

Interactive comment on “The impact of biomass burning and aqueous-phase processing on air quality: a multi-year source apportionment study in the Po Valley, Italy” by Marco Paglione et al.

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Replies to Referee #1

The authors would like to thank Anonymous Referee #1 for his/her comments.

The Referee's comments followed by our replies are listed below.

Main concerns: - Among the main findings of the study is the quantification of biomass burning SOA that is considered to result from aqueous phase reactions of biomass burning products (bb-aqSOA). This consideration, however, is mainly based on high correlations of one of the PMF OOA factors with ALWC. Even though plausible, I hesi-

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tate to take this correlation as sufficient evidence for really inferring the formation pathway of this OOA fraction, especially, as no alternative explanations are even discussed by the authors. One alternative explanation would be a strong shift in phase partitioning of water soluble organic gases during periods with high ALWC. A number of compounds like small carboxylic acids and (di)carbonyls present in the gas phase of (aged) BB plumes could be expected to preferentially partition into the particle phase only under high ALWC conditions, owing to their high volatility combined with high water solubility. These would contribute to the “OOAx_BB_aq” even without any aqueous phase chemistry taking place and OOAx_BB_aq might in fact just represent an OOA fraction with different phase partitioning behaviour than OOAx_BB”, regardless of their respective formation pathways. There might be other possible explanations for the observed correlation with ALWC and I would recommend providing a more critical discussion on the subject.

Authors Reply. The authors thank the Reviewer #1 for the critical view and suggestion. We acknowledge that a more clear explanation of our hypothesis can be profitable and it will be added in section 4.3 of the revised manuscript. We modified the manuscript in order to clarify that the attribution of OOAx_BB_aq factor to aqueous phase chemistry is not solely based on the correlation with ALWC. The consideration that the OOAx_BB_aq factors result dominantly from aqueous-phase reactions is still the most credible for two main reasons: 1- a technical one, the analyzed aerosol was dried to about 35-40% by means of a Nafion drier before sampling with the HR-TOF-AMS. So, most of the possible volatile compounds dissolved into particle phase under high ALWC conditions are expected to be volatilized again during sampling, leaving into aerosol only the most stable (complexed/oxidized by ageing) compounds; 2- linked with the previous, even if it's true that the partitioning of gaseous soluble species emitted by biomass burning is enhanced during high ALWC conditions, it is even true that these small and volatile compounds need to react to become stable components of particle phase. And this is exactly the mechanism that the Authors suggest is happening. The correlation of OOAx_BB-aq factors with HMSA is a good example of this mechanism,

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as also the Reviewer #1 suggested in the subsequent comment: “Formaldehyde would preferentially partition into particles for high ALWC conditions to form HMSA” and ONLY if it happens the products of this reaction (i.e., HMSA) will remain in the particles after water evaporation. And this is supposed to happen to other gaseous species and their specific products, changing permanently the chemical composition of the organic aerosol.

- Further evidence provided to corroborate an aqueous phase formation pathway of OOA_BB_aq is either not conflicting with the above given alternative explanation or not fully convincing to me. Formaldehyde would preferentially partition into particles for high ALWC conditions to form HMSA (P13L2), taking AMS fragment ions as evidence for specific compounds in a complex ambient mixture might be questionable (P13L22 and P13L26) and many of these are well correlated to other OOAx factors as well (Table S16), the agreement with fog processing spectra is only partial in many cases (P13L18 and Table S15) and O:C ratios are unlikely to be good indicators for specific formation pathways (P13L29). To make myself clear: I am not in general disapproving the conclusion of an important aqueous phase bbSOA fraction, but I would encourage a more critical assessment of the evidence provided, including a discussion of alternative processes that could at least in part explain the observations.

Authors Reply. In addition to the previous reply, partially answering also to this comment, authors would like to add few more specific considerations: -HMSA is the product of sulfite complexation with formaldehyde, a reaction taking place only in aqueous-phase and inhibited by photochemistry. So the correlation of OOAx_BB-aq factors with this compound is in our opinion a clear evidence of the link with aqueous-phase chemistry and not only an indication of the preferential partitioning of formaldehyde at high ALWC conditions. - we acknowledge that the AMS fragments and elemental ratios are not overwhelming evidences. For this reason we first showed that the fragments that were attributed to HMSA correlates with the HMSA concentration, quantified also with independent measurements (H-NMR). In addition, in our study the other fragments are

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used as ancillary evidences (for this reason reported in the Supplementary), not as the “main proof” that instead are the correlations with ALWC and HMSA and the variations with RH. -we acknowledge also that the variability of AMS spectra is high. However literature indicates that this can be quite common looking secondary factors (OOAs) but in any case they can be used to investigate SOA sources. This is clearly visible in Tables S7 and S14 for example where the comparison between OOAs factor spectral profiles from SUPERSITO campaigns and many correspondent reference profiles from literature is reported.

-P5L18ff: In its present form, the explanation of the alpha value approach is not really accessible to non-familiar readers. Is it important to be presented or would a reference to the method suffice?

Authors Reply. Authors thank the Referee and re-phrase the explanation of the a-value approach, removing the equation and summarizing the concept as follows: “Similarly to the classical PMF solver (e.g., PMF2, PMF3, Paatero and Tapper, 1994), the ME-2 solver (Paatero, 1999) executes the positive matrix factorization algorithm. However, the user has the advantage to support the analysis by introducing a priori information, such as known factor profiles (FP), for example within the so-called a-value approach. The a-value is a scalar (defined between 0 and 1) that determines how much the resolved factor profiles are allowed to vary from the reference ones (Canonaco et al., 2013). For instance, applying an a-value of 0.05 lets $\pm 5\%$ variability to our FP solution with respect to the reference FP during the PMF iteration.”

