Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-650-RC2, 2016

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 #2

Received and published: 6 September 2016

The manuscript presents interesting new work investigating the composition of organic aerosols using a suite of state-of-the-art mass spectrometric techniques. The results are interesting, but some interpretations are not fully supported by the data in the present version of the manuscript. The development of new instrumentation to investigate organic aerosol composition is important and exciting, but it is necessary to have a deep respect for the possible new artefacts and biases associated with the techniques.

Specific comments Check that the word "identification" is used correctly (according to Nozière et al., 2015) throughout the manuscript.

Abstract The abstract needs a thorough revision to correctly reflect the findings. Page 1 Line 20: How do you "identify a characteristic contributor"? L23-24: I would not

characterize concentrations around 10ng/m3 as "high". Please be specific instead. L24. The present data does not support the statement that terpene oxidation products dominate the organic aerosol fraction. The AMS data shows OA mass in the range 2-8 microgram/m3, while only few terpene oxidation products have been identified and quantified with a total concentration of about 1% of this mass.

L25. How high? L28: Did the air masses pass areas of high BVOC emissions such as coniferous forests? L32: How do you define "unambigious identification"? Generally authentic standards would be needed to support this.

P2 L4: The word "reveal" should generally be avoided in the scientific literature. Here you could use "indicate" instead.

P3 L4: Why is important to state that the LC-MS analysis is non-target, since most such analyses would be this? I suggest removing the term throughout the manuscript.

P4L11: Were there any size-selection? A previous paper (Brüggemann et al., EST 2015) describes an SMPS system in front of the AeroFAPA-MS. P4L3: Are all organic components evaporated at 200C? Will organosulfates evaporate at 200C? What happens to components remaining in the particle phase including inorganic species? The answers to these questions must be given in the manuscript.

P5L1: "data quality insurance" - do you mean quality control of the data?

P6L7: The extraction solvent seems relatively polar. Was the extraction efficiency of larger carboxylic acids (such as pinic acid) and organosulfates investigated? Could differences in extraction efficiency have affected the relative proportion between e.g. C7 and C10 organosulfates? P6L11-12: Is it correctly understood that the average recovery only reflects the loss during evaporation, not extraction efficiency?

P7L1- and Table 1: It is impressive that 695 individual compounds are eluted in only 4.1 minutes (according to information on the UHPLC gradient). How were possible matrix effects (leading to signal suppression during ESI) avoided or corrected? Why was pinonic acid not quantified? This would have been useful for the discussion of photochemical aging. The higher concentration of MBTCA compared to e.g. pinic acid could indicate that the BSOA components are long range transported rather than locally produced. It would be useful to compare the concentrations in Table 1 to previous measurements in similar areas. Please remove compounds below limit of detection from Table 1 and just mention them in the text.

P8L11: It is a bit surprising that Hallquist et al. already in 2009 made such general conclusions on the ubiquity of organosulfates and nitrooxy organosulfates, given the very few studies conducted at that time. Please recheck or update the reference.

P9L7: Have any of the commercially available standards for organosulfates been analyzed with AeroFAPA-MS? Since the ionization technique is known to form adducts (Brüggemann, Karu and Hoffmann, J. Mass Spectrometry 2016), how was it investigated that organosulfates or organonitrates are not formed during analysis of complex samples such as aerosols containing both organic and inorganic components?

P9L12: What do you mean by "quantify"? P9L13-26: Just because the two data sets correlate, it does not mean that the Aero-FAPA-MS signal explains the variability in the AMS organic matter data. There could be other underlying common factors involved, such as long-range transport or photochemical processes. Without any quantification of the Aero-FAPA-MS measurements, the statements that "these compounds reflect major sources" and "particle phase was dominated by BSOA markers" remains not fully documented by the data. Please correct the sentence to reflect your findings more accurately. P9L27: Concentrations of pinonic acid were not listed. P9L28-30: Since MBTCA is an oxidation product of pinonic acid (with OH) the ratio MBTCA to pinonic acid would make more sense. Please include relevant references for using this ratio.

P10L1: "transported aerosol masses" -> "transported air masses" The text on this page is quite "lengthy" and could be shortened and clarified. P10L19-24: The extraction efficiency of larger compounds with the polar solvent could also affect the ratio. Since authentic standards of highly oxidized nitrooxy carboxylic acids have probably never been measured by Aero-FAPA-MS, the statement about "reliable detection" seems speculative. Furthermore possible in-source formation should be investigated. On-line methods are certainly important for measurements of these compounds, but further work is also needed.

P11L3 and Figure 5. The purpose of Figure 5 is not clear. It seems that one compound was not "found" but rather "selected". The figure should be moved to supplementary information. The first paragraph of page 11 could be shortened and focused. P11L7: In agreement with what? P11L17-28: Are the HOOS presented and discussed here only the compounds selected in the paragraph above? Please make this more clear - also in the text of Fig. 6. Could the difference between the HOOS classes observed with LC-MS and Aero-FAPA-MS also be due to differences in ionization efficiency and the question of extraction efficiency discussed above? P11L32-35: Higher concentration of sulfate (and pH) also affects surface uptake and reactions.

P12L8-13 and L17: It is not clear how the hypothesis of "rapid phase transition" of HOMs is supported by the present data. RH is closely related to temperature, and thus time of day, which also affects emissions of BVOC. There could thus be other explanations than condensation for the variation in level of HOMs.

It is very interesting how the levels of HOOS and peroxy radicals vary together.

P12L28-31: Please clarify how this relates to previously proposed mechanisms for OS formation.

Conclusion: Please adjust according to your answers to questions stated in this review.

Figure 2 lower panel: The figure is too overloaded with information in overlying graphs. Please make the figure more clear by e.g. moving the data sets further apart.

Figure 5 should be moved to supplementary information.

Figure 6. The figure is too busy. Part A could be moved to supplementary information. The marker size is too large for high concentrations of sulfate, which gives a bias in the understanding of the number of data points. Write e.g. C7 vs. C8 to make the figures easier to understand. Are the HOOS all compounds or just the ones selected to represent each group?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-650, 2016.