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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Linking biogenic hydrocarbons to biogenic aerosol in the Borneo rainforest" *by* J. F. Hamilton et al.

Anonymous Referee #2

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Overall Comment and Recommendation:

PM2.5 samples were collected at the WMO Bukit Atur Global Atmospheric Watch station in Malaysian Borneo during June and July 2008. These samples were chemically characterized by liquid chromatography coupled to electrospray ionization ion trap mass spectrometry (LC-MS2) and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICRMS). The former technique allowed for the generation of fragment ions that could be compared to chamber samples generated from a number of biogenic VOCs and the latter technique allowed for the determination of elemental compositions of all observed ions. The authors develop the use of scripts to generate an LC/ESI-MS library from chamber samples to analyze the field samples. This is an interesting approach. It is well described by the authors why biogenic secondary organic aerosol

(BSOA) were generated in their indoor chamber for this study; specifically, they did this to generate "authentic-like" compounds since they were not able to conduct "traditional" organic synthesis. In total, the authors identify 18 BSOA tracers using their approach. Overall, this is a well written, concise, and nicely presented manuscript. The analytical methods are well utilized and the conclusions are supported by the data. The authors also do a great job in relating their findings to other field studies conducted in forested locations and are also careful in not over interpreting their findings. I only ask the authors to address my minor comments below before publication in Atmospheric Chemistry and Physics. As a result of only having minor comments, I must recommend this paper be accepted with minor revisions noted.

Minor Comments:

1.) Introduction, Page 18115, Lines 4-7:

The authors should break up citations and directly associate the ones related to boreal and temperate forests. For the boreal forest, the authors should also cite recent work by Kristensen et al. (2011, Atmos. Environ.).

2.) Section 2.2.:

Although you describe it later in the results section, you may want to go ahead and state that these were irradiation experiments and not dark reactions.

3.) Results Section, Pages 18120-18121, Lines 23-27, Lines 1-4:

I understand that you use NOx in these experiments to generate sufficient amounts of OH to react with your BVOCs, and you clearly acknowledge the issues this may cause with the oxidation mechanisms. This "classical" approach to generating SOA from VOCs requires a careful selection of the initial VOC/NOx ratio. As the first reviewer also noted, why was NOx even used if the field site was likely a lower NOx condition? I don't have issue with this as much, but I suspect that your initial nitric oxide (NO) quickly approaches zero in your experiments once you turn on the lights. In fact, in

Table 1, you need to clarify what fraction of your initial NOx is NO and NO2. As NO approaches zero, you likely begin making SOA and O3 in all of your BSOA experiments described in Table 1. However, at this same time, you likely have some unreacted BVOC remaining. Thus, this allows for the remaining BVOC to react with OH under a low-NO limit, resulting in your RO2 radicals either reacting with HO2 or another RO2 instead of NO. As a result, you are able to produce some of the same SOA constituents produced in the rainforest samples.

4.) B-caryophyllene SOA (Section 3.5):

The authors should acknowledge work by Jaoui et al. (2007, GRL) on detecting b-caryophyllinic acid (MW 254).

5.) Section 3.6 Molecular Composition, Page 18127, Line 2:

Change "(Bateman et al., 2010)" to "Bateman et al. (2010)

6.) General Notes About Composition:

a.) I just want to point out to the authors that the organosulfate of isoprene at m/z 199 (as mentioned in their Table 3) has been recently shown to form from the reactive uptake of methacrylic acid epoxide (MAE) (Lin et al., 2013, PNAS). Although epoxides of isoprene (i.e., isomeric IEPOX and MAE) explain the formation of m/z 199 and 215, which are typically the most abundant organosulfates observed in the southeastern U.S. (Lin et al., 2013, ACP, in press), the mechanism of formation of the remaining organosulfates from isoprene (as well as other BVOCs) remains unclear. Some groups (like the Turpin and Noziere groups) have postulated from lab studies that sulfate radicals may play a role in forming some organosulfates from BVOCs.

b.) In Table 2, you don't report the detection of m/z 199. Did you try extracting the m/z 199 ion out of the LC/MS TIC? Do you see it if you do that? It likely elutes very closely to the m/z 215 organosulfate. Further, you observe the nitrated organosulfate (m/z 260) in Table 3, but don't report it in Table 2. Did you try extracting the m/z 260

ion out of the LC/MS TIC? Do you see it if you do that? Lastly, I'm curious if you can see m/z 119, which is associated with 2-methylglyceric acid. 2-methylglyceric acid is another known isoprene SOA tracer and has now been demonstrated to form from the reactive uptake of MAE in the presence of sulfate aerosol (Lin et al., 2013, PNAS).

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 18113, 2013.