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Atmospheric
Chemistry
and Physics
Discussions

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.

Anonymous Referee #2

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GENERAL COMMENTS

This manuscript presents AMS data collected from aircraft- and ground-based measurements from a tropical forest in Danum Valley, Borneo, Malaysia. From their AMS data analyses, the authors find an ion at m/z 82 that appears to be well correlated with isorpene oxidation products (i.e., MACR and MVK), and thus, serves as a tracer ion (not a specific compound) in AMS datasets for isoprene SOA. This well-written paper is certainly significant and publishable in Atmospheric Chemistry Physics; however, 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

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Figure 2a and 2b. This ion seems to be so small that is almost apart of the background noise in the MS data collected from the field. 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. Although this ion appears to be due to methylfuran (MF) based on comparison to an authentic standard and smog chamber-generated isoprene SOA, MF detection is in essence an artifact of the AMS technique. 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, 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. Although the AMS and GC/MS techniques both see the m/z 82 ion, they both employ high temperature conditions and electron impact ionization to detect their molecules, and thus, it is expected that they would both observe this ion. Both of these conditions are very harsh on molecules and certainly break them down quite easily. It would be more convincing if one of these techniques was orthogonal to the other. For example, the use soft ionization MS techniques (e.g., ESI-MS or MALDI-MS) to detect intact molecules would be more helpful. If the authors could detect an intact molecule of isoprene SOA and correlate to the AMS ion detected at m/z 82, then this would be more conclusive as a source of isoprene SOA. Although there is some concerns with the dataset, I think if the authors include these caveats in their description of their dataset then I think it would be publishable in Atmospheric Chemistry and Physics in its current form. I think it is important to have this discussion of the interpretation of AMS

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datasets in the literature and to realize the limitations of what the AMS can actually do. 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.

In addition to the above, I kindly request the authors consider the specific comments below:

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-NOx conditions) observed in your PM1 samples I suspect that IEPOX-derived organosulfates could be in this aerosol. I wonder, would you suspect that these C5 compounds could contribute to your $C_5H_5O^+$ signal you observe?

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?

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?

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.

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

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