

Interactive comment on “Evidence for a significant proportion of Secondary Organic Aerosol from isoprene above a maritime tropical forest” by N. H. Robinson et al.

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1 Response to reviewer 2:

We thank the reviewer for carefully reading the manuscript and for all of their comments. Responses to all of the comments are detailed below:

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2 General Response:

The overall concern of the reviewer appears to be that we do not directly identify ambient isoprene SOA. This is correct, but at no point in the paper do we argue this. We demonstrate identification of methyl furan from the GCxGC-MS measurements and hence attribute it to the $C_5H_6O^+$ peak based on comparison with laboratory standards. We base our assertion that $C_5H_6O^+$ measurements are the result of thermal decomposition of isoprene SOA to methylfuran on two arguments: that $C_5H_6O^+$ correlates with gas phase isoprene oxidation products and that $C_5H_6O^+$ has been shown to be chemically similar to isoprene oxidation products in the literature. With regards to the precise chemical species responsible for the $C_5H_6O^+$ signal, we feel that the novel mechanism we propose (peroxyhemiacetals) is the most credible. However the reviewer is correct in saying we cannot conclusively eliminate other established isoprene SOA as possibilities. As such, we do not present this as a firm conclusion, rather as a speculative explanation. We also agree with the reviewer that care must be taken in the interpretation of single AMS peaks and we voiced these concerns in the paper. However we believe that we have evidence that $C_5H_6O^+$ is a justified marker peak for this isoprene SOA in this case.

3 General Comments:

...I think we need to be careful here as a research community to claim that this ion in AMS data is entirely from isoprene SOA, especially considering how small this ion is in Figure 2a and 2b. This ion seems to be so small that is almost a part of the background noise in the MS data collected from the field.

It is true that it may be possible to produce $C_5H_6O^+$ from aerosols other than isoprene SOA. However comparison to gas phase species show that isoprene SOA is a likely

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source in this case. It is unclear what else might be the source of such a stable molecular ion. We agree with the reviewer that care is needed in the interpretation of m/z 82 peaks and have stated this explicitly when we discuss data we consider from other projects (p25558, line 21). However, the m/z 82 peak in the OP3 dataset is substantial when compared to mass spectra from other projects in non-isoprene rich environments. It is also prominent compared to its neighboring peaks implying it is not a background fragment (p25559, line 3-4). More to the point, the 82 peak is resolved very robustly into a single PMF factor, which would not be the case if it were insignificant (p25551, line 23-27). The fact that the m/z 82 is confined to one robust PMF factor implies that, in this instance, it is of a single source.

In addition, I disagree with Reviewer 1 that this paper reports the first identification of a new isoprene SOA marker (or tracer compound). This is not a compound that Robinson et al. is seeing, but rather a degradation/fragment ion of some potential intact isoprene SOA constituent.

We agree that $C_5H_6O^+$ is a thermal degradation product but believe it to be indicative of isoprene SOA which can be used as a proxy in AMS data. While we do not directly measure the parent species, the use of thermal decomposition products (produced by the vapouriser) as markers when interpreting AMS data is already well established. While it is not indicative of specific compound in the atmosphere, the CO₂ thermal fragment has been shown to be representative of highly oxygenated organic aerosol (McFiggans et al 2004; Jimenez et al 2009). Also, through the use of PMF it is possible to account for covariant isoprene derived aerosol, even if it is not produced through the same mechanism (both atmospheric and instrumental) as the MF (p 25547, line 17-19; p 25557, line 21-23).

The authors conclude that MF is a product of a form of isoprene SOA not previously identified. This conclusion is no way supported by the current dataset and I strongly encourage the authors to revise this statement/conclusion. In order to make such a matter-of-fact conclusion, compounds previously characterized as isoprene SOA,

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such as the abundantly observed 2-methyltetrols (Hallquist et al., 2009, and references therein) and IEPOX-derived organosulfates (Surratt et al., 2010, PNAS; Froyd et al., 2010, PNAS; Chan et al., 2010, EST) found in ambient aerosol collected from isoprene-rich regions, would need to be synthesized, atomized, and sampled directly by the AMS technique. I know that Farmer et al. (2010, PNAS) recently showed that the AMS has a hard time observing intact IEPOX-derived organosulfates.

We feel that our paper is clear that we have no conclusive proof that MF is produced from previously unidentified SOA and that we do not draw that as a conclusion. We speculate on possible sources other than established isoprene SOA, and convey this speculation through words such as “potential”, “could” and “suggest”. This sentiment is expressed throughout the paper e.g:

- “One such potential condensable MF precursor could be peroxyhemiacetal oligomers, derived from gas-phase isoprene photo-oxidation products such as unsaturated 1,4-hydroxycarbonyls. However, the actual specific MF precursor (or precursors) require laboratory identification.” (p25560, line 7-8)
- “This suggests that the MF is a product of a form of isoprene SOA not previously identified.” (p25555, line 11-12).

