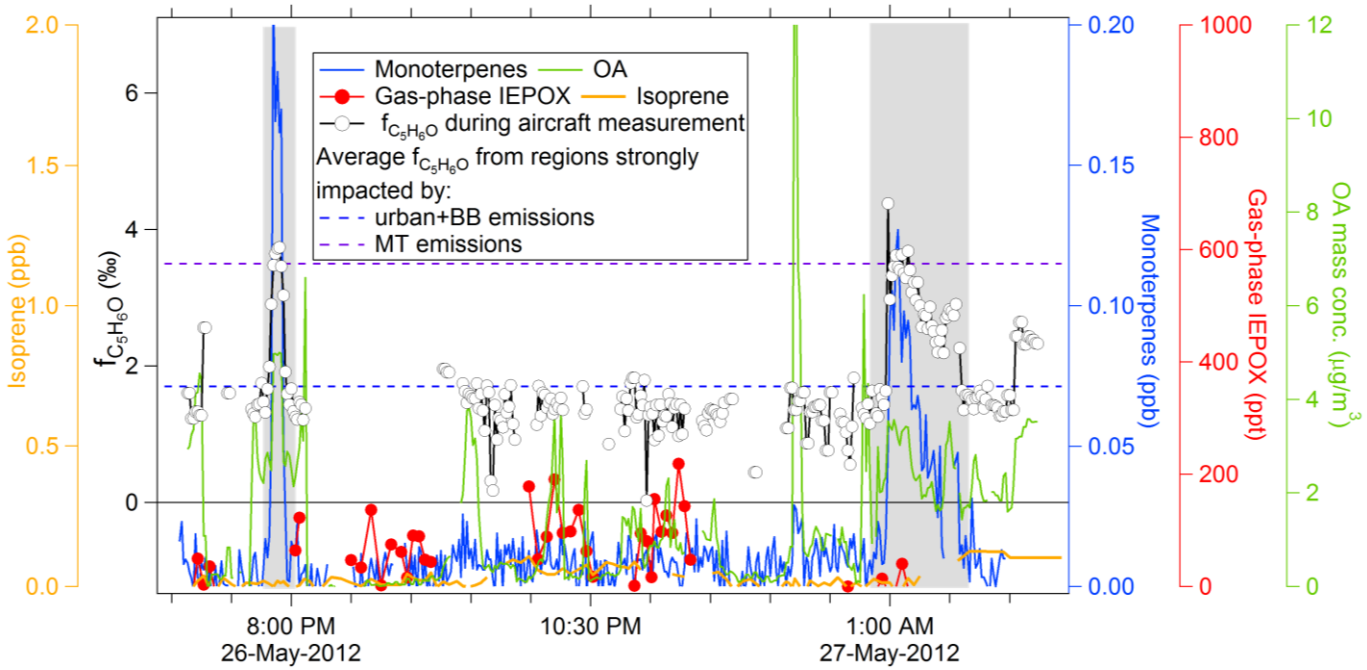


Figure 6. Time series of ambient $f_{C_5H_6O}^{OA}$, gas-phase IEPOX, monoterpenes and isoprene in DC3 aircraft measurement. Average $f_{C_5H_6O}$ from regions strongly impacted by urban and biomass-burning emissions and MT emissions are also shown for reference. Two areas with grey background indicate the periods when $f_{C_5H_6O}^{OA}$ increases when monoterpene concentrations increase.

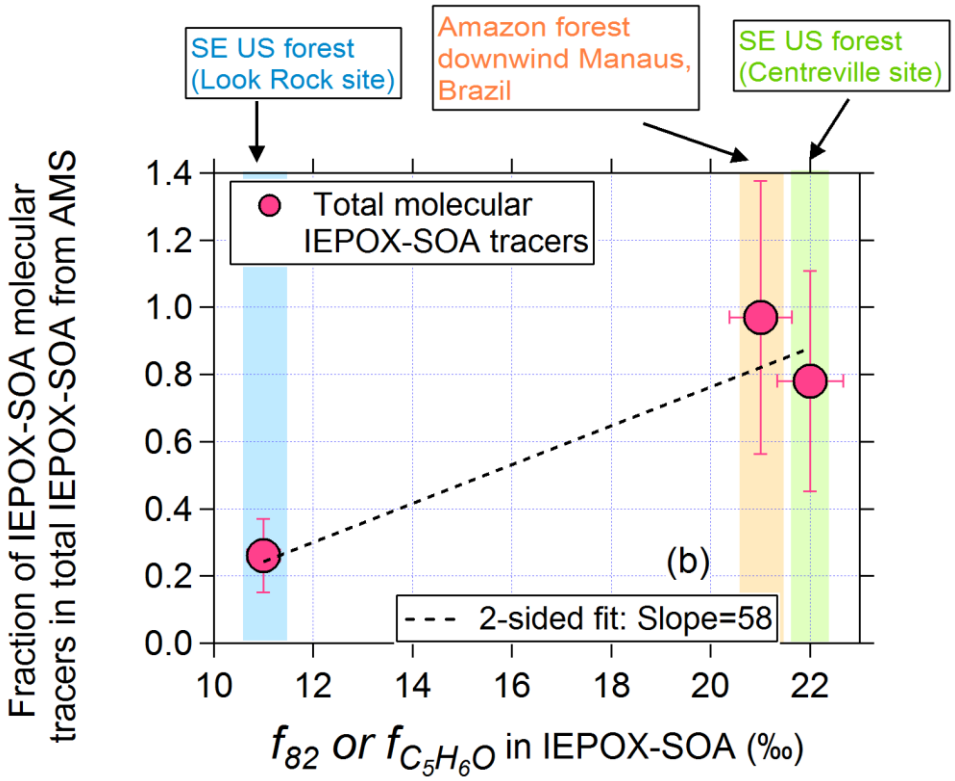


Figure 7. Scatter plot between total IEPOX-SOA molecular tracers (=Methyltetrol + C5-alkene triols +IEPOX-derived organosulfates and dimers) in IEPOX-SOA$_{PMF}$ and $f_{82}^{IEPOX-SOA}$. Besides SOAS, the other two datasets in the graph are from Budisulistiorini et al. (2015) and de Sá et al.(2015). The relative uncertainty value estimated for the SOAS study is applied to the other two datasets.

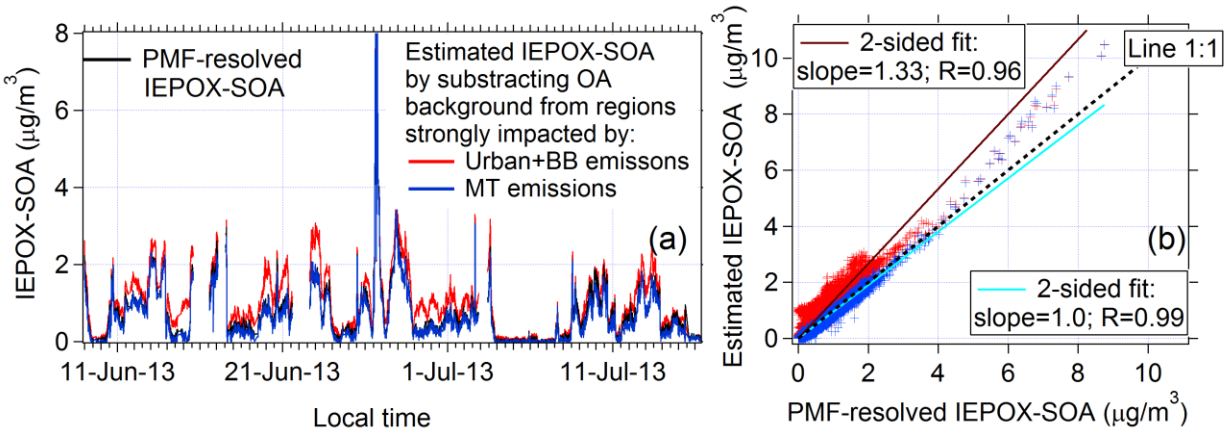
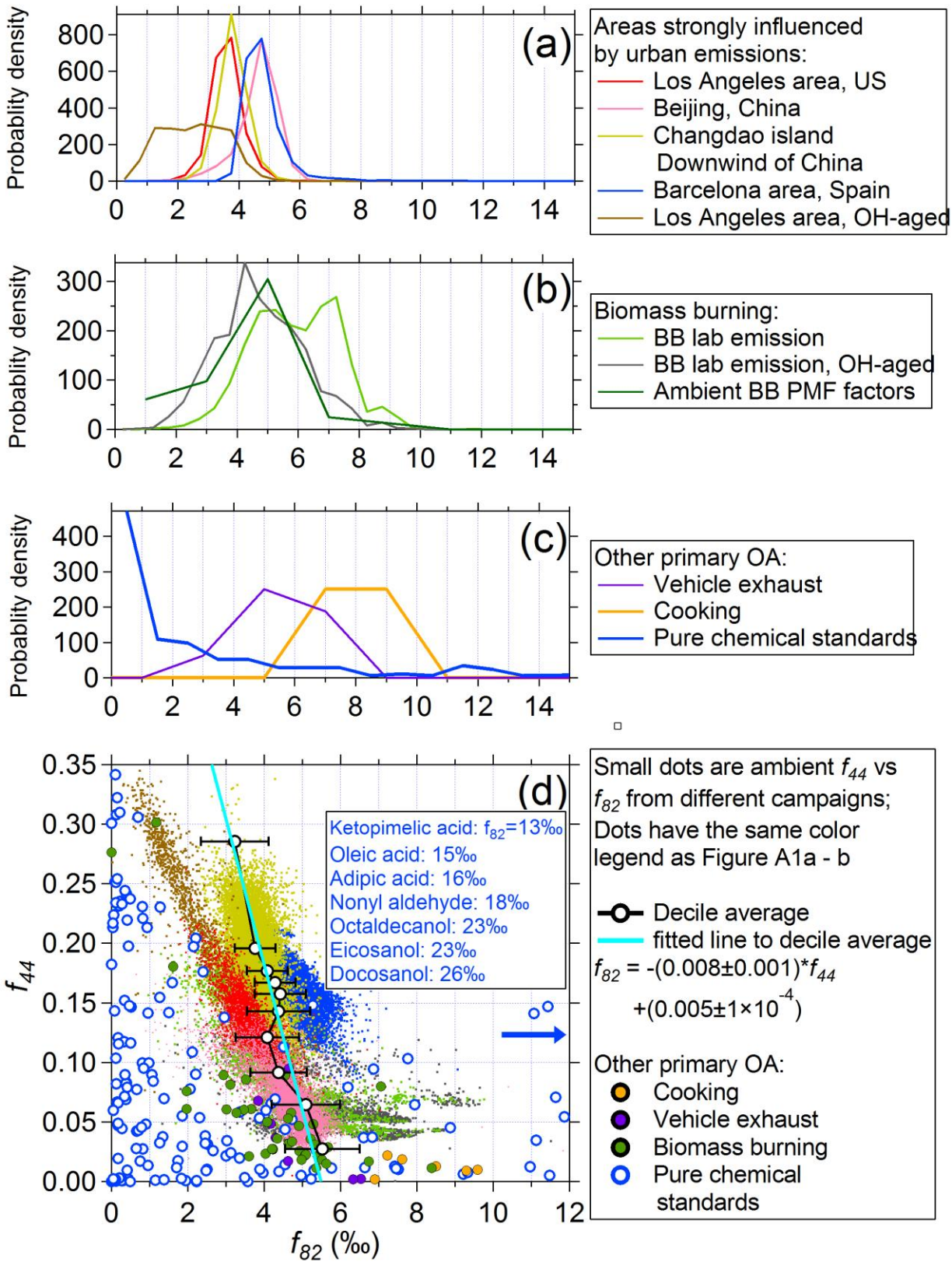


