

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.

Marco Paglione et al.

m.paglione@isac.cnr.it

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Replies to Referee #2

The authors would like to thank Anonymous Referee #2 for his/her comments.

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

-I must say here that the uploaded text font of the ACP manuscript is too small read offline. I suggest authors to take care of this part when uploading the revision.

Authors Reply. ACP has specific rules about the submission format (e.g., font size, line numeration, etc.). The Authors simply followed these rules to satisfy the requirements

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of the journal. The same is applicable for the last comment of the Referee #2: Please provide line numbers continuously and also increase the font size of the text so that it will help us to properly evaluate the manuscript.

-Grey shades in figures should be in 'black' with increase in font size for all the figures.

Authors Reply. We apply all the Referee's suggestions in the revised version of the paper.

-P2 L13: Is it 400 or 400,000 premature deaths??

Authors Reply. We thank the Referee to have notice the misspelled number. The correct number is four-hundred-thousand (400,000) of course. In order to avoid any confusion we completely remove the separator (putting 400000) in the revised version.

-P2 L20: replace 'proved' with 'established'

Authors Reply. Done.

-P3 L16: Aerosol Chemical Monitor (ACSM)??

Authors Reply. We thank the Referee to have notice the misspelling. The correct definition - Aerosol Chemical Speciation Monitor (ACSM) – is replaced in the revised version.

-P9L25-29: I could not follow the logic of arguments here? Do authors mean HOA are embedded/occluded in water-soluble OA components at SPC, which are scavenged by the fog and left behind the HOA, thus increasing the fossil-based emission contribution to SPC?? Some additional explanation is needed here.

Authors Reply. This behavior is better discussed in a previous publication by Gilardoni et al. (2014), specifically focused on SPC fall2011 campaign and cited at P9, L29. In the revised version we add a clearer linkage to this paper and we re-phrase the paragraph in order to clarify the concept, Here we just want to quickly explain the peculiarity of this specific campaign, representative of irregular meteorological conditions,

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and so not completely comparable with the others in term of relative contributions of the different OA components. We would like to clarify that during the fall2011 campaign SPC was affected by persistent fogs during 14 days (out of the total 17). And (as reported in Gilardoni et al., 2014) fog scavenges aerosol components selectively, based on their solubility. For this reason, after fog formation, the interstitial aerosol (i.e., the fraction of the aerosol that is not scavenged and was measured in particle-phase) was dominated by particles enriched in carbonaceous aerosol, mainly black carbon and water-insoluble (or poorly soluble) organic aerosol. Moreover, analyzing the functional group composition and OA elemental ratios, Gilardoni et al. indicated that more oxidized OA was scavenged more efficiently than less oxidized OA. HOA is the less oxidized (O:C ratio = 0.29) and less soluble fraction of OA, so it is likely the one that is scavenged less efficiently and therefore its fractional contribution in the interstitial aerosol increases. So, the aerosol composition and concentrations for this campaign at SPC referred to a mixture of total OA and interstitial OA in fog conditions not fully comparable with the other campaigns.

-From Table 1, it is apparent that OA contribute almost 50% at both sampling sites (BO and SPC).

Authors Reply. Even if the comment is not clear, we think it refers to our sentence at P4, L22-23 “the organic aerosol (OA) component that represents the major fraction of submicron particles for most of the campaigns”. We don’t see any problem in this sentence: even when the OA fraction is less than 50% of the total mass there’s not any other single component (NO₃, SO₄, NH₄, etc.) accounting for a higher fraction of the PM₁ mass. To clarify, we modified the sentence as follows: “the organic aerosol (OA) component that represents the most abundant fraction of non refractory submicron particles mass for most of the campaigns. . .”

-It is bit confusing to see some places OOA and other places as SOA. Please maintain consistency throughout the manuscript.

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Authors Reply. We partially accept the suggestion of the Reviewer. In the revised manuscript we use always “OOA” when we are talking about the PMF factors. However sometimes we keep also the “SOA” abbreviation when we refer to more general arguments, like potential sources and formation pathways.

-In Table 2, I understand the reason of HOA share decrease between BO and SPC. But the BBOA component show more at BO site compared SPC during spring 2013 but also somewhat higher or comparable for other seasons too. Some explanation is need in the manuscript.

Authors Reply. Unfortunately we don't have enough reliable data to indicate a clear trend for BBOA concentrations between urban and rural site in all the seasons. The campaigns carried out in parallel at the two sites were only 4 (summer 2012, spring 2013 and fall 2011 and 2013). Among these: during the summer 2012 PMF didn't identify any BBOA (no domestic heating during summer); the fall 2011 had its meteorological peculiarity linked with fog events (already discussed in a previous reply here above and in the revised text at P9, L21-26) and so it is considered not comparable; the spring 2013 was characterized by very low and intermittent BBOA levels (as better discussed in some other replies below) and so it is not clear how it is representative of background conditions. The only campaign reliable to say something about differences in BBOA concentrations between urban and rural site is the fall 2013, suggesting “a higher contribution of BBOA in the rural areas, probably due to the more spread use of fire-places and wood-stoves for domestic heating and to additional possible sources, such as agricultural burning”, as clearly stated in the text.

