ACP-2018-773
Answer to Anonymous Referee #3 comments

We thank the reviewer for his/her attention to our manuscript. We reworked and rearranged it in many places, in order to take into account all the general remarks and specific comments below, as well as those of the reviewer # 4. Particularly, we are now providing a more in-depth presentation of the overall PMF methodology and results. The detailed responses to the comments are given below, point by point, *in blue color*, including changes directly made to the manuscript, *in red color.* A list of references used to address Reviewer's comments is given at the end of the present response letter.

This manuscript presents an interesting data set, treating aerosol PM10 and PM2.5 composition for a number of Traffic, Urban and Rural sites across France that is important for the understanding of aerosol sources over continental west European areas. From this data set the manuscript focus specially in the polyols and sugar components with the objective of determining the importance of this group of organics and their sources in the atmospheric aerosol loading. Unhappily the manuscript is not well presented. The first part, 3.1 to 3.4 sections, is mostly descriptive, showing average values and variability for polyols and glucose across sizes, seasons and regions. The authors try to evidence the importance and contribution of those compounds to the aerosol loading in a somehow enthusiastic and forced way. They have the tendency to present more maximum concentrations than average values. The second part, section 3.5, deals more specifically with the evaluation of the Polyols source composition and contribution to the aerosol loading, using mainly PMF analysis. However the authors only show the PMF results concerning the source associated to polyols, remitting the reader to an unpublished manuscript for further scrutinizing of the aerosol total source apportionment and this is not acceptable. Furthermore, the so-called PMF calculated PBOA source factor has a mass that is more than 30 times higher than the measured polyols without a clear explanation about how can this result from primary particulate biomass emissions. I have some doubts about the correctness of this source factor as discussed further in the Specific Comments part. Therefore, I recommend that the manuscript is reorganized and modified in order to provide a more detailed information and discussion of the sources of the atmospheric aerosol and the contribution and importance of polyols and sugars as sources of the particulate pollution.

Specific comments:

Line 174- "130 Different chemical species"? I only counted around 40.

The reviewer is right that this table only presented around 40 chemical species, since not all of the analyzed chemical species were included in the PMF runs. This is now explained in the manuscript: line 195, page 6.

Line 175- Table S2 instead of S1?

This has been rephrased. It now corresponds to the Table SI-6.

Line 194- "BC" instead of "EC"?

Filter analysis for EC-OC and aethalometer measurements were conducted simultaneously for the 3 DECOMBIO sites within the Arve valley (Chevrier, 2016). Aethalometers give the total BC, thus enabling the decomposition of BC concentrations into its two main constituents: wood-burning BC (BC_{wb}) and fossil-fuel BC (BC_{ff}) (Sandradewi et al., 2008). Considering the very specific context of this mountainous valley (with a large influence of meteorology on atmospheric concentrations in winter),

the PMF runs with better results in term sof statistical stability and geochemistry were the one with BC_{wb} and BC_{ff}. However, for graphical simplicity, BC_{wb} and BC_{ff} are summed up and labelled as EC in the present study. This point is further detailed in the response to the comment 14 of Anonymous Referee #4

Line 200-204- The imposition of these constrains may not influence artificially the composition results? Anyway, the PBOA source calculated still has important contributions of unexpected EC.

The PMF runs take advantage of the ME2 algorithm to add constraints to different chemical profiles (see the tables SI-3 to SI-5 for in-depth details). Mainly soft constraints were applied in order to add some prior "expert knowledge" about the emission sources and their chemical profiles, and "*clean*" the different profiles without forcing the model toward an explicit solution. This is now classical in many PMF work (Bozzetti et al., 2017; Daellenbach et al., 2017; Srivastava et al., 2018a, 2018b; Weber et al., 2018). This point is also further detailed in the response to the comment 15 of Anonymous Referee #4.

Also, details about the contribution and uncertainties of EC over the sampling sites have now been addressed in Fig. SI-7. As evidenced in Fig. SI-7, EC apportioned by PBOA appears to be variable both within and between the sites under consideration. Indeed, the average contribution of EC calculated for this profile is largely influenced by two values of about 25% for the traffic site at Strasbourg and 18% at Chamonix (2 sites influenced by direct and indirect traffic emissions), but 6 other sites present no EC in this factor (hence the large standard deviation 9±7 % mentioned in the main text, Fig.11). In term of mass (SI-7a), the PBOA factor is making up between 0 to 400 ng m^{-3} of EC on yearly average depending on the site, which is close to the background value of remote sites in rural France of about 300 ng m^{-3} (Golly et al., 2018). There are indeed some uncertainties on how the PMF method is redistributing the components of this background PM with no strong specific chemical signature among all the extracted factor. Further, one should keep in mind that the factors defined in a PMF are characteristic of a "source", a mixing of sources and/or atmospheric processes as seen at the receptor site. Hence, they may be somewhat influenced by processes taking place during atmospheric transport (i.e., aging, mixing, etc.) and may not present a chemical signature as pristine as that right at the emission point. All of these could justify the presence of EC in the chemical profiles.