Figure 8. (a) Time series of IEPOX-SOA$_{PMF}$ and estimated IEPOX-SOA based on $C_5H_6O^+$ for the SOAS data in SE US. Two different estimates of background $C_5H_6O^+$ are shown, using values from regions strongly impacted by urban and biomass-burning emissions vs. regions with strong monoterpene emissions. (b) Scatter plot of estimated IEPOX-SOA vs. IEPOX-SOA$_{PMF}$. Note that the largest IEPOX-SOA plume on 26-Jun-13 had a slightly higher $f_{C_5H_6O}^{OA}$ of 24‰, resulting in a slight overestimation of IEPOX-SOA for those data points.


(a)
Probablity density
Areas strongly influenced by urban emissions:
Los Angeles area, US
Beijing, China
Changdao island Downwind of China
Barcelona area, Spain
Los Angeles area, OH-aged
(b)
Probablity density
Biomass burning:
BB lab emission
BB lab emission, OH-aged
Ambient BB PMF factors
(c)
Probablity density
Other primary OA:
Vehicle exhaust
Cooking
Pure chemical standards
(d)
Ketopimelic acid: f82=13‰
Oleic acid: 15‰
Adipic acid: 16‰
Nonyl aldehyde: 18‰
Octaldecanol: 23‰
Eicosanol: 23‰
Docosanol: 26‰
f44
f82 (‰)
Small dots are ambient f44 vs f82 from different campaigns; Dots have the same color legend as Figure A1a - b
Decile average
fitted line to decile average
f82 = -(0.008±0.001)*f44 +(0.005±1×10-4)
Other primary OA:
Cooking
Vehicle exhaust
Biomass burning
Pure chemical standards

1211

Figure A1. Probability density distributions of f_{82} in studies (a) strongly influenced by urban emissions; (b) biomass-burning emissions; (c) other anthropogenic primary OA sources and pure chemical standards. Several pure chemical species showing higher f_{82} between 15 – 30‰ are labeled with arrow. (d) Scatter plot of f_{44} (f_{44}=*m/z* 44/OA) vs. f_{82} for all studies shown in panels (a) − (c), using the same color scheme. Quantile averages of f_{82} across all studies sorted by f_{44} are also shown, as is a linear regression line to the quantile points.

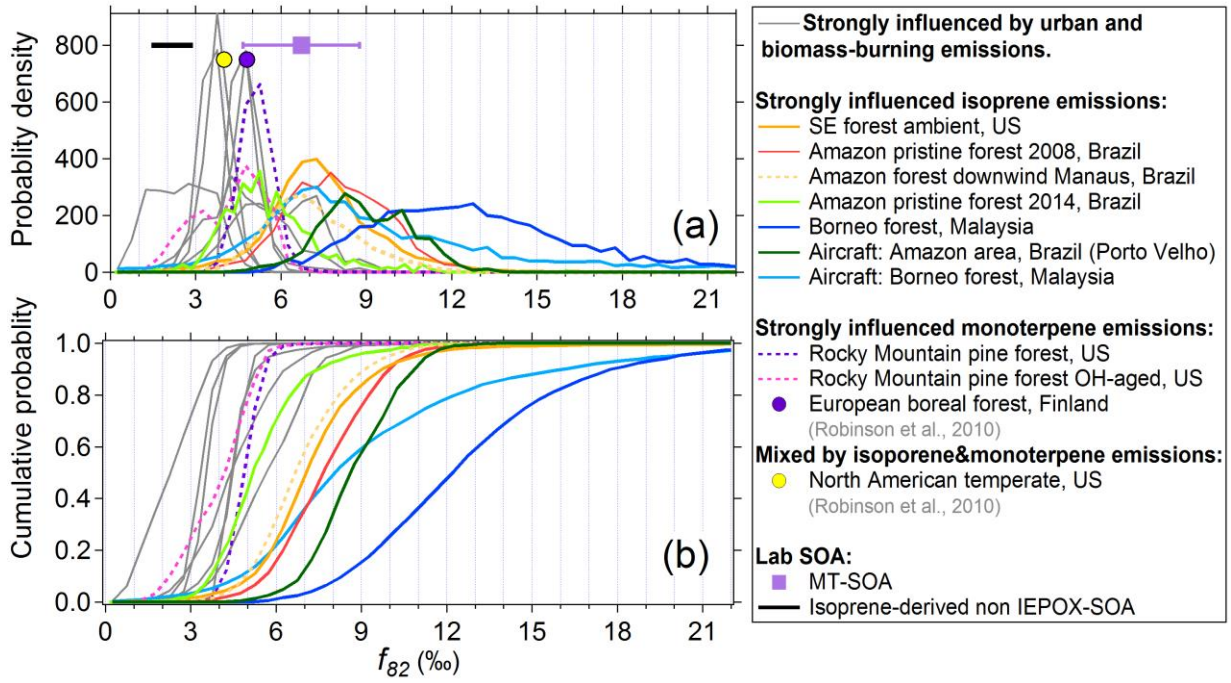


Figure A2. (a) Probability density and (b) cumulative probability distributions of f_{82} in studies strongly influenced by isoprene and/or monoterpene emissions. The ranges of f_{82} from other non IEPOX-derived isoprene-SOA and MT-SOA are also shown. The background grey lines are from studies strongly influenced by urban and biomass-burning emissions and are the same data from Fig. A1a − b.

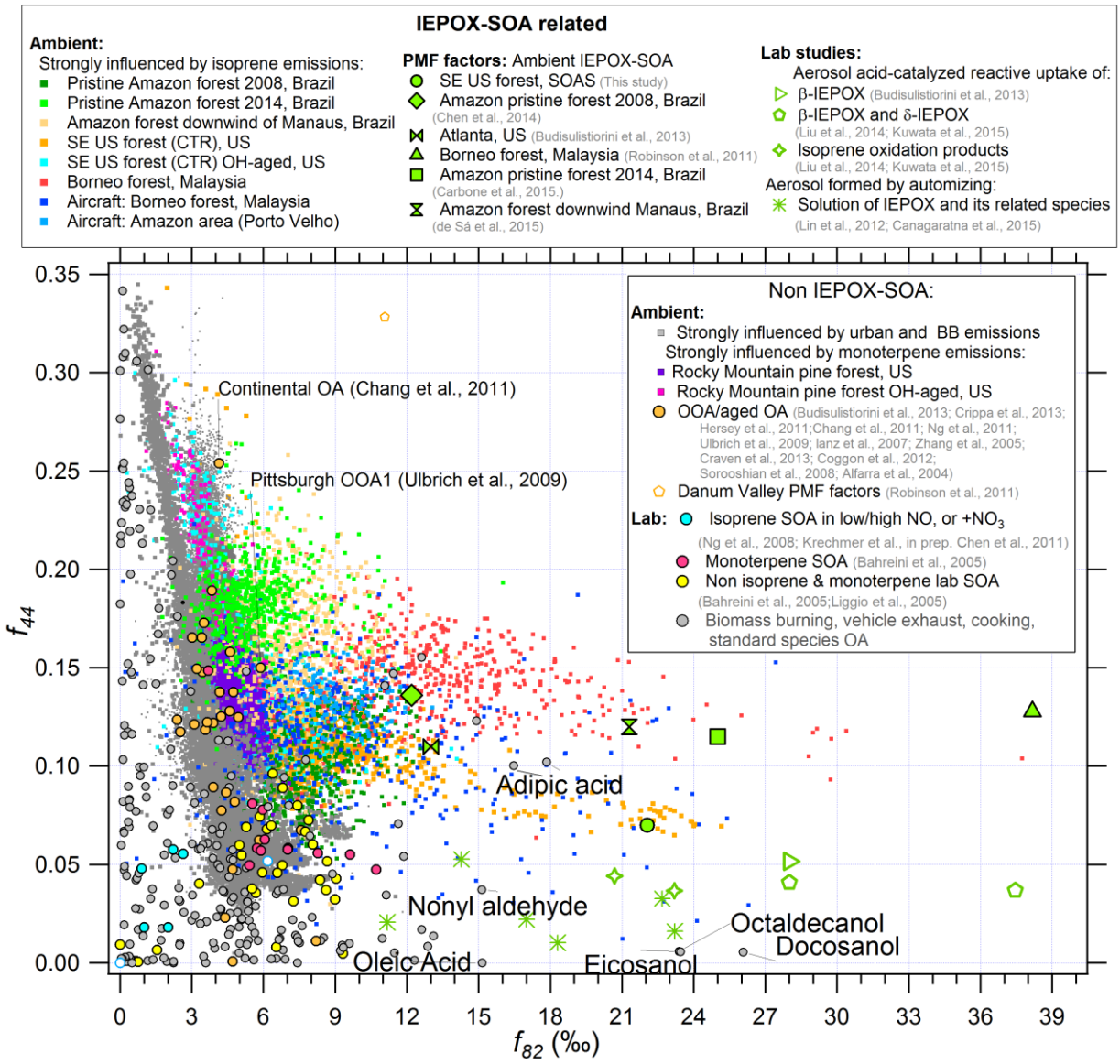


Figure A3. Scatter plot of f_{44} and f_{82} in studies strongly by isoprene and monoterpene emissions, as well as other OA sources. The grey dots represent background levels from studies strongly influenced by urban and biomass-burning emissions in Fig. A1d. f_{44} and f_{82} values from multiple sources of OA (Jimenez-Group, 2015) are also shown, together with IEPOX-SOA from different ambient PMF factors and chamber studies.

