

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 #3

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The manuscript presents interesting investigation on the chemical characterization of organic aerosols collected in southeast Germany. Large variety of mass spectrometry techniques (online and offline) was deployed and the results proposed in this study could provide new insights in the organosulfate chemistry. However, the discussion/interpretation of the results are not well supported and most of the discussion is focus on the comparison of the methods. I suggest major revisions of the manuscript to better discuss the different findings of this study. In particular, the discussion on the potential formation of organosulfates from the heterogeneous oxidation of RO₂ radicals is not well sustained and requires deeper investigation. For instance, only one RO₂ radical was considered in the discussion (while 4 were identified) and the authors

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did not consider the other pathways recently reported in the literature (i.e. heterogeneous reactivity of organic hydroperoxides). In general, the authors should better compare/discuss their results with the existing literature.

Please revise the abstract to highlight the findings of this study

Page 2: lines 27-32: The authors mentioned the different pathways leading to the organosulfate formation but some reaction pathways are missing. Indeed, organosulfates could be formed by either nucleophilic substitution of an organic nitrate group by sulfate (Darer et al., 2011; Hu et al., 2011), or by heterogeneous chemistry of gas-phase organic hydroperoxides, which might undergo acid-catalyzed perhydrolysis followed by reaction with sulfate ions (Riva et al., 2016a; 2016b).

In addition, the authors should also include the following references: - Reactive uptake of epoxides: Shalamzari et al., 2014; 2016 - Sulfate radicals: Schindelka et al., 2013. - SO₂: Passananti et al., 2016

Page 3: lines 1-5. It has been recently reported that HOM monomers formed from the oxidation of α -pinene are unlikely to be ELVOCs even when their O:C ratios are close to 1 (Kurten et al., 2016). Please correct.

Lines 16-19: Since Mutzel et al., 2015; several studies have discussed the reactivity of organic hydroperoxides. For example, Surratt and co-workers have reported recently the formation of organosulfates from the acid catalyzed hydrolysis of organic hydroperoxides (e.g. isoprene dihydroxydihydroperoxides). Please revise this sentence.

Line 24: Please specify the reagent ion used: NO₃-

Page 4: Lines 13-14: How does the temperature impact the integrity of the compounds (acids, organosulfates)? Indeed, it has been reported recently that accretion products could decompose at high temperatures (Lopez-Hilfiker et al., 2016).

Page 7: Lines 11-14: The authors should better discuss this point and the potential artifacts of their measurements. The ionization efficiency could be impacted by the

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structure of the compounds but also by the composition of the mobile phase (organic phase enhances the ionization efficiency). Is it the reason why the authors decided to use the mobile phases (i.e. water spiked with ACN and ACN spiked with water) described page 6? In addition, the authors should point out the potential matrix effect (i.e. ion suppression). Have they investigated this aspect?

Lines 18-21: Please add references: Glasius and co-workers.

Lines 22-24: Could the authors provide the concentration of isoprene since they also identified some isoprene-derived organosulfates (e.g. m/z 213; 215)?

Page 8: Lines 1-2: I agree that measurements of sesquiterpenes required special setup due to their high reactivity but it is not clear why the oxidation products cannot be measured due to their "high reactivity and low volatility". If they are low volatile the techniques used in this study should allow the detection of such products in gas and particle phases. In addition, could the authors provide the reference(s) reporting the reactivity of sesquiterpene oxidation products? Have the authors compared the products identify in this study with previous works, such as Chan et al. (2011)?

Lines 5-6: The mass accuracy (formula determination) obtained from the UHPLC/ESI-HRMS cannot be solely used to validate the presence of organosulfates. MS2 data of organosulfur compounds such as organosulfate lead to specific fragment ions such as m/z 97 or 80. As recently reported by Riva et al. (2015), other organosulfur compounds such as sulfonate could be distinguished by analyzing the MS2 spectra. Therefore, the authors should use the MS2 data generated from the UHPLC/ESI-HRMS to further support their assignments.

Lines 7-9: This sentence is a bit confusing. Are the contributions of CHON, CHOS and CHONS based on the number of compounds identified? The relative abundance? Please clarify.

Line 28: The authors wrote "since inorganic species are typically not volatilized and

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ionized by the AeroFAPA ion source." Please support this statement by a reference.

Lines 33-34: Could the authors further discuss the event identified during the night of the 21st of July? Why are the particles with relative large diameters attributed to a regional source? Did the authors observe any increase on the concentration of inorganic species during that night (sulfate)? Any anthropogenic tracers exhibit a larger concentration?

