

Black = reviewer comment

Blue = author response

## Reviewer 2:

“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.”

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.

Specific comments:

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

According to the reviewer’s suggestion the manuscript was checked for the use of the word “identification”. The only sentence in which it was used was in the abstract, which was thoroughly revised. The word “identification” is no longer used now.

2-9) “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/m<sup>3</sup> 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/m<sup>3</sup>, 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 "unambiguous 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.”

According to the reviewer’s suggestion, the abstract was thoroughly revised. Please, see the new version of the manuscript for all changes made.

10) “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.”

The term “non-target” is commonly used in the analytical chemistry community to describe a certain data analysis approach of high resolution data. The common approach for LC-MS analyses is to look for specific/known signals, i.e. “targeted”, in the obtained chromatograms and mass spectra. In contrast, for a “non-target” analysis no such information is used, but the data is analyzed solely by finding signals which show significant abundances above the background. Due to the huge amount of data that are obtained using high resolution LC-MS, this is only possible using specialized software (see also the Experimental section of the manuscript).

Since the word is in any case not misleading but may even help in understanding the different data analysis approach used here, the authors would prefer to keep this term in the manuscript.

11) "P4L11: Were there any size-selection? A previous paper (Brüggemann et al., EST 2015) describes an SMPS system in front of the AeroFAPA-MS."

In this work no SMPS was used in combination with the AeroFAPA-MS. The authors decided not to use such a size selective system prior to the instrument, since the generation of a monodisperse aerosol might have led to concentrations below the detection limits of the instrument.

12) "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."

To the best of the authors knowledge, inorganic compounds, i.e. salts, are not vaporized in the ionization region of the AeroFAPA-MS. In contrast, laboratory experiments showed that heating the inlet of the AeroFAPA to 200 °C leads to a complete vaporization of secondary organic aerosol particles, which were produced by  $\alpha$ -pinene ozonolysis. Nonetheless, due to ambient conditions the authors cannot exclude the possibility of uncomplete vaporization of the aerosol particles. Therefore, the authors decided to use the word "supported" instead of "ensured". The sentence now reads as follows (P4L15):

**Evaporation of organic aerosol components prior to ionization was supported by heating the inlet to 200 °C.**

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

Indeed, the authors want to make this statement. 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).**

14) "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? "

The authors agree with the reviewer, since differences in extraction efficiencies are an inherent problem of filter analysis by LC-MS. However, since authentic standards for organic aerosol compounds are typically not commercially available and have to be self-synthesized if possible, it is difficult to assess these uncertainties. In order to clarify these uncertainties, the following sentence was added (Supplemental Material, S-1.1):

**It should also be noted that differences in extraction efficiencies and matrix effects might have had a significant effect on the observed signal abundances, which is an inherent problem for aerosol analysis by LC-MS.**

15) "P6L11-12: Is it correctly understood that the average recovery only reflects the loss during evaporation, not extraction efficiency?"

The recovery rate actually also includes losses due to extraction efficiencies. The method description was revised accordingly and now reads as follows (see Supplemental Material):

**To compensate for losses during the sample processing, i.e. extraction efficiency and evaporation, an average recovery rate was determined for pinic acid, which served as a surrogate for the quantification of other monoterpene oxidation products.**

16) “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? “

The authors agree with the reviewer that it is not possible to exclude possible matrix effects for the LC-MS measurements. However, it should be noted that this is an inherent problem of measurements using LC-MS. The only way to account for matrix effects is to know the composition of the matrix. Unfortunately, this is difficult to achieve (especially for aerosol samples), since the filter samples were taken in the field. In order to clarify this point, the following sentence was added to the detailed method description, which can be found in the revised Supplemental Material:

**It should also be noted that differences in extraction efficiencies and matrix effects might have had a significant effect on the observed signal abundances, which is an inherent problem for aerosol analysis by LC–MS.**

17) “Why was pinonic acid not quantified? This would have been useful for the discussion of photochemical aging. “

The authors agree that in several studies pinonic acid concentrations are used to discuss photochemical aging of SOA particles. Therefore, the authors decided to add pinonic acid concentrations to Table 1. However, as suggested by Müller et al. (ACP, 2012), MBTCA is formed from pinonic acid with a yield of only 0.012–1.6% and several other compounds with similar chemical structures might serve as additional precursors for this aging marker. Furthermore, pinonic acid concentrations in the particle phase are easily affected by temperature variations due to the high volatility (SIMPOL.1 model calculated vapor pressure is  $5.5 \cdot 10^{-3}$  Pa at 298 K). Therefore, the authors decided to follow the approach of Vogel et al. (EST, 2016) and to discuss the ratio of MBTCA to pinic acid, which is also an early-generation oxidation product of  $\alpha$ -/ $\beta$ -pinene but less volatile by a factor of 5 (SIMPOL.1 model calculated vapor pressure is  $10^{-4}$  Pa at 298 K).

