

Black = reviewer comment

Blue = author response

Reviewer 1:

“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.”

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) “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.”

As explained in section 3.2, the signals for the representative HOOS were selected based on several strict criteria in order to avoid wrong assignments. Therefore, only the signals that matched the criteria the best were selected eventually for further data analysis. Since the AeroFAPA-MS exhibits only unit mass resolution, it is difficult to unambiguously identify and monitor HOOS from the data of this instrument alone. A comparison to the LC-HRMS data is, thus, necessary. However, most of the signals from the LC-HRMS measurements show additional significant signals on the same nominal mass as the HOOS. Assuming that AeroFAPA-MS is measuring the same compounds, this means that a differentiation between HOOS and other compounds is not possible for such signals. Therefore, the authors believe that examining more ion markers from the AeroFAPA-MS data would lead to unnecessary high uncertainties for the discussed results.

2) “Additional discussion of the methods and comparison of the methods are suggested to be moved to the supplemental.”

In agreement with comments made by referee 2, the authors believe that a discussion and comparison of the methods is necessary, since the AeroFAPA-MS is a rather new and not well-established technique. Therefore, the authors would prefer to keep this part in the main text. However, details of the analysis of filter samples by LC-MS were moved to the Supplemental Material, since these procedures are well-known in the literature.

3) “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 authors agree with the referee and the abstract as well as the conclusion section were revised according to the helpful suggestions made.

(Please see the revised manuscript for the changed abstract and conclusions sections.)

4) “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.”

Since MBTCA and 3-carboxyheptanedioic acid are well-known and widely used marker compounds in laboratory as well as field studies for the oxidation of α -/ β -pinene and d-limonene, respectively (Jaoui et al., 2006; Szmigielski et al., 2007; Müller et al., 2012), the authors do not see an oversimplification here.

5) “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?”

In order to set the expression “rather low” in context, the authors added the results and the reference of another field study at the site (Plewka et al., Atmos. Env., 2006). With regards to their volatilities, these compounds can be regarded as semivolatile, meaning a significant fraction should partition into the particle phase. In agreement, compounds such as pinic acid are well-known SOA marker compounds resulting from α -/ β -pinene oxidation.

The following sentence was added to the text (P7L32):

Despite these relatively high mixing ratios for monoterpenes and isoprene, Plewka et al. (2006) already observed that early-generation oxidation products of isoprene and terpenes account only for a small part of the total organic carbon content of the particles at the site. In agreement to this work, similar concentrations in the lower $\text{ng}\cdot\text{m}^{-3}$ range were found during the F-BEACH study for early-generation monoterpene oxidation products, e.g. pinic acid ($c = 4.7 (\pm 2.5) \text{ng}\cdot\text{m}^{-3}$).

6) “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 authors are aware of the uncertainties, however, believe that sufficient evidence is given for this statement because of the high abundances of signals for photo-oxidation products (see also the references given in the manuscript). In order to account for these uncertainties, the expression “might indicate” was used in the text (see P7 L31). Moreover, a more detailed discussion of these compounds is also given a bit later in the text when the real-time measurements of the aerosol particles are discussed. Nonetheless, to give more evidence for photochemical processing the authors added the mean solar radiation observed at the site throughout the campaign.

The following sentence was added to the text (P8L6):

This hypothesis is also in agreement with high solar radiation values observed at the site, typically showing a maximum around midday at an average of $393 (\pm 15) \text{W}\cdot\text{m}^{-2}$. In addition, real-time measurements of the organic aerosol fraction and trajectory calculations also suggest a photochemical source for these compounds, as it will be discussed later on in the text.

7) “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.”

The authors agree with the reviewer and the description of standard procedures for the LC-HRMS measurements were moved to the supplemental material. Only a small section containing important and specific information was kept in the main text.

8) “Additionally, the list of previous papers on line 14 (page 8) is not comprehensive as currently implied.”

Here, the authors’ intention is not to give a comprehensive review on studies on organosulfates but just to highlight some studies which are related to the work. Nonetheless, in order to give a broader overview several references were added.

The sentence was changed as follows (P8L24):

Several of the identified sulfur-containing compounds were already studied in the past and found in field and laboratory studies (Liggio and Li, 2006; Surratt et al., 2007; Surratt et al., 2008; Altieri et al., 2009; Kristensen et al., 2011; Nguyen et al., 2012; Lin et al., 2012; Kristensen et al., 2016).

9) “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.”

As already mentioned above and in agreement with comments made by Referee 2, the authors believe that a discussion and comparison of the methods is necessary due to the novelty and unique combination of the applied methods.

10) “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.”