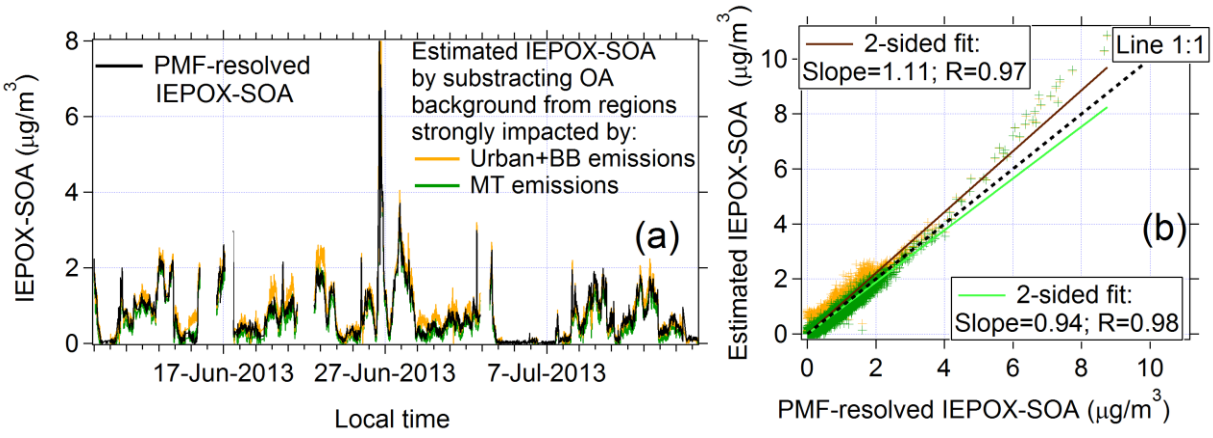


Figure A4. (a) Time series of IEPOX-SOA$_{PMF}$ and estimated IEPOX-SOA based on *m/z* 82 for the SOAS-CTR data in SE US forest. Two different estimates of background *m/z* 82 are shown, using values from regions strongly impacted by urban and biomass-burning emissions vs. regions with strong monoterpene emissions. (b) Scatter plot of estimated IEPOX-SOA vs. IEPOX-SOA$_{PMF}$. Note that the largest IEPOX-SOA plume (> 4 µg m^{-3}) on 26-Jun-13 had a slightly higher f_{82}^{OA} of 24‰, resulting in a slight overestimation of IEPOX-SOA for those data points.

The Supporting information of "Characterization of a Real-Time Tracer for Isoprene Epoxydiols-Derived Secondary Organic Aerosol (IEPOX-SOA) from Aerosol Mass Spectrometer Measurements"

Weiwei Hu[1,2], Pedro Campuzano-Jost[1,2], Brett B. Palm[1,2], Douglas A. Day[1,2], Amber M. Ortega[1,3], Patrick L. Hayes[1,2*], Jordan E. Krechmer[1,2], Qi Chen[4,5], Mikinori Kuwata[4,6], Yingjun Liu[4], Suzane S. de Sá[4], Karena McKinney[4], Scot T. Martin[4], Min Hu[6], Sri Hapsari Budisulistiorini[7], Matthieu Riva [7], Jason D. Surratt[7], Jason M. St. Clair[8**,***], Gabriel Isaacman-Van Wertz[9], Lindsay D. Yee[9], Allen H. Goldstein[9,10], Samara Carbone[11], Joel F. de Brito[11]

Paulo Artaxo[11], Joost de A. Gouw[1,2,12], Abigail Koss[2,12], Armin Wisthaler[13,14], Tomas Mikoviny[13], Thomas Karl[15], Lisa Kaser[16,14], Werner Jud[14], Armin Hansel[14], Kenneth S. Docherty[17], M. Lizabeth Alexander[18], Niall H. Robinson[19****], Hugh. Coe[19], James D. Allan[19,20], Manjula R. Canagaratna[21], Fabien Paulot[22,23], and Jose L. Jimenez[1,2].

1 Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
2 Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
3 Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO, USA
4 School of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA
5 State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China
6 Earth Observatory of Singapore, Nanyang Technological University, Singapore7 Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill, Chapel Hill, NC, USA
8 Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA
9 Department of Environmental Science, Policy, and Management, University of California, Berkeley, CA, USA
10 Department of Civil and Environmental Engineering, University of California, Berkeley, CA, USA
11 Department of Applied Physics, University of Sao Paulo, Sao Paulo, Brazil
12 NOAA Earth System Research Laboratory, Boulder, CO, USA
13 Department of Chemistry, University of Oslo, Oslo, Norway
14 Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria
15 Institute of Atmospheric and Cryospheric Sciences, University of Innsbruck, Innsbruck, Austria
16 Atmospheric Chemistry Division (ACD), National Center for Atmospheric Research, Boulder, CO, USA
17 Alion Science and Technology, Research Triangle Park, NC, USA
18 Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA
19 School of Earth, Atmospheric and Environmental Sciences, University of Manchester, UK
20 National Centre for Atmospheric Science, University of Manchester, UK
21 Aerodyne Research, Inc., Billerica, MA, USA
22 NOAA Geophysical Fluid Dynamics Laboratory, Princeton, NJ, USA
23 Program in Atmospheric and Oceanic Sciences , Princeton University, Princeton, NJ, USA.

*Now at: Department of Chemistry, Université de Montréal, Montréal, QC, Canada
** Now at: Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, USA
*** Now at: Joint Center for Earth Systems Technology, University of Maryland Baltimore County, Baltimore, MD, USA.
**** Now at: Met Office, Exeter, UK

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

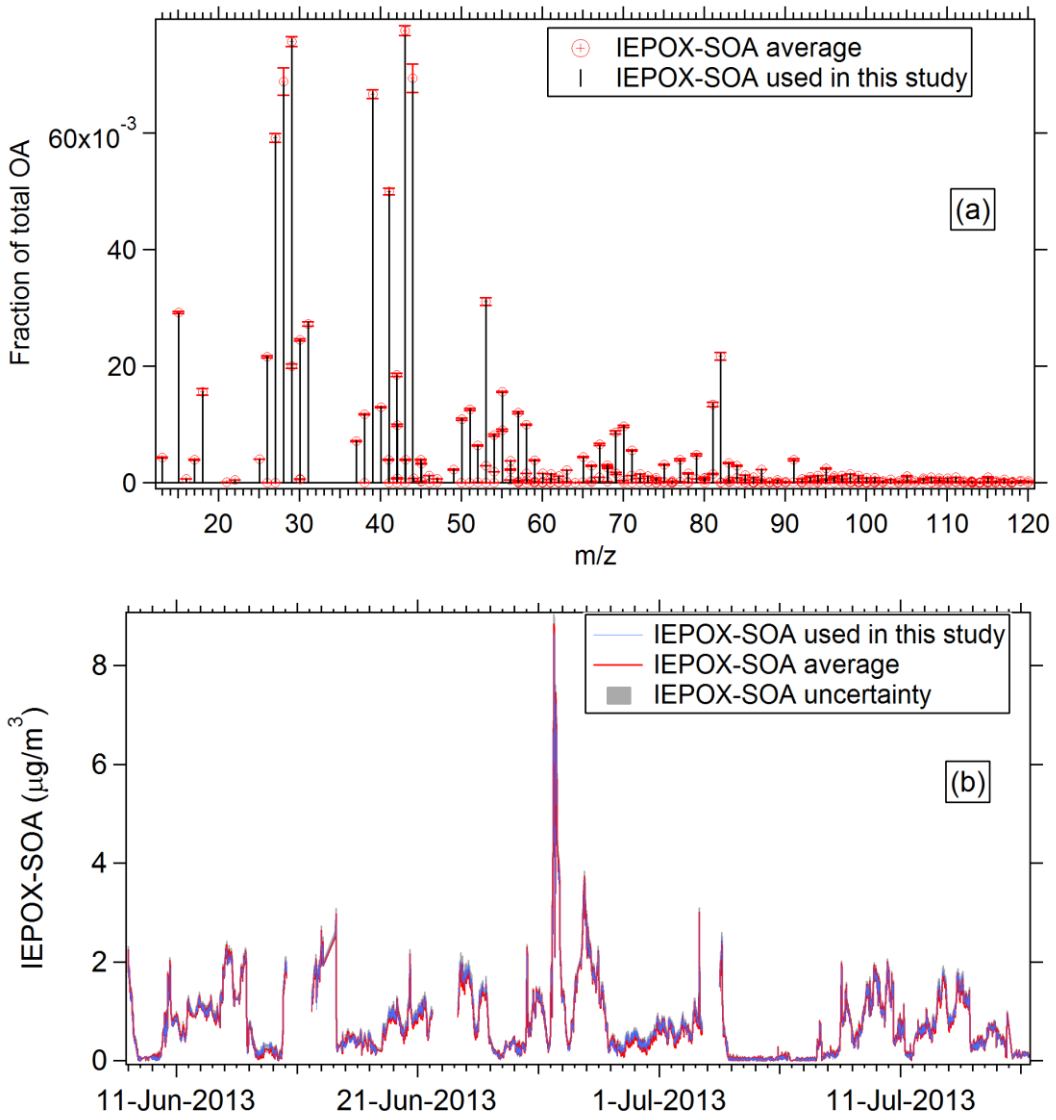


Figure S1. Results from bootstrapping analysis of the 4-factor solution of the SOAS dataset. Average IEPOX-SOA, with standard deviation, are shown for IEPOX-SOA (a) mass spectrum and (b) time series.