-P10 L8: Is it because of the differences in the ambient temperature and photochemical activity between winter and summer controls their abundance whether it is NH_4NO_3 in winter/fall vs. $(\text{NH}_4)_2\text{SO}_4$ in summer and, hence, their correlation with OOA component. Add some additional explanations here.

Authors Reply. We believe that there are two possible explanations. As suggested by

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the Reviewer, the differences in temperature and relative humidity between winter and summer shift the partitioning of nitrate toward gas-phase (due to its volatility) during warm season. In addition, the different correlation suggests the possibility of a different oxidation pathways in secondary species formation between cold and warm season: a pathway characterized by cold temperature and high relative humidity (dominated by aqueous-phase processing and correlating more with nitrate) and another one more related with higher temperature and photochemical activity (correlating more with sulfate). We add in the revised manuscript a short explanation introducing the subsequent sections in which we developed more the concept.

-P10 L10: Instead of calculating based on the overage, I recommend authors' to show the ratio of each fraction of OA between BO and SPC based on the box plots. This will give us a brief idea about the relative increment of emissions/formation processes contributing to observed compound classes of OA between both sites.

Authors Reply. A more rigorous assessment of emission/formation processes would need a more detailed statistical treatment of the data variability between urban and rural sites, which is beyond the scope of the present manuscript. "Urban increment" here is not intended as a source apportionment tool but only as an instrument to discuss the differences observed between the urban and the rural sites. For this reason, even if we acknowledge the limitations of our urban increment assessment, we believe the calculation based on the average values is enough to have a rough idea of the most evident differences between the sites. In any case, we calculated the same ratios using Median value (reported in the table in Fig.1 here below), showing not substantial differences with Table 3. The high value corresponding to Spring 2013 (even higher than in Table 3) is consistent with the idea of few and intermittent high BBOA spikes, better discussed in the subsequent reply to the comment on Table 3.

-P10 L13: Authors mentioned previously that in summer traffic is less at BO because of the shutdown of schools and public institutions, in which case, why the HOA fraction increased over BO compared to SPC in summer.

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Authors Reply. As the Urban increment clearly show (Table 3 and also previous comment), the HOA trend is constantly shifted toward higher concentrations at the urban site (BO) with respect to the rural one (SPC). This is quite expectable and already mentioned in the text: the urban site is closer to the HOA primary sources (traffic) with respect to the rural site and for this reason HOA concentrations are always higher at BO than at SPC, even when (during summer) are depleted (compared to the winter) due to the activities shutdown and increased dilution.

-In Table 3, why BBOA fraction is almost 6 fold higher at BO (urban) compared to the SPC (rural). This implies there exists a very strong local source of biomass combustion at BO compared to SPC, please clarify. Higher share of BBOA(%) over SPC in fall, why not is the case for winter or other seasons?

Authors Reply. Overall both the measurement sites are representative of background conditions: BO is representative of urban background, while SPC of the rural background. This because of two main reasons: 1- both the field stations are located quite far from any kind of direct local source and 2- 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 is supposed to be diffusive in the studied area (http://www.arpae.it/sim/?osservazioni_e_dati/climatologia ; Ricciardelli et al., 2017). The high BBOA urban increment during spring 2013 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 colder temperature (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 especially in SPC (average values of $0.05 \mu\text{m}^{-3}$), something not strange during May. So this very low and intermittent BBOA levels affect the concentrations for this specific campaign, which is considered for this reason not representative. About winter seasons: unfortunately our dataset is not comprising a winter

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campaign carried out in parallel at both the sites and for this reason we can not argue nothing about the urban increment during winter.

-P11 L6: Why focus only on these two factors?

Authors Reply. Considering the big amount of data already reported in the paper, the Authors decided to focus more only on the two most innovative aspects emerged from this study, namely the biomass burning influence on SOA components and the aqueous-phase processing affecting some of these components. These two aspects are represented by the OOA_BB factors deeper examined, indeed.

-P11 L30-31: How this fraction of OOA_BB was estimated here?

Authors Reply. This fraction is represented by the mass contribution of the OOA factors which, looking the f60 vs f44 space, resulted influenced by biomass burning. 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 OOA_x_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).

-Figure 6 panel resolution and font sizes need to be improved? This figure is not readable at all offline. Grey shade text in panel d should be converted to black.

Authors Reply. A new version of the Fig. 6 is reported in the revised manuscript.