As stated in the manuscript the authors think that RO₂ might be a direct or indirect precursor (see P12 L27). Due to ambient conditions and the limited dataset it’s not possible to discriminate an exact reaction mechanism from the presented measurements. In order to clarify this, the passage was revised as follows (P13L32):

While the observed coinciding concentration profiles are not unambiguous for the limited available dataset, there might be a certain connection between RO₂[•] and the observed HOOS. In contrast, time series for a possible closed-shell HOM precursors, such as C₁₀H₁₆O₁₀ (*m/z* 358, [M+NO₃]⁻), show only a weak agreement with signals for HOOS (Fig. S-14). As previously suggested, e.g. by Kurtén and co-workers (2015), RO₂[•] contain acylperoxy-functionalities which might possibly undergo a nucleophilic attack by HSO₄⁻, 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 RO₂[•] 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.

The publication suggested by the reviewer (Xu et al., 2015, PNAS) is very interesting; however, it’s mainly focusing on the reactions of isoprene and organosulfates formed in reactions of this compound. However, the focus of this work is on the formation of organosulfates from monoterpenes (as discussed in the text). Therefore, the authors think that the aforementioned publication is only of limited relevance for the manuscript.

Specific Comments:

11-12) “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?”

The abstract was thoroughly revised according to the helpful suggestions made by the reviewers.

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

The authors agree with the referee that biomass burning cannot be solely considered as anthropogenic. Therefore, this expression was removed from the manuscript.

The sentence now reads as follows (P2L5):

Depending on the source of these VOCs the resulting SOA can be classified as anthropogenic SOA (ASOA), e.g. from fossil fuel combustion, or biogenic SOA (BSOA), e.g. from terrestrial or marine ecosystems (Hallquist et al., 2009; Nozière et al., 2015).

14) “Page 3, 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.”

In order to clarify that no structural elucidation will be discussed in this work, the sentence was changed as follows (P3L6):

Although a comprehensive structural elucidation of HOMs was not possible until now, it is assumed that these compounds largely contribute to both particle formation and growth (Riipinen et al., 2011; Donahue et al., 2012; Zhao et al., 2013, Tröstl et al., 2016).

15) “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.”

In order to avoid misunderstandings regarding refractory material, the sentence was changed as follows (P5L7):

The quality control of the data acquired by the AMS was made according to Poulain et al. (2014).

16) “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.”

As suggested by the reviewer, the missing information were added to the manuscript. The following phrases were added to section 2.1 to give a better overview of the field site (P4L3):

The canopy height and displacement height are ~23 m and ~15 m, respectively. A mixture of larch, beech, maple, and pine accounts for the rest of the tree population (Staudt and Foken, 2007). All instruments were arranged closely with inlet heights of 4–6 m above ground and at a distance of less than 10 m. Solely, VOC cartridges were sampled in and above canopy level at a distance of ~200 m from the other instruments.

17) “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?”

According to the reviewer's suggestions, the passage was revised and more information on the instrument were added.

For details, please see the revised passage (P5L9) of the manuscript.

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

In this configuration only monoterpenes were quantified. According to the reviewer's comment, the following information were added to the manuscript (P6L10):

Monoterpenes (i.e. α -/ β -pinene, *d*-limonene, Δ -3-carene, camphene) were quantified using authentic standards.

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

In this part of the manuscript, correlations between the data of the AeroFAPA-MS and the AMS are discussed. In a first step, all signals of the AeroFAPA-MS (in the m/z range 150–500) are correlated to the organic compounds that were measured by the AMS – but no quantification of the compounds is intended. Then, in a second step, only the signals of the previously discussed 93 compounds are taken into account for this correlation. Therefore, the authors believe that it is not necessary to discuss the fraction of the total OA here.

Furthermore, the authors did not discuss the fraction of the total OA mass for these 93 compounds in more detail because the exact chemical structures are not available from the measurements performed here. Thus, a quantification by standards is impossible and even a concentration estimation, as it is done for a few marker compounds, using a surrogate compound seems not reliable.

20) "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?"

The authors believe that a big advantage of the AeroFAPA-MS is the high time resolution. Using data from the filter sample extracts will lead solely to two data points for each day of the campaign period, while using the AeroFAPA-MS signals provides insights into dynamic changes on the timescale of hours or even minutes. Moreover, as discussed earlier in the manuscript, the AeroFAPA-MS shows a good agreement with the LC-MS data. Therefore, it is believed that an additional aging ratio from filter sample measurements would not add significant value to the manuscript.

21) "Page 9, line 33: By "low altitudes", do you mean within the boundary layer?"

The HYSPLIT trajectories (see Supplemental Material) show that at least some of the trajectories reaching the site were travelling within the boundary layer. In order to clarify this point the sentence was changed as follows (P10L12):

In agreement, HYSPLIT trajectory calculations reveal that arriving air masses typically traveled several days over land with distances of >1,500 km at low altitudes, often within the boundary layer (Figures S-1 to S-6).

22) "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."

As already mentioned above, the authors are very grateful for the suggestion of this interesting publication. However, due to the focus on reactions of isoprene in this work the authors believe that it is questionable to apply the same conclusions to the observations discussed in the presented manuscript.