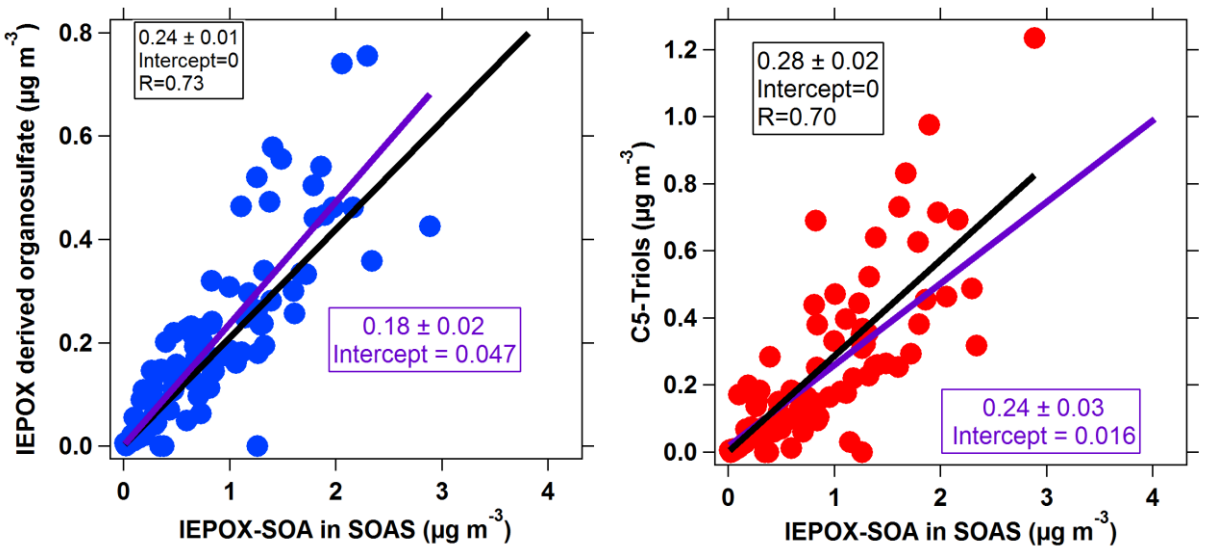


Figure S2. Scatter plots between IEPOX-derived organosulfate and C5-triols vs IEPOX-SOA_{PMF} in the SOAS study. The IEPOX-derived organosulfate and C5-triols were measured in GC/MS and LC/MS analysis of filter extracts (Lin et al., 2014;Budisulistiorini et al., 2015).

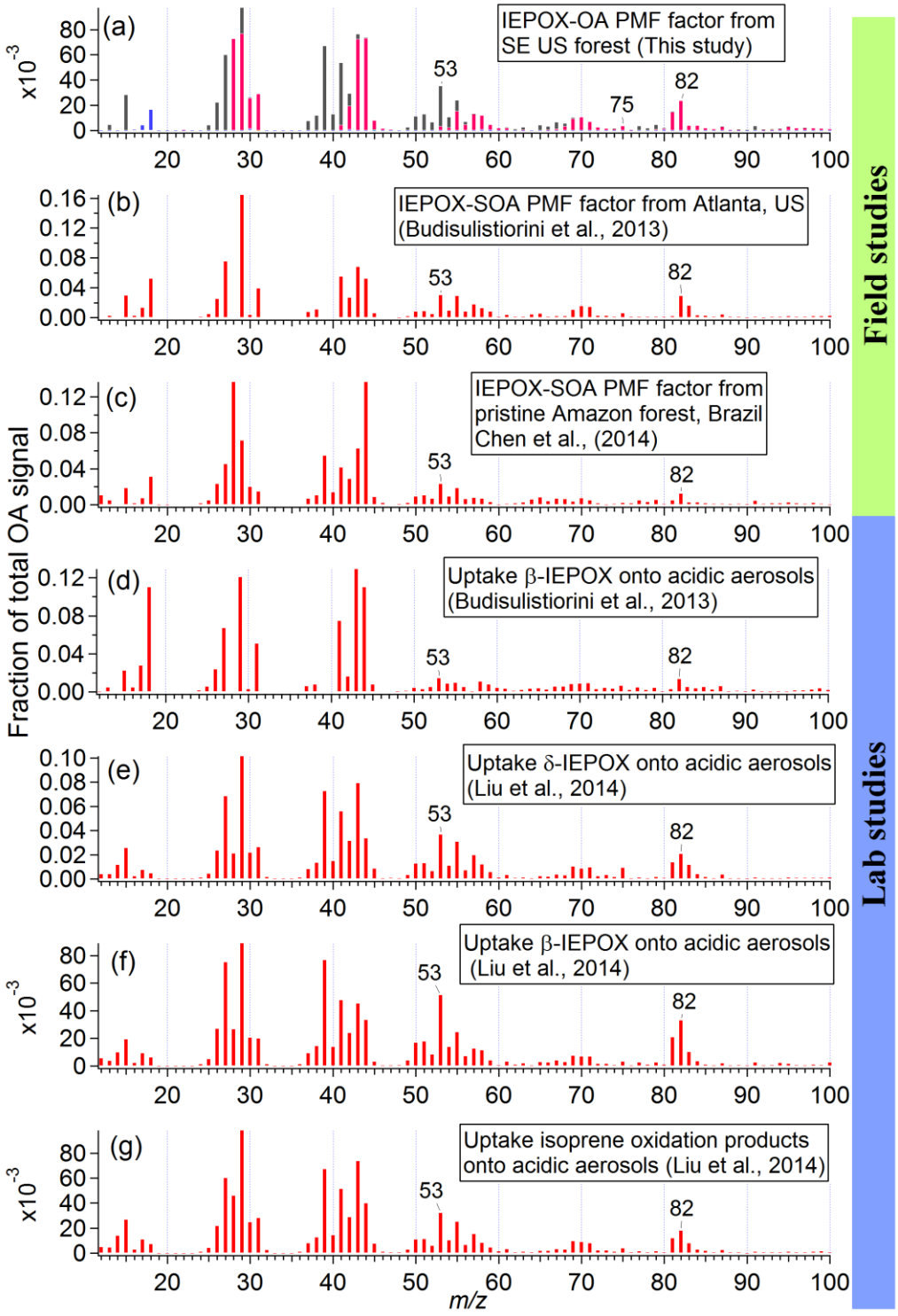


Figure S3. Mass spectra of IEPOX-SOA from different studies. Panel (a) − (c) are the results from field studies. Panel (d) − (g) are the results from lab studies.

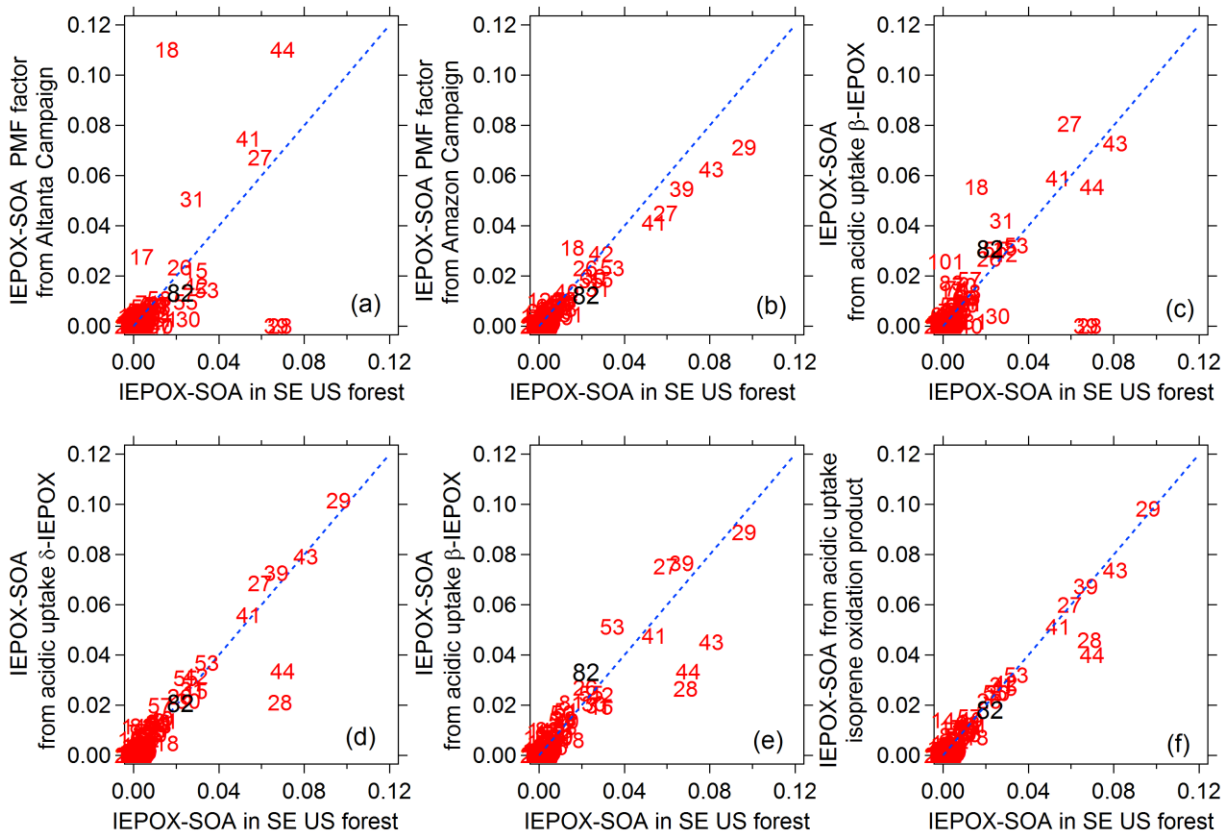


Figure S4. Scatter plots of IEPOX-SOA spectra in other studies vs IEPOX-SOA spectrum from this study (SOAS, SE US forest). The spectra on the y-axes are in the same order as Figures S1 (b) to (g).

