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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Real-time detection of highly oxidized organosulfates and BSOA marker compounds during the F-BEACh 2014 field study" *by* Martin Brüggemann et al.

Anonymous Referee #1

Received and published: 5 September 2016

Brüggemann et al. describe a detailed mass spectrometric analysis of organic aerosols during a field study in a forest in southeast Germany in July 2014. The array and novelty of the gas- and particle-phase analyses completed were impressive. The opportunity to compare trends in HOMs, sulfate, and HOOS is exciting and has the potential to improve our knowledge of organosulfate chemistry. However, much of the discussion is general with more focus on the methods and comparison of those methods rather than the science. I suggest major revisions with focus the results pertaining to advancing our knowledge of biogenic SOA. In particular, the detailed comparison of specific HOMs and HOOS in section 3.2 is exciting and should be expanded and examined in greater detail with additional ion markers examined and compared to the LC-HRMS results.

Additional discussion of the methods and comparison of the methods are suggested to be moved to the supplemental.

The abstract can be improved significantly. Much of the abstract reads as a list of methods and types of compounds measured with only vague, general aspects of the results stated, such that the unique findings and implications are not as clear as possible. It would be improved by focusing more on the main details of the scientific results and implications of the study, rather than the analytical aspect of the study. Similar advice should be considered for the conclusions section.

The discussion in section 3.1 is general within minimal in-depth analysis and much focus on the methods, rather than the results. The statement on lines 21-24 (page 7) oversimplifies the pathway from emission to SOA formation and does not account for oxidation pathways, reaction kinetics, and reaction yields. Then on line 28 it is stated that "rather low abundances were found for early-generation oxidation products". What is considered "rather low" compared to expected based on other studies? Do the volatilities of the expected compounds suggest that they should be significantly in the particle phase? On line 31 (page 7), it is stated that "…fast photochemical aging processes, eventually result[ed] in high abundances…"; without knowledge of the oxidant concentrations or reference to solar radiation measurements, is difficult to assess this general statement. The discussion of organosulfates and related compounds (lines 3-11, page 8) is general, focusing most on the method. However, many papers have been published using UPLC-HR-MS to study organosulfates, so this level of detail about the method is not necessary to include in the main text. I would suggest moving elsewhere (supplemental?) and combining this and the following paragraph. Additionally, the list of previous papers on line 14 (page 8) is not comprehensive as currently implied. This section suffers most from a lack of discussion of the properties of the HOOS, which appears to be a focus of the paper. Again, the text on lines 21-24 and 27-28, for example, focuses on the methods, rather than the scientific results. Other examples can be provided. Overall, the authors might consider reorganization of section 3.1 to first discuss MEGAN results, then VOC results, then met/HYSPLIT information, and finally SOA results to provide justification first for the observed biogenic SOA markers. The case study of July 21 seems useful, and it might be helpful to also include LC-HRMS individual compound results in this examination for greater interpretation. Overall, the authors should focus on the scientific results rather than explanation of the methods, information about which should be in the methods and supplemental. Similar issues are present in section 3.2 and should be considered.

Are the authors suggesting that the RO2 directly reacts with sulfate in an implied heterogeneous reaction (Page 12, lines 30)? Why does the RO2 need to be the immediate precursor? This would contradict work of Surratt and most others in the consideration of the formation of organosulfates. However, as summarized by Xu et al 2015 (PNAS) in Fig 3, RO2 can be a precursor of organosulfates through the subsequent formation of an epoxide, followed by nucleophilic addition.

Specific Comments: Page 2, lines 2-3: It is unclear what “a good agreement” means here.

Page 2, lines 4-5: What aspect of HOOS is implied to be increased here?

Page 2, line 11: Is biomass burning SOA really considered anthropogenic? Wildfire smoke is not necessarily human-caused.

Page 2, line 8: The phrasing “Yet, until now a comprehensive structural elucidation of HOMs was not possible” implies that the structures, rather than just elemental formulas, of HOMs were determined in this study; this seems misleading.

Page 5, lines 2-3: The statement that PM1 mass closure was achieved is not necessary and is misleading, as it suggests that refractory material did not at all contribute to the aerosol at this site, which is difficult to believe.

Section 2.1: What is the forest canopy height at the field site, and what height does the canopy start at? This is needed to understand whether various measurements were

located within, below, or above the forest canopy. Also, please provide measurement heights in Sections 2.4 and 2.5. It would be helpful if an overview of measurement locations could be provided in Section 2.1.

Section 2.4: Please provide details regarding the sampling inlet. What are the transmission losses of the HOMs and sulfuric acid through the inlet? What were the uncertainties and limits of detection for sulfuric acid during this study?

Section 2.6: What VOCs were able to be investigated in this configuration?

Page 9, line 17: What fraction of the total OA mass did the 93 compounds comprise?

Page 9, lines 29-30: Since both MBTCA and pinic acid were quantified by LC-HR-MS, why can’t these concentrations be used to calculate the “aging” ratio, rather than the raw AeroFAPA-MS signals?

Page 9, line 33: By “low altitudes”, do you mean within the boundary layer?

Page 11, lines 30-32: The authors should consider the work of Xu et al 2015 (PNAS) who examined in detail correlations between organosulfates, RH, and sulfate concentrations. This may improve interpretation of these results.

Figure 4: The results of this figure should be discussed in greater detail in the text, taking the LC-HRMS data into greater consideration.

Figure 5: This figure could be moved to the supplemental, as the main scientific point is not clear.

Technical Comments: Page 3, lines 7-8: Fix reference location.

Page 4, Section 2.2: The first two sentences should be combined with the following paragraph to be one full paragraph.

Section 2.6: The two paragraphs in this section can be combined to avoid the presence of a two sentence paragraph.

Page 6, line 11: Why is the ratio listed as 2:8 instead of 1:4?

Page 6, lines 16-17: The phrasing of this sentence does not make sense.

Page 6, line 24: Given the mass resolving power and tolerance (given on lines 21 and 31), for what m/z range can compounds be unambiguously determined?

Page 6, line 29: The “signal threshold. . .for the detection of significant signals” is stated and in arbitrary units. It would be more meaningful if a S/N threshold were listed.

Page 7, lines 4-6: Similar to the previous comment, there is no context given for “integrated peak areas of >10ˆ7 a.u.”. Some relationship to S/N thresholds would be useful here.

Page 7, lines 6-7: Does this mean that the previously mentioned 695 compounds (on line 3) were not within a mass accuracy range of +/- 5 ppm? This would be concerning. In addition, it would be useful to provide the m/z range of the identified compounds.

Page 7, line 11: I am guessing that the authors mean “and” instead of “or” here.

Page 7, lines 11-15: This calibration information could be moved to the methods or supplemental so that the authors can focus on science here. Also, it is not clear here whether all 93 compounds were calibrated with pinic acid or just pinic and terpenylic acid.

Table 1: Why are m/z 255 and 357 listed here if they were below the LOQ? Was there any day/night difference observed?

Page 7, lines 19-21: This suggests that MBTCA is a minor (in terms of yield) pinene oxidation product. Is this correct? Please clarify the comparison.

Page 7, lines 23-24: Were these the only VOCs quantified? This information is not provided in the methods, so it is difficult to fully interpret this result.

Page 8, lines 1-2: Move this statement to the methods section.

Supplemental, Page 1: For clarity, please add a header with the title and author names to the supplement.

Fig S-7, bottom panel caption: For clarity, please indicate the instrument used.

Fig S-8, caption: Additional information for interpretation of the figure would be helpful.

Fig S-9: A legend would be helpful.

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