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

The authors agree with the reviewer and the passage was revised. According to the reviewer's suggestion the LC-MS data were taken into greater consideration and compared to the signals of the AeroFAPA-MS.

Please see the manuscript for the revised passage (P10L22).

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

The authors agree with the reviewer and the figure was moved to the Supplemental Material.

Technical Comments:

25) Page 3, lines 7-8: Fix reference location.

The reference was fixed.

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

As suggested, the first two sections were combined.

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

As suggested, the first two sections were combined.

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

As suggested, the ratio was changed to 1:4 (note that this section is now in the Supplemental Material).

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

The section was revised and the sentence rephrased (note that this section is now in the Supplemental Material).

30) 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?

The authors think that it is not possible to give an exact answer to this question since it depends on the definition of "unambiguous". As written in the manuscript several assumptions had to be made regarding possible formula assignments. Furthermore, all assignments were within a mass accuracy of 5 ppm. The authors believe that these restrictions allow a quite unambiguous formula assignment for the observed signals, however, in order to avoid misunderstandings, the expression "unambiguous" was removed from the manuscript.

31) 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.

The authors agree with the reviewer and the sentence was changed as follows (Supplemental Material, S-1.1):

The threshold for signal abundance was set to $2.5 \cdot 10^6$ a.u. (i.e signal to noise ratio ≥ 3) for the detection of significant signals in the obtained chromatograms after background subtraction by the software.

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

The authors agree with the reviewer and the sentence was changed as follows (P7L5):

[...] only those signals were selected for the subsequent analysis which showed an integrated peak area of $>10^7$ a.u. for at least two separate filter samples, resembling a signal to noise ratio of ≥ 12 .

33) 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.

The authors are very grateful for this comment, since the actual value that was set here was ± 2 ppm for the formula assignment. Furthermore, the authors would like to stress that the threshold for the signal abundance (i.e. S/N ratio) was more important for the selection of characteristic compounds, since still a large number of assignments was in the range of ± 2 ppm. Therefore, the sentence was changed as follows (P7L4):

In order to identify characteristic compounds for the organic aerosol fraction from this relatively large number only those signals were selected for the subsequent analysis which showed an integrated peak area of $>10^7$ a.u. for at least two separate filter samples, resembling a signal to noise ratio of ≥ 12 . As an additional criterion, the formula assignment for these signals had to show a mass accuracy in the range of ± 2 ppm.

34) “In addition, it would be useful to provide the m/z range of the identified compounds.”

The following sentence was added to the manuscript (P7L7):

Eventually, these thresholds led to 93 compounds in the nominal mass range of m/z 133–387 which were identified from the data analysis (Fig. 1 and Supplemental Material).

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

The authors agree and the sentence was changed according to the suggestion.

36) 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.

The authors believe that the information on the calibration is very important here since not all compounds were quantified by authentic standards. To clarify that pinic acid served as surrogate for all SOA markers, the sentence was changed as follows (P7L12):

The concentrations of all SOA marker compounds in $PM_{2.5}$ were estimated using pinic acid as calibration standard.

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

The authors agree with the reviewer and the signals at m/z 255 and 357 were removed from the table.

38) 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.

Here, it is only said that MBTCA is a later-generation oxidation product. Previous studies showed that it is produced with relatively high yields from oxidation of α -/ β -pinene. For example, Müller et al. (2012, ACP) show in chamber experiments that the formation MBTCA can explain up to 10% of newly formed SOA mass.

In order to clarify the expression “later-generation oxidation product” was changed to “major oxidation product”. The sentence now reads as follows (P7L21):

While MBTCA depicts a major oxidation product of α -/ β -pinene (Szmigielski et al., 2007; Müller et al., 2012), 3-carboxyheptanedioic acid is a major oxidation product of *d*-limonene (Jaoui et al., 2006).

39) 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.

As already stated above (see comment 18), in this configuration only monoterpenes were quantified. However, published data on other VOC emissions from previous field campaigns are available. The following sentence was added to the manuscript (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 ppb_v. 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).

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

In agreement with the suggestions made by reviewer 3, the passage was changed as follows (P8L9):

Besides several monoterpene oxidation products, also a marker compound for sesquiterpene oxidation, i.e. β -nocaryophyllinic acid, could be identified (van Eijck et al., 2013). However, the contribution of sesquiterpene oxidation products on particle composition cannot be estimated here because the observed concentrations were typically below the quantification limits.

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

According to the manuscript preparation guidelines of ACP no such header or title is necessary. As written on the ACP website: “Supplements will receive a title page added during the publication process including title (“Supplement of”), authors, and the correspondence email. Therefore, please avoid providing this information in the supplement.”

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

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

According to the reviewer’s suggestion, the caption was revised and additional information were added to facilitate the interpretation of the figure.

44) Fig S-9: A legend would be helpful.

The authors do not see the necessity to add an additional legend since the axes already explain all signals.