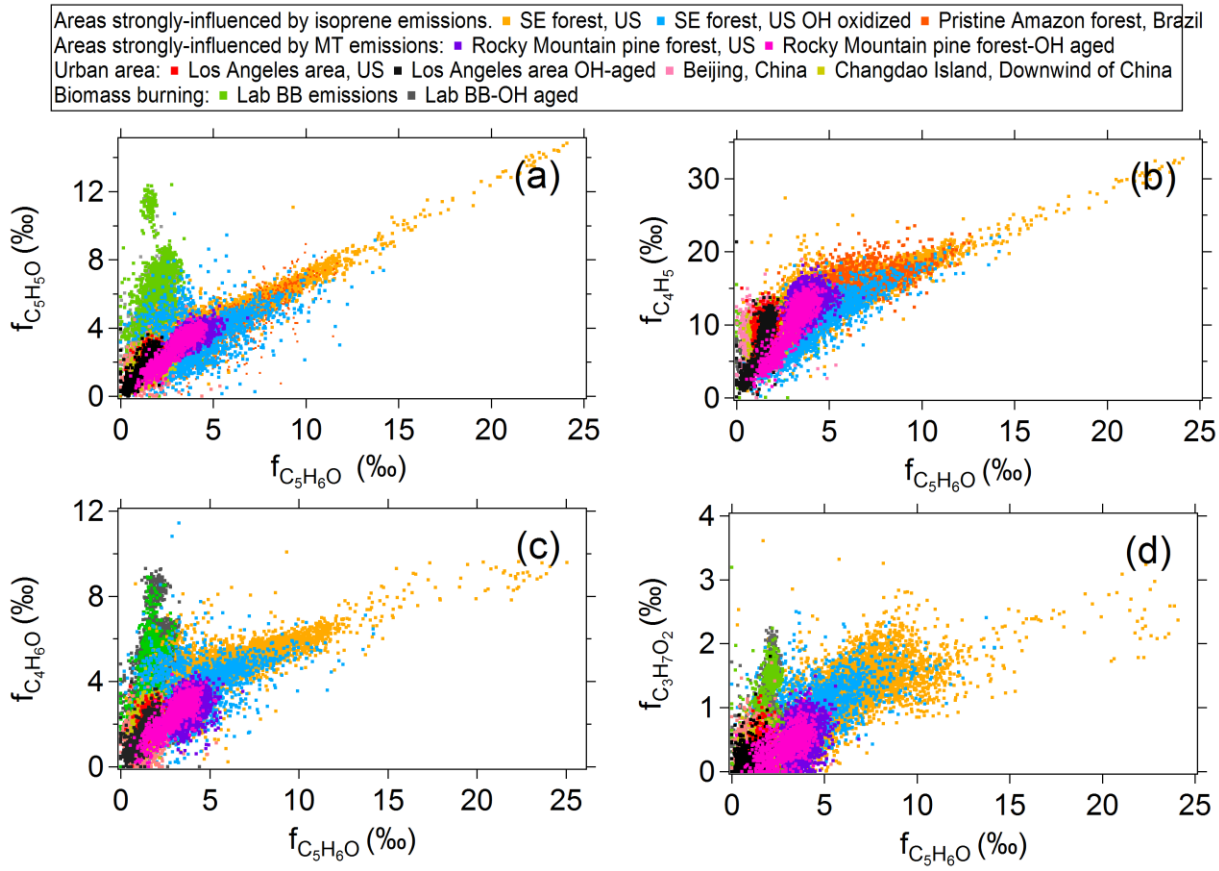


Figure S5. Scatter plots of abundance of ions versus $f_{C_5H_6O}^{OA}$ obtained in different studies: (a) $f_{C_5H_5O}^{OA}$,(b) $f_{C_4H_5}^{OA}$, (c) $f_{C_4H_6O}^{OA}$, and (d) $f_{C_3H_7O_2}^{OA}$. Compared to $f_{C_5H_6O}^{OA}$, $f_{C_4H_5}^{OA}$, $f_{C_4H_6O}^{OA}$, and $f_{C_5H_5O}^{OA}$ have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

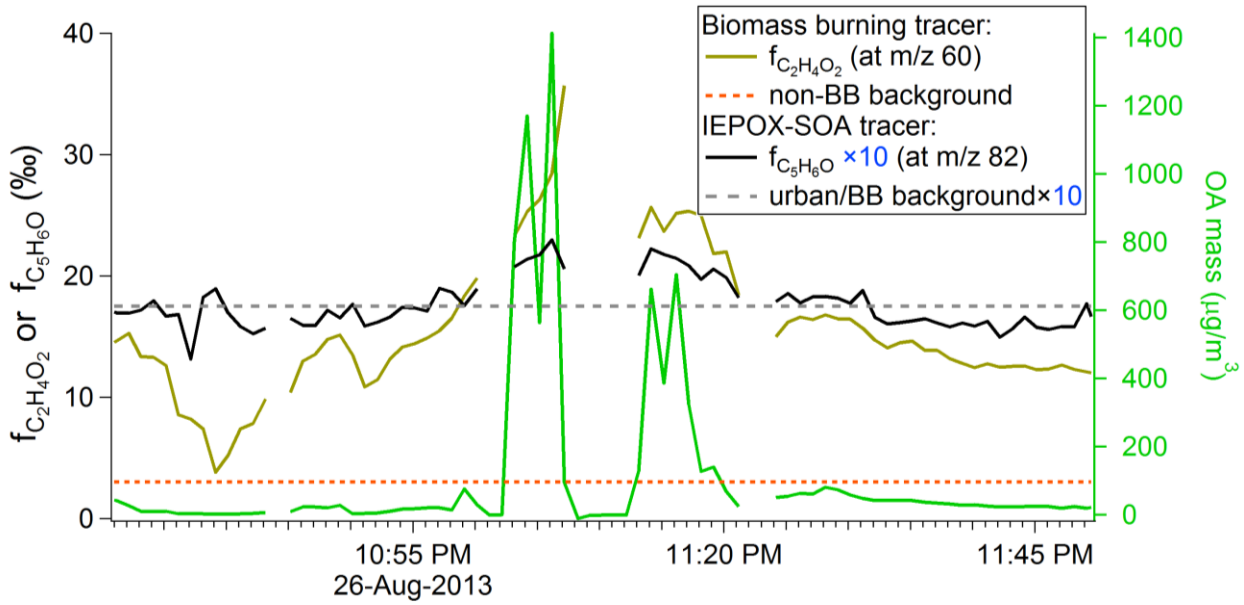


Figure S6. Time series of OA mass concentration, and of tracers for IEPOX-SOA ($f_{C_5H_6O}$) and biomass-burning ($f_{C_2H_4O_2}$, *m/z* 60.0211) compared to their respective backgrounds on the research flight on Aug 26, 2013 during the SEAC4RS campaign. The biomass-burning tracer indicates extensive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

