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Atmospheric
Chemistry
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Discussions

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.

Anonymous Referee #1

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The paper by Paglione et al. presents a detailed analysis of AMS data obtained in several campaigns at Bologna and San Petro Capofiume throughout 2011 – 2014. The authors focus on source apportionment of OA by PMF and report a number of interesting findings, especially related to the impact of biomass burning and aqueous-phase processing. Generally, the methods and procedures applied are state-of-the-art, the paper is well structured and well written, and the results will certainly be welcomed with considerable interest by the readership of ACP. I have one major concern regarding the validity of "bb-aqSOA" identification (see below) and a few further minor issues. Overall, I recommend the paper for publication after the following issues have been addressed.

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 hesitate 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.

- 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.

Other issues:

- 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?

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

- P5L23: "…represented by f." What does f mean?

- P6L21: "inorganic ions"?

- P6L23: ion charges are missing

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

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

- P10L19: Is agricultural burning common in the area?

- 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".

- 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?

- P15L14: "ambient air"?

- P15L24: erase "extremely"

- 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.

- 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"?

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

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