We believe that it is possible MF is the result of sampling some previously identified isoprene SOA, however we cannot envisage a condensed phase molecular structure by which this would occur (page 25555, line 7). The fact that Farmer et al reported difficulty measuring IEPOX-derived organosulphates is consistent with this. We will make this sentiment clearer by adjusting page 25560, line 7-8 to read:

“However, the actual specific MF precursor (or precursors) require laboratory identification. **Future work will attempt to detect the m/z 82 in the laboratory, both from established isoprene SOA and from the compounds suggested here.**”

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Also we will adjust the following (removing “as yet unknown”), as the discussion between established and un-established isoprene SOA is presented more clearly elsewhere in the paper:

“Instead, we hypothesise that MF measurements are a result of decomposition of some condensed phase isoprene photo-oxidation product upon the thermal vaporization used in the GC×GC and AMS analyses reported here.” (p25554, line 23-26)”

I have always worried that trying to associate specific ions to specific compounds with AMS might happen and is difficult to do especially considering the fact that there is no chromatographic separation of aerosol constituents before MS detection.

We agree with the reviewer to the point that this work would not have been possible without the GCxGC measurements. We believe that we are clear that extreme care must be taken when interpreting single peaks from AMS data. MF is a marker and should not be considered completely representative of the composition of the parent aerosol.

4 Specific Comments:

1.) Page 25548, Lines 15-17: *This sentence is mostly true; however, a study by Froyd et al. (2010, PNAS) that was just published showed the real-time detection and quantification of IEPOX derived organosulfates in ambient aerosol collected from several flight campaigns near isoprene-rich regions using the NOAA PALMS instrument. Their results show significantly high concentrations of this single compound. In fact, considering the high amounts of sulfate (and likely low-NO_x conditions) observed in your PM₁ samples I suspect that IEPOX-derived organosulfates could be in this aerosol. I wonder, would you suspect that these C₅H₅O₊ signal you observe?*

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We thank the reviewer for bringing this interesting paper to our attention and will include a reference to it as follows:

“While previous work has identified a number of potentially important mechanisms (Chan et al., 2010; Paulot et al., 2009), the ambient measurements are **largely** based on offline analysis of bulk samples. **However, one recent study has measured isoprene SOA online, with IEPOX-derived organosulphates being detected using Particle Analysis by Laser Mass Spectrometry (PALMS; Froyd et al 2010).**”

As stated in the responses above, we believe it is possible that some established isoprene SOA (such as the isoprene derived organosulphates) could be the source of the observed *m/z* 82 peak, however we cannot envisage an appropriate mechanism. Specifically the condensed phase compounds detailed in Surratt et al. 2009 are highly functionalized with hydroxyl groups and it is not clear how they would be defunctionalised and cyclised to form MF. We hope that future work nebulising isoprene SOA will shed light on this (as indicated by the addition of the sentence detailed above).

2.) Page 25549, Lines 14-17: *It isn't clear to me why the air was dried before sampling at the ground site. Why was this done? Couldn't this affect the aerosol and potentially its chemical constituents?*

Drying of aerosol was necessary in Borneo due to the very high ambient RH and changes in temperature between canopy top, where the sample was taken, the understorey and the laboratory, which would have led to condensation in the lines as their temperature reduced. Whilst this may affect the sampled aerosol, it is necessary in order to make any successful measurements. We will change page 25549, line 14-16 to the following for clarity:

“Air was then sub-sampled isokinetically from the centre of this flow at 35 l min⁻¹. **To avoid condensation in the lines**, sampled air was dried using a 780 tube Nafion drier using a dry air counter flow, where the air was decelerated to the laminar flow regime”

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3.) Page 25559, Lines 17-20: Can the authors provide any insights into the sources of sulfate (i.e., marine or anthropogenic)? How acidic might these particles be?

We believe the vast majority of sulphate aerosol to originate outside the island. It appears there are both anthropogenic and marine sources of sulphate. It also appears that, while sulphate is largely neutralized by its arrival at the measurement site, it is acidic over marine environments. These assertions will be presented in two coming papers. They will be summarized with relevant references to papers in preparation as follows (also some spelling corrected):

“Sulphate levels in Borneo are around four times greater than in the Amazon. **Inspection of back trajectories suggests marine and anthropogenic sources of sulphate external to Borneo (Robinson et al 2011a). A charge balance of sulphate and ammonium ions show excess sulphate over the oceans (Robinson et al 2011b) compared to the ground site where charge is usually balanced.**”

4.) Pages 25560-61 Lines 29-30 and Line 1. This conclusion should be revised or removed all together. Even though it is currently unclear how MF could be produced from established isoprene SOA constituents, no tests were done in this study to confirm that these compounds don't make MF signals in these harsh techniques. Thus, there is no clear data to support that unidentified isoprene products are producing MF signals in your techniques.

Again, we feel that we are transparent that we are speculating that MF is from previously unseen isoprene SOA. To make this clearer, we will change the indicated line to: **“While established isoprene SOA such as IEPOX derived organosulphates may be the precursor aerosol to MF measurements, it is unclear what mechanism could produce MF from these species. It is possible therefore that MF is produced from previously unidentified isoprene product(s).”**

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 25545, 2010.

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