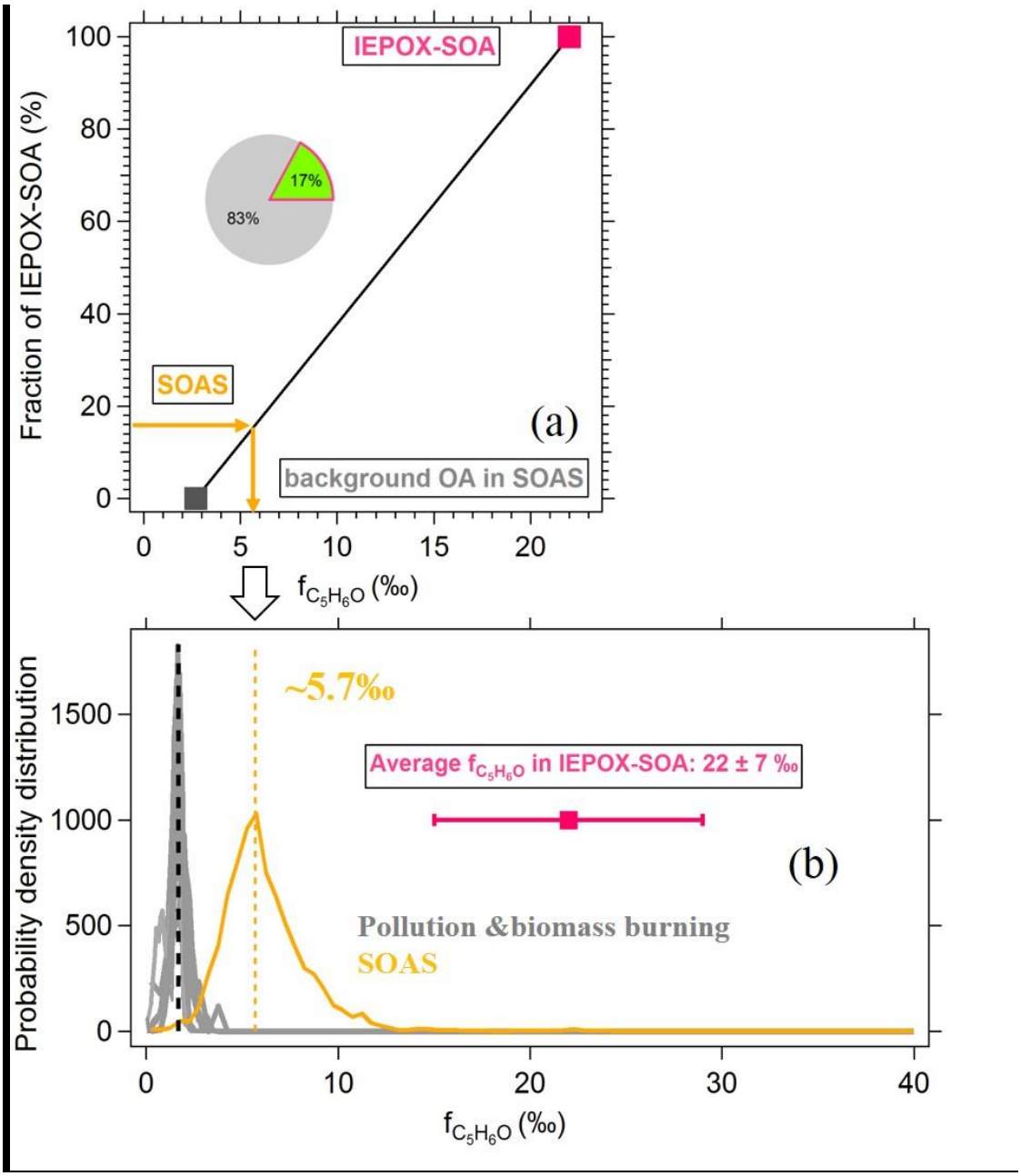
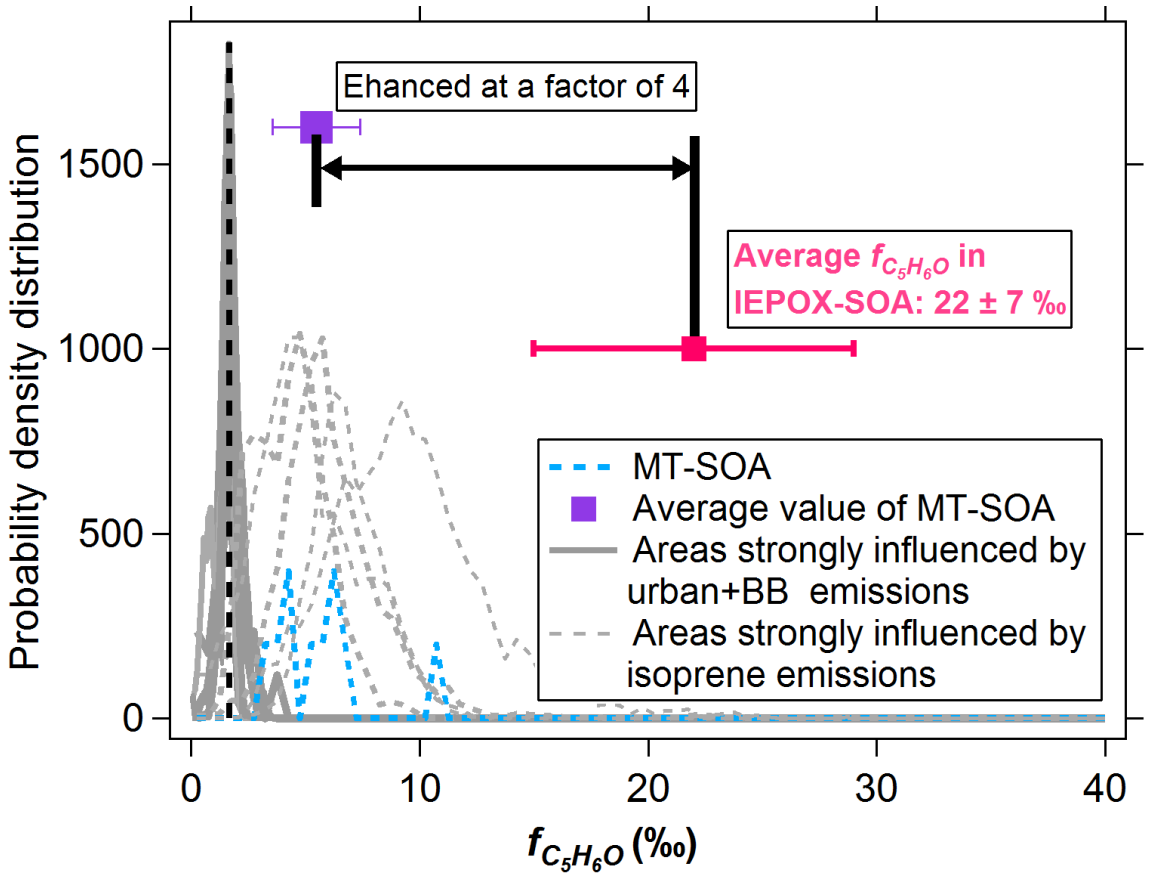


Figure S7. Schematic of the estimation method of IEPOX-SOA based on ambient $f_{C_5H_6O}$. (a) Fraction of IEPOX-SOA in total OA vs ambient $f^{OA}_{C_5H_6O}$ (b) probability distribution of $f^{OA}_{C_5H_6O}$ in SOAS and in background studies. The average background of $f^{OA}_{C_5H_6O}$ -from SOAS-CTR 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‰.



118

119 **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
120 influenced by urban + biomass burning and isoprene emissions are also shown.

121

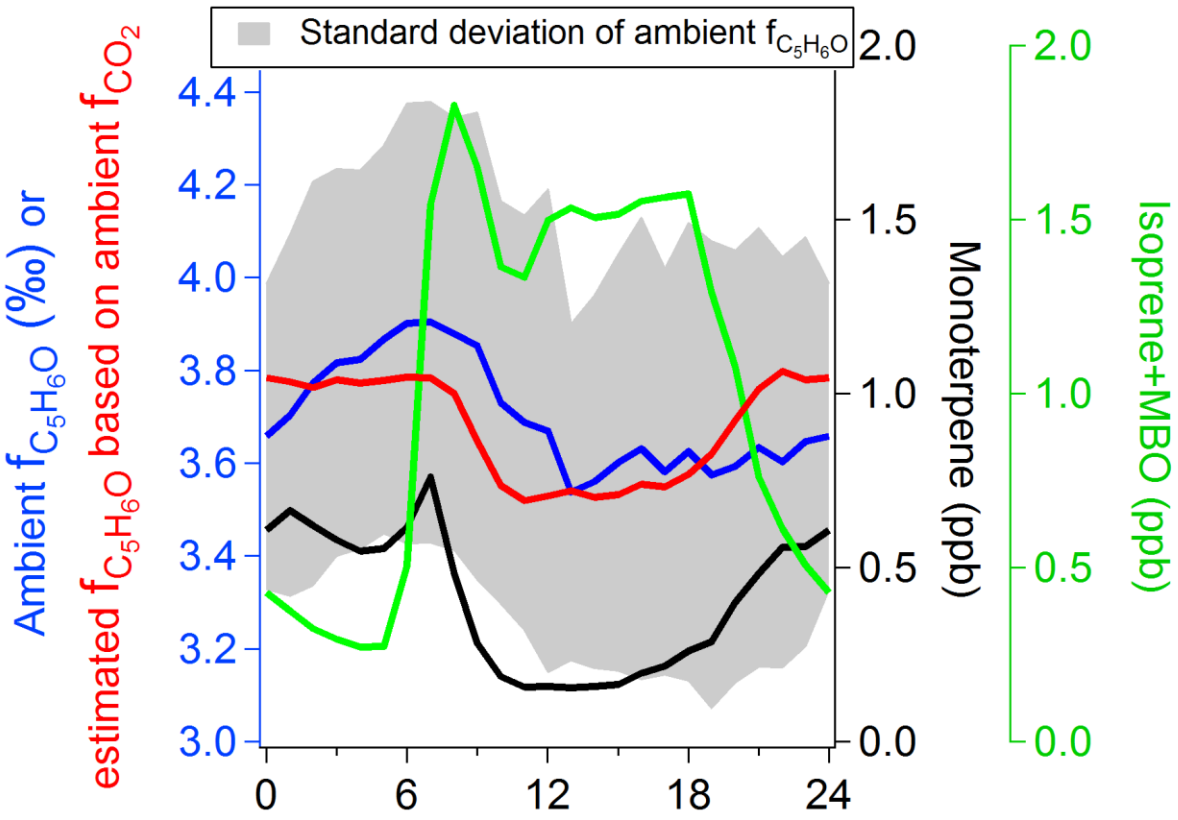


Figure S9. Diurnal variation of ambient $f_{C_5H_6O}^{OA}$ at the Manitou Forest pine forest site in the Rocky Mountains during the BEACHON-RoMBAS 2011 field study, together with diurnal variations of estimated $f_{C_5H_6O}^{OA}$ from $f_{CO_2}^{OA}$ based on regression results between $f_{C_5H_6O}^{OA}$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

