

Black = reviewer comment

Blue = author response

Reviewer 3:

“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 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.”

The authors thank the reviewer for taking the time to comment on our manuscript. The authors have taken the reviewers comments into account in a revised version of the manuscript. The details given below show how each comment was addressed in the revised manuscript.

1) “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). “

The authors agree with the reviewer and the following sentence was added to the manuscript (P2L26):

Furthermore, it was shown that such compounds are formed by nucleophilic substitution of nitrate groups 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).

2) “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”

The authors thank the reviewer for these additional references. The following sentence was changed as follows (P2L22):

Studies have shown that OS and NOS are formed in the condensed phase, either from VOC gas-phase oxidation products with sulfuric acid in acidic sulfate aerosols (Iinuma et al., 2005; Liggió and Li, 2006; Iinuma et al., 2007; Surratt et al., 2007; Surratt et al., 2008; Shalamazari et al., 2014; Shalamazari et al., 2016), or also directly by the reaction of gaseous SO₂ with unsaturated carboxylic acids (Shang et al., 2016, Passananti et al., 2016).

3) “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.”

To account for these recent findings, the following sentence was added to the text (P3L2):

Nonetheless, recently it was shown that HOM monomers formed from the oxidation of α -pinene are unlikely to exhibit saturation vapor pressures in the range of ELVOCs – even when their O:C ratios are close to 1 (Kurten et al., 2016).

4) “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.”

The authors agree with the reviewer and the following sentence was added (P3L18):

Nonetheless, recently Riva et al. (2016a) reported on the formation of organosulfates from the acid catalyzed hydrolysis of organic hydroperoxides.

5) “Line 24: Please specify the reagent ion used: NO₃-“

The sentence was changed according to the reviewer’s suggestion (P3L23):

[...] and Chemical Ionization Atmospheric-Pressure interface Time-of-Flight Mass Spectrometry (CI-API-TOFMS) using nitrate (NO₃⁻) as ionization reagent (Jokinen et al., 2012).

6) “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).”

Unfortunately, at this point the authors cannot completely rule out the decomposition of accretion products during the analysis. However, the authors believe that such contributions to the number and abundance of signals are rather small since a good agreement to AMS and LC-MS measurements is observed. Furthermore, it should be noted that the temperature given in the text (i.e. 200 °C) is solely the temperature of the inlet but not the temperature that is reached for the aerosol flow. Nonetheless, in order to clarify this point the following passage was added to the section (P4L16):

Although heating is a common approach for aerosol evaporation and analysis, it should be noted here that recently Lopez-Hilfiker et al. (2016) reported on the decomposition of accretion products upon heating. Therefore, contributions of such decomposition products cannot be completely ruled out here.

7) “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 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?”

The authors agree with the reviewer and added information on potential artifacts and ionization efficiencies. For this point, please also read the answer to comment 14 of reviewer 2. Furthermore, the following sentence was added to the main text (P7L15):

Furthermore, the composition of the LC eluent can have additional effects on the actual ionization efficiencies.

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

The authors do not see any missing references here. Thus, no changes were made. If some essential references are missing here, please specify more clearly.

9) "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)?"

For the campaign period, no data on isoprene concentrations are available. However, previous studies at the site showed that isoprene mixing ratios are in the range of 0.27–0.50 ppbv (Klemm et al., Atmos Env, 2006). To give the reader an estimate on the contribution of isoprene to BVOC emissions at the site the following sentence was added to the text (P7L29):

Beside monoterpene emissions, previous studies at the site have shown that average mixing ratios for isoprene are typically in the range of 0.27–0.50 ppbv. An overview on typically VOC mixing ratios at the site can be found in Klemm et al. (2006) and others (Grabmer et al., 2006; Graus et al., 2006).

10) "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)?"

The authors agree with the reviewer and the statement was changed as follows (P8L10):

However, the contribution of sesquiterpene oxidation products on particle composition cannot be estimated here because the observed concentrations were typically below the quantification limits.

11) "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."

The authors agree that using MS2 data allows to distinguish between organosulfates and compounds such as sulfonates. However, in this case no MS2 data are available. In order to increase the time resolution of the LC-MS method (i.e. to decrease the cycle time of the Orbitrap-MS), which is beneficial in non-target approaches (e.g. Hun et al., 2016, Anal. Bioanal. Chem.), no MS2 data were acquired during the analysis. Nonetheless, to clarify that sulfonates might have a certain contribution here, the following sentence was added to the manuscript (P8L17):

It should, however, be noted that hydroxysulfonates are isobaric with organosulfates, and thus, might contribute to a certain extent to this class.