-P5L15 and P5L22: There is a contradiction in the range the alpha values can take.

Authors Reply. Re-phrased and contradiction removed.

-P5L23: “. . .represented by f.” What does f mean?

Authors Reply. Sentence removed rephrasing the concept.

- P6L21: “inorganic ions”?

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Authors Reply. Replaced as suggested

- P6L23: ion charges are missing

Authors Reply. Ion charges added as suggested

- P9L15: "...in the summer period analyzed by itself" What does it mean? Please rephrase.

Authors Reply. Rephrased removing "analyzed by itself".

- P10L15: Are local sources important for the urban increment, i.e. does wind direction play a role for the high variability?

Authors Reply. In general, due to very low winds intensity (average values for all the campaigns of 1.89 ± 0.32 and 2.06 ± 0.17 m/s for BO and SPC respectively), the transport of pollutants along the two sites is supposed to be diffusive. So, the two sites are representative of two different background conditions (urban and rural), both poorly affected by really local sources in most of the cases (background sites) (http://www.arpae.it/sim/?osservazioni_e_dati/climatologia ; Ricciardelli et al., 2017). The high variability affecting BBOA urban increment is something not expected, but (as expressed in the text, P10 L11, and showed in Section S2) probably it is due to the fact that the spring 2013 campaign was characterized by few nights with temperature colder (8°C) then the monthly average for May (18.5°C). These nights correspond to very sharp and intermittent peaks in BBOA concentrations (probably due to domestic heating active just for those few nights). For the rest, the BBOA concentrations during the campaign were really low (average values of 0.29 and $0.05 \mu\text{m}^{-3}$ at BO and SPC respectively), something not strange during May. So this very low and intermittent BBOA levels affect the urban increment value for this specific campaign and it is considered not representative.

- P10L19: Is agricultural burning common in the area?

Authors Reply. Actually agricultural burning is limited by the law: every Regional ad-
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ministration and sometimes also the different municipalities have a specific regulation on the topic especially during definite periods (e.g., dry summer, for fires prevention). However the open burning of agricultural waste is allowed for most of the year and continues to be a practice fairly common and difficult to regulate in rural areas (data confirmed by Regional Environmental Protection Agency of Emilia Romagna, ARPAE-ER). For this reason it is not possible to exclude the contribution of agricultural burning to the total BB aerosol burden at the rural background site (SPC), even if it is not possible to estimate its importance.

- P12L21ff: I do not follow these conclusions. Both carboxylate as well as hydroxyl group formation can in principle take place both in the gas and in the aqueous phase. The references cited all relate to aqueous phase chemistry. Please elaborate. Also, in Fig. 6d it is the circles that show a negative slope and in contrast to what the text says in L21 and L23, these are the ones labelled "BB-aq".

Authors Reply. Authors thank the Reviewer to highlight the discrepancies. We agree that in the present form the paragraph can be misleading for the reader. Our intention here is only to highlight the possible different oxidation pathways observed in the biomass burning ageing. Then in the subsequent paragraph we focus on the aqueous-phase chemistry. We rephrased the paragraph clarifying the message. We also add references of carboxylate formation not related to aqueous chemistry.

- P13L6ff: Given the very different emission strengths of POA during a day, I doubt it can be used as a surrogate of the PBL. Also, which "above conclusion" (L9) is supported by similar variations and why?

Authors Reply. Authors accept the Referee's suggestion: the sentence about POA as PBL surrogate is removed as well as the panel d) in Figures 7 and S5.

- P15L14: "ambient air"?

Authors Reply. Added

- P15L24: erase “extremely”

Authors Reply. Done

- Fig. 6 is hard to digest. Please structure the legend according to the different campaigns and increase panel sizes of a) – d). Maybe make d) a separate figure to gain space for a) – c)? Check readability of greyish color (really “gold-green”?) Consider using a consistent color code for OOAx_BB and OOAx_BB-aq. Right now, identifying the points in the scatter plot is a headache. Check the grey square for “no BB influence” for correct positioning. Text says 0.05 max, but the shaded area is < 0.05 in the plot.

Authors Reply. Done. A new version of the Fig. 6 is reported in the revised manuscript. The legend is now structured according to the different campaigns; the panel size is increased and the grey area for “no BB influence” is located in the right position. We prefer to leave the color distinction between different OOAs based on their O:C ratios and not on the formation process (which is instead highlight by the name of the factor). We prefer also to leave the panel d) in the same figure, even if increased in dimension.

- Fig. 6a) Some of the points are just at the edge of “BB influenced”, based on f60. Is this considered in data interpretation and what does it imply for their assignment as “OOAx_BB”?

Authors Reply. As reported in the Supplementary section S2.2.3 (Validation of by Biomass Burning influenced OOAs) we performed additional tests in order to validate the attribution of the C₂H₄O₂⁺ fragment (corresponding to the f60) to the OOA factors. In the end, factors considered as OOAx_BB are only those for which both average values and error bars (representing the standard deviation of all the additional tests performed) are located out of the gray shaded area indicating no influence of biomass burning (Fig. S3).

- Fig. 8: Check formatting of unit in axis labels.

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Authors Reply. Done.

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