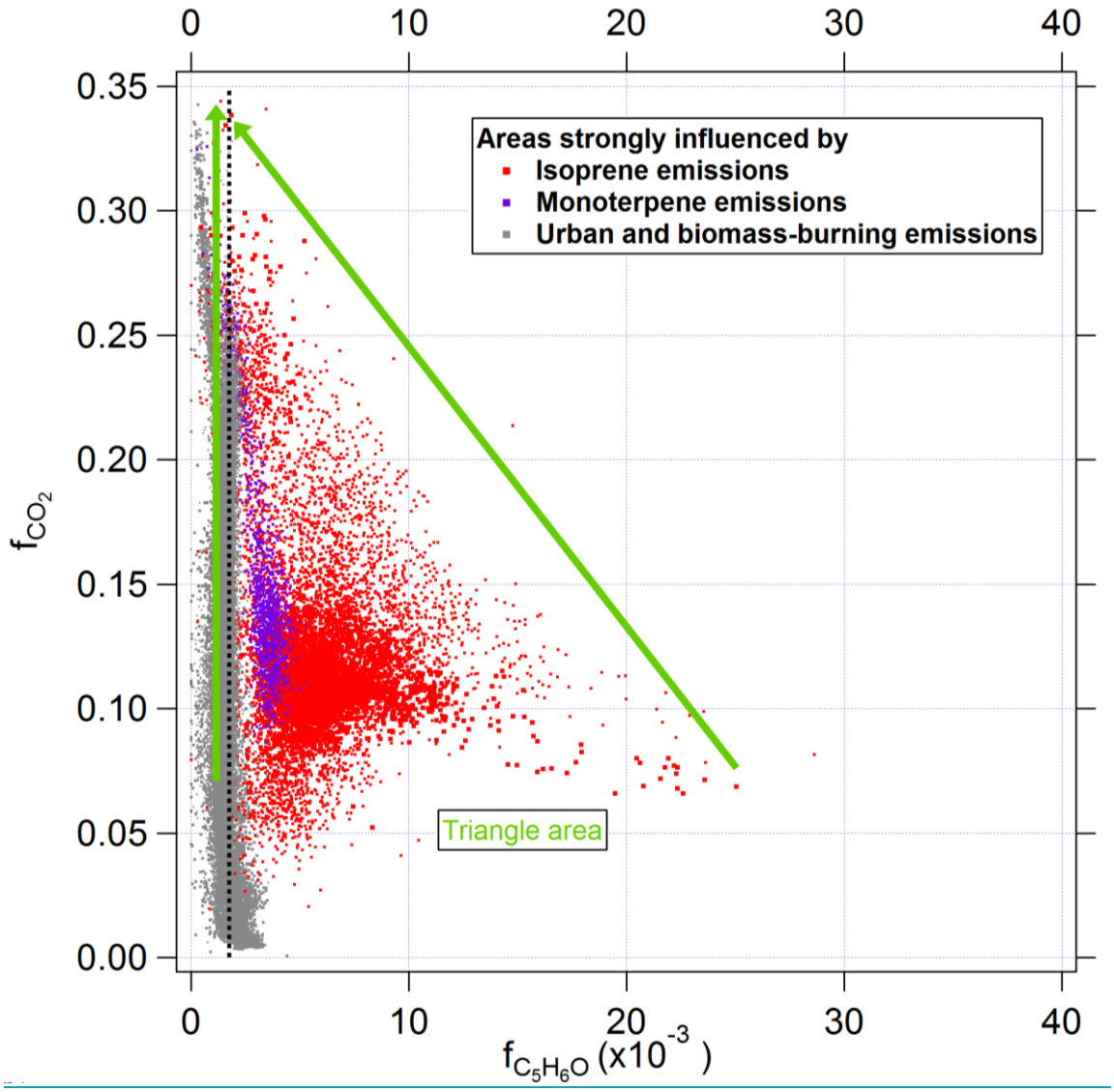


Figure S10. Scatter plot between $f_{CO_2}^{OA}$ and $f_{C_5H_6O}^{OA}$ for all the ambient OA dataset. Green arrows are added to guide the eye.

.

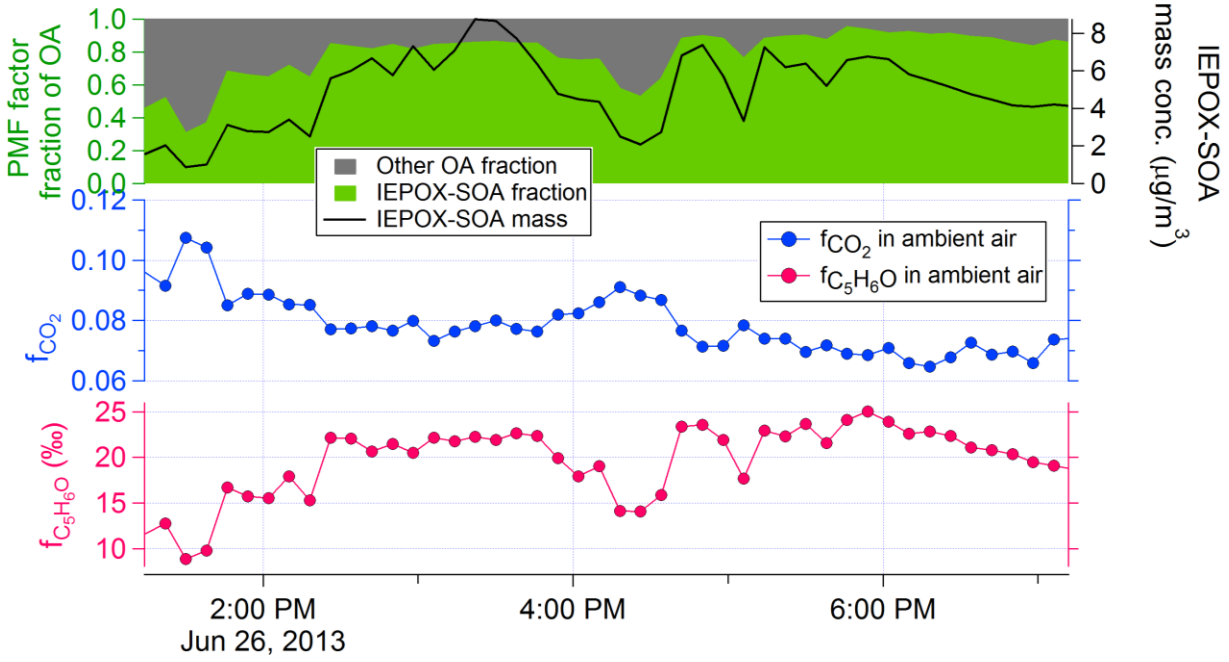


Figure S11. Time series of ambient $f_{C_5H_6O}^{OA}$, $f_{CO_2}^{OA}$, and IEPOX-SOA mass concentrations, together with the IEPOX-SOA fraction of OA during the SOAS-CTR campaign in a SE US forest. During this period, high sulfate and IEPOX-SOA mass concentrations and mass fractions are observed.

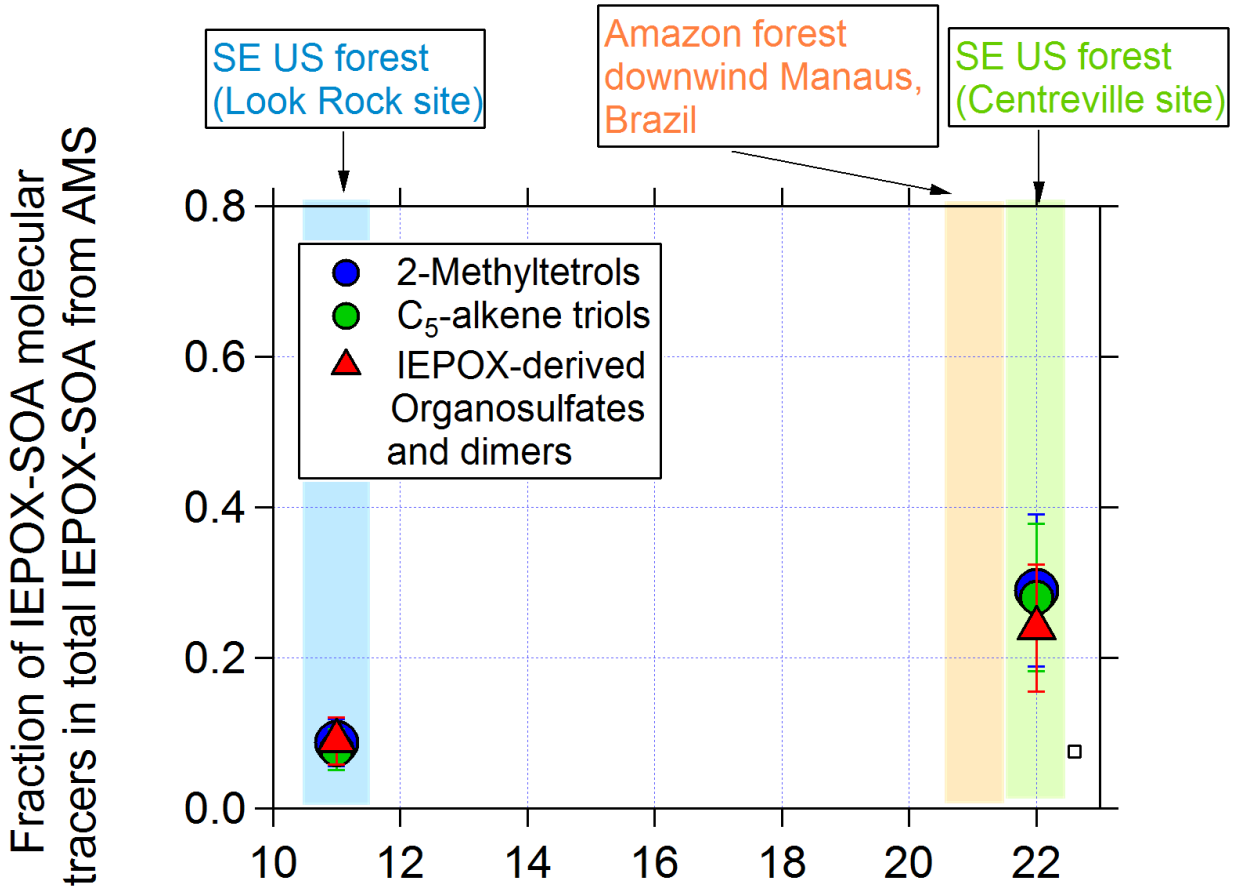


Figure S12 Scatter plot between different IEPOX-SOA molecular tracers (Methyltetrol, C5-alkene triols and IEPOX-derived organosulfates and their dimers) vs IEPOX-SOA$_{PMF}$ and f_{82} in IEPOX-SOA