18) “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. “

The authors agree with the reviewer and like to point out that this is already discussed in the original version of the manuscript (see P10 L11): “[...] these extremely high values [of the ratio MBTCA/pinic acid] suggest that mainly air masses with aged aerosol reached the site. 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).”

19) “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.”

The authors added the results and the reference of another field study at the site (Plewka et al., Atmos. Env., 2006). In agreement with the reviewer’s suggestion, compounds below the limit of detection were removed from Table 1.

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. pinonic acid ( $c = 2.9 (\pm 2.8) \text{ ng}\cdot\text{m}^{-3}$ ) and pinic acid ( $c = 4.7 (\pm 2.5) \text{ ng}\cdot\text{m}^{-3}$ ).**

20) "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."

It is true that at that time knowledge on such compounds was not as detailed as today. However, several sections in Hallquist et al. (2009) are already discussing the abundance and formation of organosulfates and nitrooxy organosulfates in ambient aerosols (e.g. p5183–5186). Therefore, the authors believe that it is correct to cite this reference here.

21) "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?"

The authors agree with the reviewer that the offline application of this ionization technique was shown to produce adducts (as discussed in the given reference). However, this adduct formation was only observed to a very small extent for the AeroFAPA (i.e. online) setup (see also Brüggemann et al., ES&T, 2015). Moreover, adduct formation was never observed with sulfate but only with nitrate ions. Therefore, the authors believe that the signals for organosulfates are not affected by such processes in the ionization region. This is also supported by the time trends of AeroFAPA-MS and LC-MS signals for HOOS (see Figure S-9), which show a similar pattern over the campaign period. The signals of the AeroFAPA-MS for organonitrates are not further discussed in the manuscript, since this is not the focus of this work.

22) "P9L12: What do you mean by "quantify"?" "

The authors agree with the reviewer that the word "quantify" might lead to misunderstandings here. Therefore, the word "estimate" was used instead. The sentence was changed as follows (P9L25):

**In order to estimate the portion of organic compounds in aerosol particles that was measurable by AeroFAPA-MS, the signals of AMS organics and the TIC of the AeroFAPA-MS were plotted against each other.**

23) "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. "

The authors disagree with the reviewer in this point. It is a widely-used and well-established interpretation of the square of the 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, 3<sup>rd</sup> Ed., Routledge, 2014).

Of course, the correlation coefficient alone cannot be used to prove causality; however, in this case both instruments were measuring at the same time the same aerosol mass. Moreover, the time series of the instruments also suggest a good agreement. Therefore, the authors believe that causality is given here and the observed correlation gives evidence for a linear association between the observed signals of the two instruments. Furthermore, the authors do not state that this value will give any information on underlying common factors such as the chemical composition of the aerosol mass, which might be influenced e.g. by long-range transport or photochemical processing.

24) “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.”

The authors agree with the reviewer and the sentences were changed as follows (P9L29 and P10L3):

**Furthermore, the AeroFAPA–MS signals ( $[M-H]^-$ ) of the 93 compounds, which were previously identified from 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).**

**As can be seen from this figure, the AeroFAPA–MS spectra support the aforementioned hypothesis that the composition of the particle phase reaching the site were influenced by BSOA marker compounds such as [...].**

25) “P9L27: Concentrations of pinonic acid were not listed.”

As suggested by the reviewer, the concentration of pinonic acid was added to Table 1 (please see also the answer to comment 17).

26) “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.”

Since not only pinonic acid but also pinic acid is a major early-generation oxidation product the authors think that it is reasonable to use the ratio MBTCA/pinic acid as a proxy for aging processes. This ratio was already used in the literature before (e.g. Vogel et al., ES&T, 2016). Furthermore, due to the higher volatility the partitioning of pinonic acid into the particle phase is stronger affected by temperature variations as it is the case for pinic acid.