12) "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."

In order to clarify this point the sentence was changed as follows (P8L19):

While only 4% of the number of compounds were classified as CHON compounds about 47% of the compounds are either belonging to the CHOS or the CHONS group.

13) "Line 28: The authors wrote "since inorganic species are typically not volatilized and ionized by the AeroFAPA ion source." Please support this statement by a reference."

The authors cannot provide a reference for this statement, however, believe that this assumption is rather trivial. Since inorganic species, i.e. salts, can be considered as non-volatile, it seems unlikely that such species can be volatilized in the ionization region which exhibits maximum temperatures of merely 150 °C. Furthermore, a volatilization of inorganic species was never observed by the authors in any measurements.

14) "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?"

In agreement with HYSPLIT back trajectories (see Supplemental Material) and a strong increase of sulfate during the night (see Fig. 6, panel b) the authors are convinced that mainly particles from regional sources reached the site. To improve the discussion of the data, the following phrase was added (P9L11):

This observation is further supported by HYSPLIT backward trajectories, exhibiting rather low altitudes and trajectory lengths (Supplemental Material), as well as a strong increase in sulfate during the night (see also Fig. 5, panel b).

15) "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."

To clarify what is meant by "deviations between the signals", the sentence was revised as follows (P9L17):

Deviations between the signals for organics of the AMS and the total signals of the AeroFAPA-MS are mostly observed during nighttime [...].

Regarding the reference suggested by the reviewer, the authors do not see how this work fits into the discussed data. While in Yan et al. (2016) gas-phase measurements of HOMs and a subsequent source apportionment are discussed, here the focus lies on the composition of aerosol particles. Moreover, it is well known that ozonolysis of monoterpenes is occurring day and night. Therefore, this reaction cannot explain the deviations observed during nighttime for the AMS and AeroFAPA-MS measurements.

16) "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."

The authors agree with the reviewer and the expression "major contribution" was changed to "characteristic contribution". Furthermore, these compounds were identified from the

LC–MS measurements and not from AeroFAPA–MS data. In order to clarify, the sentence was restructured as follows (P9L29):

Furthermore, the AeroFAPA–MS signals ($[M-H]^-$) of the 93 compounds, which were previously identified from the LC–MS data as characteristic contributors to the organic aerosol fraction, were plotted as a function of the organic aerosol mass, determined by the AMS (Fig. 3, panel b).

17) “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.”

The authors disagree with the reviewer in this point. It is a widely-used and well-established interpretation of the squared correlation coefficient (i.e. R^2) to take it as a measure for the explained variability of a two-dimensional dataset. As an example, a quote from a course on statistics from Yale University:

“The square of the correlation coefficient, r^2 , [...] represents the fraction of the variation in one variable that may be explained by the other variable. Thus, if a correlation of 0.8 is observed between two variables [...], then a linear regression model attempting to explain either variable in terms of the other variable will account for 64% of the variability in the data.” (see: <http://www.stat.yale.edu/Courses/1997-98/101/correl.htm>)

More information can easily be found in standard textbooks on statistics (e.g. page 254 in “Statistics Explained”, Perry R. Hinton, 3rd Ed., Routledge, 2014).

Of course, the correlation coefficient alone cannot be used to proof causality, however, in this case both instruments were measuring at the same time the same aerosol mass. Therefore, the authors believe that causality is given here and the observed correlation gives evidence for the linear association of the observed signals of the two instruments.

18) “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).”

The discussion of the selection procedure was revised and additional information added to the passage. However, and also in agreement with comment 29 by referee 2, the authors believe that the discussion on the selection criteria of the signals for HOOS should not be extended further in order to avoid distraction from the focus of the work.

Please see P11L21f for the revised passage.

19) “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 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.”

The authors agree with the reviewer and additional information on aerosol acidity were added and compared to time series of different organosulfates. As a proxy for the aerosol

acidity molar concentrations of H^+_{Aer} were used, calculated from AMS data as previously shown by Zhang et al. (EST, 2007). In general, no correlation between aerosol acidity and organosulfate formation was observed here. However, it should be noted that the aerosol acidity was quite low over the entire campaign period. In order to give the reader more details on particle acidity and possible effects on organosulfate formation, the following passage was added (P12L28):

Furthermore, it should be noted that for the entire campaign period the particle acidity was very low and rather stable (average of $H^+_{Aer} = 7.4 \text{ nmol m}^{-3}$), indicating the presence of partially or even fully neutralized particles (Fig. S-11). In contrast to previous studies, which suggest aerosol acidity to be one of the main factors driving organosulfate formation (Surrat 2007, 2008; Iinuma et al., 2009, Gaston et al., 2014), no such effect was observed here. This result is, however, not contradicting previous findings, but rather indicating that even at low particle acidities HOOS formation can be observed, as it will be discussed in the following.