-P12 L19-20: These sentences are not clear, please rewrite. The slope line between triangles and circles seems to be zero (i.e., OOA_x_BB-aq) and those between triangles and squares (OOA_x_BB) is like between -0.5 and one. P12 L24: This is contradicting the above classification on L19-20. Please check.

Authors Reply. Authors thank the Reviewer to highlight the discrepancies. The text was mixed up during writing and so the description of the figure is not consistent. We

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rephrased the paragraph clarifying the message.

-P12 L29: What are the input parameters to ISORROPIA-II, which mode is used, please provide.

Authors Reply. Info provided in section 2.3 of the revised manuscript.

-P13 L7: sentence should read like this, 'Dividing the individual OOA fractions with the total POA'

Authors Reply. Authors, accepting a comment from Referee #1, removed the sentence about POA as PBL surrogate and removed also the panel d) in Figures 7 and S5.

-In Figure 8, what is the OOA2, OOA3, OOA refers to, Please clarify.

Authors Reply. OOA factors are numerically ordered based on their O:C ratios, independently on the influence of a specific source, as explained in the text (P11,L5) and in the captions of Figure 6, showing for the first time in the paper the different OOAs. To improve clarity we add this information in the revised manuscript also in the caption of Figure 8.

-P13 L16: I can see m/z 29 signal but not 58 from figure 8 (left panel). Did I miss something here?

Authors Reply. The ion at m/z 58.01 01 (C₂H₂O₂⁺) is associated in literature to aqueous-phase reactions because is one of the typical fragments of precursors of SOA via cloud processing, like methylglyoxal and glyoxal (Carlton et al., 2007; Altieri et al., 2008). We state this clearly in the text (P13, L27-29 of revised manuscript). Since m/z 58.01 has much lower fractional abundances (f₅₈) with respect to other fragments in the spectra this ion is not easily distinguishable in Figure 8 (where the spectra are reported in a very synthetic way). We acknowledge this but we prefer to avoid adding more information in Figure 8 (already quite packed). Anyway the f₅₈ is always higher in all the OOA_BB-aq with respect to the others OOA_BB factors (as showed in the additional graph here below, Fig. AR1). This feature, associated with the abundance of

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m/z 29 (CHO⁺), can help in the identification of the BB-aqSOA factors, even if it is not a sufficient proof (because the correlation with ALWC and HMSA together with the study of the variations with RH are more important to unambiguously identify those factors).

-P13 L21: mention those specific fragment ions here within parenthesis.

Authors Reply. They are mentioned in the subsequent sentences. The Authors don't see the need to add them also before within parenthesis.

-In Figure 9, why there is no such presence of aq-SOA despite more sunlight and having precursors at both sites. Some explanations needed in the manuscript.

Authors Reply. The question is hard to understand because no specific reference to the text or the figure is provided. Anyway, we think the comment is referring to the absence of a BB-aqSOA at SPC during Spring 2013. We believe it is probably related to the very low and intermittent BBOA levels affecting this specific campaign (already discussed above) and not allowing an important BB-SOA formation.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-274>, 2019.

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Urban Increment using Median values	HOA	BBOA	OOA	OA TOT
SPRING 2013	1.73	8.85	1.28	1.42
SUMMER 2012	2.94		1.60	1.64
FALL 2013	1.70	0.64	1.20	1.11

Fig. 1. Urban increment, calculated as the ratio between the campaign Median concentration in urban and rural site, for each season and OA fraction considered.

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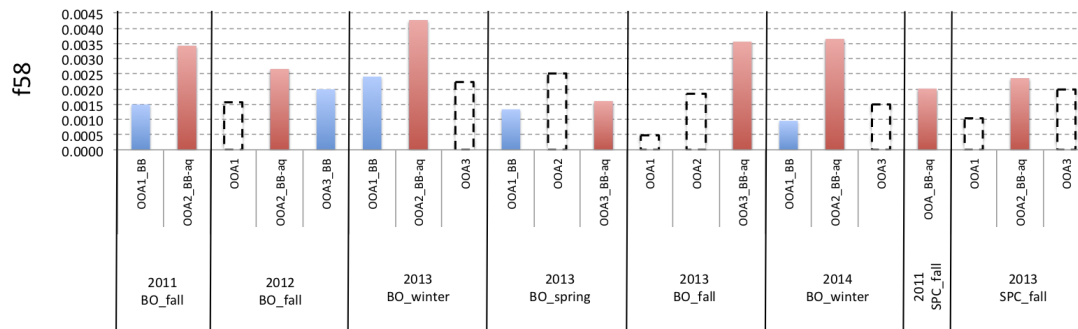


Fig. 2. Fractional abundance of m/z 58.01 (f_{58}) in the spectral profiles of each OOA factor identified by PMF analysis in all the campaigns where a BB-aqSOA factor is identified. Blue bars represent

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