Page 9 Lines 4-6: This sentence is not clear. What do the authors mean by "deviations between the signals of the instruments"? The authors should also consider the ozonolysis of monoterpenes in the formation of oxygenated species. As recently reported by Yan et al. (2016) ozonolysis of α -pinene is an important pathway in the oxidation of monoterpenes during the night. Finally organic hydroperoxides could also be formed from the oxidation of monoterpenes. Please revise this sentence.

Lines 16-18: How do the authors know that the 93 compounds have a major contribution to the organic aerosol? Indeed, no quantification has been performed and Aero-FAPA-MS is not sensitive (as mentioned by the authors paragraph 2.2) to a large variety of non-acidic compounds such alcohols, hydroperoxides, or aldehydes.

Lines 19-21: Please revise this sentence. It is not because the two data sets correlate that means the Aero-FAPA-MS explains the variability in OA measured by the AMS.

Page 10. Line 30: Further information/discussion should be added in the new version of the manuscript to better justify the choice of the selected organosulfates. Indeed, the choice appears arbitrary and is not well justified. Why did the authors consider only the organosulfates from C7 to C10? Finally the authors should cite the previous laboratory studies that have identified the precursors for the different organosulfates/biogenic tracers identified in this work (c.f. Table S5).

Page 11. Lines 29-34: The authors should estimate the aerosol acidity and correlate the different class of organosulfates vs the aerosol acidity. As written in the manuscript

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their results suggest that organosulfate formation is higher under high RH and high concentration of sulfate periods. As reported in previous works the aerosol acidity significantly enhances the formation of organosulfate. However, smaller effects were observed under high-RH and is attributed to dilution of aerosol acidity by additional particle water (Gaston et al., 2014). Therefore, as presented in the manuscript the results appear different than those previously reported and the impact of aerosol acidity should be further discussed.

Page 12. Lines 5-7 and 21-24: Formation of HOMs has been proposed to occur through auto-oxidation reactions, which could lead to the formation of organic hydroperoxides. Recent works have reported the hydrolysis of organic hydroperoxides in the aerosols and the formation of oligomers as well as organosulfates (Lim and Turpin, 2015; Riva et al., 2016a; b). In addition to the proposed reactive pathway, the authors should further discuss the potential formation of organosulfates from the hydrolysis of organic hydroperoxides, especially since they suggest that “aqueous-phase chemistry plays a major role for HOOS production” (Page 11, line 32-34).

Line 15: Why did the authors focus the discussion on only one RO₂ radical (i.e. C₁₀H₁₅O₈) while they have identified 4 RO₂ radicals? Do they have the same profiles? Is the lifetime of RO₂ long enough to be transferred to the particle phase and react with sulfate? Is the concentration of C₁₀H₁₅O₈ large enough to explain the formation of the parent ion at m/z 327? If the authors expect/propose the RO₂ radicals to be the precursors of the HOOS a box model is needed to evaluate the possibility of such reactive pathway.

Finally, the authors should also provide similar time series for the ion at m/z 326 (C₁₀H₁₆O₈ + NO₃) and compare the time-series of HOMs with the different RO₂ radicals.

Please update/correct according to your answers the abstract as well as the conclusion.

References:

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Chan et al., 2011; *Atmos. Chem. Phys.*, 11, 1735–1751. Darer et al., 2011; *Environ. Sci. Technol.*, 45, 1895–1902. Gaston et al., 2014; *Environ. Sci. Technol.*, 48, 11178–11186. Hu et al., 2011; *Atmos. Chem. Phys.*, 11, 8307–8320. Kurten et al., 2016; *J. Phys. Chem A*, 120, 2569-2582. Lim and Turpin, 2015; *Atmos. Chem. Phys.* 15, 12867-12877. Lopez-Hifliker et al., 2016; *Environ. Sci. Technol.*, 50, 2200-2209. Passananti et al., 2016; *Angew. Chem. Int. Ed.*, 55, 10336-10339. Riva et al., 2015; *Environ. Sci. Technol.*, 49, 5407-5416. Riva et al., 2016a; *Environ. Sci. Technol.*, DOI: 10.1021/acs.est.6b02511. Riva et al., 2016b; *Atmos. Chem. Phys.*, 16, 11001-11018. Schindelka et al., 2013; *Faraday Discuss.*, 165, 237–259. Shalamzari et al. 2014; *Environ. Sci. Technol.*, 48, 12671–12678. Shalamzari et al. 2016; *Atmos. Chem. Phys.*, 16, 7135–7148. Yan et al., 2016; *Atmos. Chem. Phys. Disc.*, DOI:10.5194/acp-2016-367.

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

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