20) "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)."

The authors agree with the reviewer and are grateful for this suggestion and the corresponding references. The following sentence was added to the passage (P13L7):

An additional or alternative pathway for the formation of HOOS might be the hydrolysis of hydroperoxide-containing HOMs as recently reported for methylglyoxal-, isoprene-, and alkane-derived hydroperoxides (Lim and Turpin, 2015; Riva et al., 2016a, 2016b).

21) "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."

The authors focused on the discussion of this single RO₂ radical (C₁₀H₁₅O₈) because it showed the highest abundances during the campaign. In addition, three of the four identified RO₂ radicals show very similar time trends and are all possible precursors for the C₁₀ HOOS (i.e. m/z 293 = C₁₀H₁₅O₆; m/z 311 = C₁₀H₁₇O₇; m/z 325 = C₁₀H₁₅O₈). Only the RO₂ radical at m/z 393 (i.e. C₁₀H₁₅O₁₀) shows a different behavior. To clarify this point, the time traces of the missing RO₂ radicals were added to the Supplemental Material. Furthermore, the passage was revised and now reads as follows (P13L25):

Remarkably, the signals for three of the four identified RO₂[•] (i.e. C₁₀H₁₅O₆[•], C₁₀H₁₇O₇[•], C₁₀H₁₅O₈[•]) and HOOS follow the same trends during the dry periods, possibly revealing a connection between these species. Solely the signals for C₁₀H₁₅O₁₀[•] (i.e. m/z 357, [M+NO₃]⁻) exhibit a different behavior (Fig. S-13).

Although it is argued that there might be a direct or indirect link between these species and HOOS formation, the authors believe and emphasize that further laboratory work under controlled conditions is necessary to discriminate possible underlying reaction mechanisms. The application of a box model with large uncertainties would, thus, only add little additional evidence here and is beyond the scope of this work.

Nonetheless, to clarify that future work is needed to identify underlying formation pathways, the passage was revised as follows (see P13L32):

While the observed coinciding concentration profiles are not unambiguous for the limited available dataset, there might be a certain connection between RO_2^\bullet and the observed HOOS. In contrast, time series for a possible closed-shell HOM precursors, such as $\text{C}_{10}\text{H}_{16}\text{O}_{10}$ (m/z 358, $[\text{M}+\text{NO}_3]^-$), show only a weak agreement with signals for HOOS (Fig. S-14). As previously suggested, e.g. by Kurtén and co-workers (2015), RO_2^\bullet contain acylperoxy-functionalities which might possibly undergo a nucleophilic attack by HSO_4^- , forming the corresponding HOOS, which has been discussed for closed-shell HOMs earlier by Mutzel et al. (2015). Such a mechanism would explain HOOS formation coupling to RO_2^\bullet in the particle-phase and/or at the interface. However, knowledge on the existence of such formation pathways still needs to be much better explored.

22) “Finally, the authors should also provide similar time series for the ion at m/z 326 ($\text{C}_{10}\text{H}_{16}\text{O}_8 + \text{NO}_3$) and compare the time-series of HOMs with the different RO_2 radicals.”

The authors agree with the reviewer and an additional time series for the HOM species at m/z 326 (i.e. $\text{C}_{10}\text{H}_{16}\text{O}_8 + \text{NO}_3$) was added to the Supplemental Material. Nonetheless, since the focus of this work is not to investigate connections between closed-shell HOMs and RO_2 radicals, the authors compared the time series to the formation of HOOS. Furthermore, Figure S-12 is already comparing the time series for closed-shell HOMs and RO_2 radicals over the campaign period. The following sentence was added to the manuscript (P13L34):

In contrast, time series for a possible closed-shell HOM precursors, such as $\text{C}_{10}\text{H}_{16}\text{O}_{10}$ (m/z 358, $[\text{M}+\text{NO}_3]^-$), show only a weak agreement with signals for HOOS (Fig. S-14).