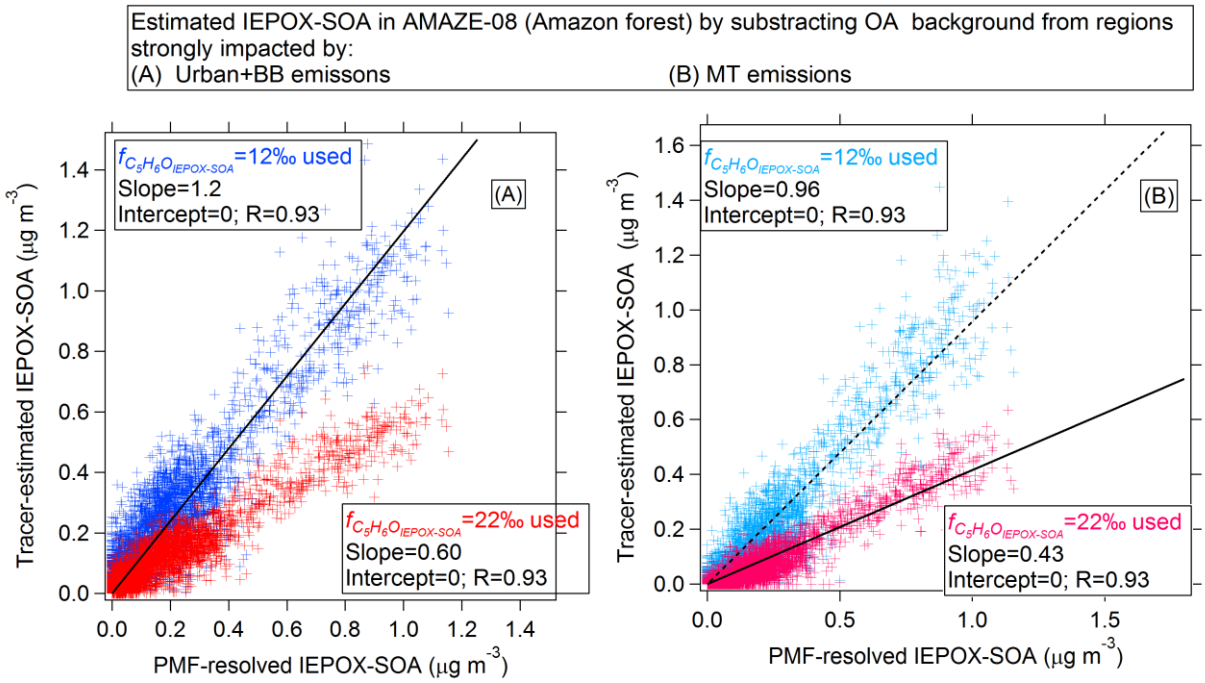


Figure S13. Scatter plot between tracer-estimated IEPOX-SOA and IEPOX-SOA$_{PMF}$ at a pristine Amazon forest site (AMAZE-08). The tracer-based IEPOX-SOA was estimated using OA background from regions strongly influenced by (A) urban and biomass-burning emissions and (B) monoterpene emissions. In each 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‰).

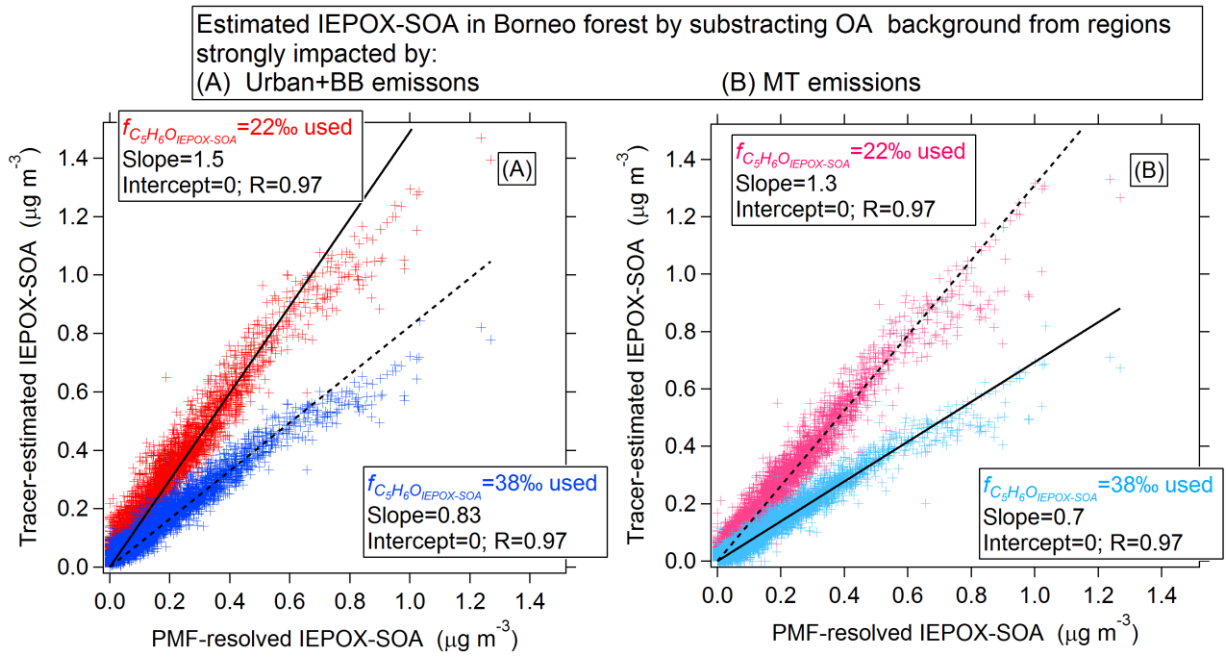


Figure S14 Scatter plot between estimated IEPOX-SOA and IEPOX-SOA$_{PMF}$ at a Borneo forest site. The tracer-based IEPOX-SOA was estimated using OA background from regions strongly influenced by (A) urban and biomass-burning emissions and (B) monoterpene emissions. In each plot, we used two $f_{C_5H_6O}^{IEPOX-SOA}$,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

References

Aiken, A. C., Salcedo, D., Cubison, M. J., Huffman, J. A., DeCarlo, P. F., Ulbrich, I. M., Docherty, K. S., Sueper, D., Kimmel, J. R., Worsnop, D. R., Trimborn, A., Northway, M., Stone, E. A., Schauer, J. J., Volkamer, R. M., Fortner, E., de Foy, B., Wang, J., Laskin, A., Shutthanandan, V., Zheng, J., Zhang, R., Gaffney, J., Marley, N. A., Paredes-Miranda, G., Arnott, W. P., Molina, L. T., Sosa, G., and Jimenez, J. L.: Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) - Part 1: Fine particle composition and organic source apportionment, Atmos Chem Phys, 9, 6633-6653, 2009.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, 10.5194/acp-15-253-2015, 2015.

Chen, Q., Farmer, D. K., Rizzo, L. V., Pauliquevis, T., Kuwata, M., Karl, T. G., Guenther, A., Allan, J. D., Coe, H., Andreae, M. O., Pöschl, U., Jimenez, J. L., Artaxo, P., and Martin, S. T.: Submicron particle mass concentrations and sources in the Amazonian wet season (AMAZE-08), Atmos. Chem. Phys., 15, 3687-3701, 10.5194/acp-15-3687-2015, 2015.

Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, Atmos. Chem. Phys., 10, 4111-4131, 10.5194/acp-10-4111-2010, 2010.

Crippa, M., El Haddad, I., Slowik, J. G., DeCarlo, P. F., Mohr, C., Heringa, M. F., Chirico, R., Marchand, N., Sciare, J., Baltensperger, U., and Prévôt, A. S. H.: Identification of marine and continental aerosol sources in Paris using high resolution aerosol mass spectrometry, Journal of Geophysical Research: Atmospheres, 118, 1950-1963, doi: 10.1002/jgrd.50151, 2013.

Docherty, K. S., Aiken, A. C., Huffman, J. A., Ulbrich, I. M., DeCarlo, P. F., Sueper, D., Worsnop, D. R., Snyder, D. C., Peltier, R. E., Weber, R. J., Grover, B. D., Eatough, D. J., Williams, B. J., Goldstein, A. H., Ziemann, P. J., and Jimenez, J. L.: The 2005 Study of Organic Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition, Atmos. Chem. Phys., 11, 12387-12420, 10.5194/acp-11-12387-2011, 2011.

Dunlea, E. J., DeCarlo, P. F., Aiken, A. C., Kimmel, J. R., Peltier, R. E., Weber, R. J., Tomlinson, J., Collins, D. R., Shinozuka, Y., McNaughton, C. S., Howell, S. G., Clarke, A. D., Emmons, L. K., Apel, E. C., Pfister, G. G., van Donkelaar, A., Martin, R. V., Millet, D. B., Heald, C. L., and Jimenez, J. L.: Evolution of Asian aerosols during transpacific transport in INTEX-B, Atmos Chem Phys, 9, 7257-7287, 2009.

Robinson, N. H., Hamilton, J. F., Allan, J. D., Langford, B., Oram, D. E., Chen, Q., Docherty, K., Farmer, D. K., Jimenez, J. L., Ward, M. W., Hewitt, C. N., Barley, M. H., Jenkin, M. E., Rickard, A. R., Martin, S. T., McFiggans, G., and Coe, H.: Evidence for a significant proportion of Secondary Organic Aerosol from isoprene above a maritime tropical forest, Atmos. Chem. Phys., 11, 1039-1050, 10.5194/acp-11-1039-2011, 2011.

Setyan, A., Zhang, Q., Merkel, M., Knighton, W. B., Sun, Y., Song, C., Shilling, J. E., Onasch, T. B., Herndon, S. C., Worsnop, D. R., Fast, J. D., Zaveri, R. A., Berg, L. K., Wiedensohler, A., Flowers, B. A., Dubey, M. K., and Subramanian, R.: Characterization of submicron particles influenced by mixed biogenic and anthropogenic emissions using

high-resolution aerosol mass spectrometry: results from CARES, Atmos. Chem. Phys., 12, 8131-8156, 10.5194/acp-12-8131-2012, 2012.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, Atmos Chem Phys, 9, 2891-2918, 2009.