The above-mentioned reference was added to the sentence (P10L8):

**The ratio of signals for MBTCA and pinic acid, which can be used as aging proxy for organic aerosols (Vogel et al., 2016), [...].**

27) “P10L1: “transported aerosol masses” -> “transported air masses” The text on this page is quite “lengthy” and could be shortened and clarified. “

As suggested by the reviewer, the expression was changed to “**transported air masses**”. Moreover, the text of this paragraph was revised and, as suggested by reviewer 1, some additional information were added to facilitate the interpretation of Fig. 4. (Please see the revised manuscript for the new paragraph, P10L5.)

28) “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.”

In agreement with the reviewer’s suggestion, the authors added the following sentence to the method description to clarify possible influences of extraction (Suppl. Material):

**It should also be noted that differences in extraction efficiencies and matrix effects might have had a significant effect on the observed signal abundances, which is an inherent problem for aerosol analysis by LC–MS.**

Furthermore, to weaken the statement of “reliable detection” and to account for yet unknown in-source mechanisms this part was changed as follows (P11L12):

**Thus, online detection methods such as AeroFAPA–MS might allow a more reliable detection of such highly oxidized nitrooxy carboxylic acids in organic aerosols. Nonetheless, different ionization efficiencies and in-source formations might also have a significant effect on the detection of such compounds and should be investigated further in the future.**

29) “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.”

This first paragraph might not directly give the reader additional information on the aerosol composition, but the authors believe that this part is essential for understanding on how signals for HOOS were chosen. As explained in the manuscript, these compounds were indeed “selected” from the LC–MS data set, according to the given criteria. Since referee 3 suggested to give an even more detailed discussion here, the paragraph was not shortened but a few additional information were added. Nonetheless, in order to avoid distraction from the focus of the work, Figure 5 was moved to the Supplemental Material.

30) “P11L7: In agreement with what? “

To clarify this point, the sentence was changed as follows (P11L33):

**This finding is also in agreement with previous studies in which the C7 and C9 HOOS have been identified in laboratory and field measurements by Surratt et al. (2008).**

31) “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?”

In order to clarify that only the four previously identified/selected compounds are discussed, the following sentence was added to the text (P12L10):

**In the following only the signals of these four representative HOOS are discussed.**

32) "P11L32-35: Higher concentration of sulfate (and pH) also affects surface uptake and reactions."

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.**

33) "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."

The authors agree that RH is closely related to temperature, and thus, time of day. However, during the discussed period of July 21 the concentrations of HOMs differ strongly from the diurnal cycle which is observed for the rest of the campaign period (see Fig. S-12). RH values reached much higher values during this time (>90% for midday) compared to other days. As shown by Shiraiwa et al. (PNAS, 2011), RH might be a major factor for uptake of gas-phase species into the particle phase. Therefore, the authors believe that phase transition of HOMs was playing an important role for the low HOM concentrations observed. In order to clarify these points, the passage was revised and now reads as follows (P13L9):

**Assuming that RH is one of the main factors driving the uptake of gas-phase species into the particle phase (Shiraiwa et al., 2011), the required rapid phase transition of gas-phase HOMs is further supported by the observed trend for the sum of HOMs, measured by the CI-API-TOF-MS. In contrast to the diurnal behavior observed for other days of the campaign, the HOM concentrations show very low concentrations during this high humidity period (Fig. S-12).**

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

In order to relate the proposed connection between RO<sub>2</sub> radicals and organosulfates to mechanisms previously reported, the manuscript was revised and several information on organosulfate formation were added where necessary.

Please see the following comments and corresponding answers for more details: comment 10 by reviewer 1; comment 32 by reviewer 2; comments 2, 19, and 20 by reviewer 3.

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

According to the reviewer's helpful suggestions the conclusion section was thoroughly revised. Please see the manuscript for the new version of this section.

36) "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. "

The authors agree with the reviewer and the figure was revised.

37) "Figure 5 should be moved to supplementary information."

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

38) "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?"

The authors agree with the reviewer and the figure was revised. The marker size was decreased to increase the visibility of data point for higher sulfate concentrations. Moreover, the figure labels in panel a) were changed to C7 vs. C8, etc. To clarify that here only the previously selected HOOS are discussed the caption of the figure was changed as follows:

**Figure 5. (a) Correlations among the selected HOOS signals as well as the effect of RH (color code) and particulate sulfate on their abundance (marker size, range: 0.8–7.2  $\mu\text{g}\cdot\text{m}^{-3}$ ). [...].**