Line 2017- Which is the necessity of having a Figure S3 that is very similar to Figure 2? Substitute Figure 2 in the text by Figure S3.

The Fig. S3 has now been removed, as suggested by the reviewer.

Line 232 Figure 3- If possible harmonize colors in this Figure with colors in Figure 2, for Mannitol, Arabitol and Glucose.

We agree with reviewer#3 and harmonized the colors between Fig.2 and Fig.3, for glucose, arabitol and mannitol.

Line 233 Add "Average" initially to the sentence.

The term "average" has been added

Line 256- Could you give some more information and reasoning about the removal of glucose from the PMF treatment?

We can note that the papers dealing with glucose in atmospheric PM are really rare and, to the best of our knowledge, there is currently no discussion or hypothesis on the origin or the stability of glucose in PM. As mentioned in the text, adding glucose in the PMF treatment always led to PMF solutions that were unstable or did not make sense in a geochemical way. Particularly, glucose showed no tendency

to mix with the other polyols in a single factor. So far, we are not able to provide a proper explanation for this behavior, despite many investigations on the data base. It may be that the factor that would include the larger part of glucose (if any) could present a really variable chemical profile across the year, while stability is a strong hypothesis underlying the PMF method. This would prevent getting a well identified factor.

Line 258- Change to ". . .the variability in the slope of the regressions between the chemical concentrations is most probably. . ."

This information has been added.

Line 269- change to "to-PM2.5 ratios were. . ."

This correction has been added.

Line 356-366- There is a lack of information concerning average Polyols and glucose concentration values for the total sampling sites and perhaps either to each one of the four classified station types. A column to the right of the Figures 6 -8 with average values for the station ensemble would be informative.

The information concerning the annual average polyols and glucose concentrations for the total sampling sites, and for each one of the four classified station typologies is now provided in Table SI-2. This information is now discussed in the manuscript (lines 341-344, page 11; lines 373-375, page 12).

Line 429 Figure 10- Which is the meaning of "*" in OC?

OC* corresponds to the bulk organic carbon fraction minus individual molecular weight of characterized organic species. This information has been added in lines 496-497, page 17.

Line 447-449- The mass of EC contribution to the PBOA factor shown in Figure 11 is 3 times higher than the mass of soil estimated. Then, it is impossible to conclude anything about EC in soil from this data.

The reviewer is right and it was not our intention to mention that EC in this factor could be entirely linked to the resuspended dust fraction. We changed the text to be clearer on this point (please see below).

Also, we are now more precise in the text and the SI (SI-7a in mass and SI-7b in $\mu g_{EC}/\mu g_{PM}$) on the amount of EC in the PBOA factor. Indeed, (as mentioned above) the average contribution calculated for the profile is largely influenced by two values of about 25% for the site in Strasbourg and 18% at Chamonix, but 6 other sites present no EC in this factor (hence the large standard deviation mentioned in Figure 11 of 9 ±7 %). Moreover, the internal variability of EC according to bootstrap is now presented in SI-7 for all the sites thanks to 100 bootstrap solutions for each site. For the sites of Strasbourg and Chamonix, EC contributions can be quite high but also very uncertain (between 5% - 30% of EC in PBOA mass for Strasbourg for instance). All of this information indicates that the amount of EC is generally less important than the average value presented in the PBOA factor.

The text is now changed accordingly, in order to take into account these elements (lines 510-527, page 17):

"The large value for the contribution of EC is driven by two high values obtained at the sites of Strasbourg (that reaches 25%) and Chamonix (18%) both influenced by direct and indirect traffic emissions. However, 6 other sites present no EC in PBOA. Moreover, the uncertainties of EC in the PBOA profile of Strasbourg and Chamonix is rather high (between 5 to 30% of PM mass at Strasbourg, see SI-7). On a yearly average, EC apportioned by this factor (0 to 400 ng m^{-3} depending on the site) is close to the rural EC background in France of about 300 ng m^{-3} (Golly et al., 2018).

Line 453 Figure 11- The PBOA factor has an important contribution of EC (ratio of OC/EC equal to approximately 4.8, similar to values found in secondary organic aerosol formation). Therefore in my opinion this PBOA factor is probably highly contaminated with secondary organic material. That may explain the more than 30 times higher PBOA mass than the mass of polyols. However a more well based evaluation is impossible given the lack of complementary information from the PMF source apportionment.

We thank the reviewer for this interesting question. Indeed, it is a major drawback of most of the dozens of PMF studies published every year, based on molecular tracers, that PBOA and Biogenic SOA (BSOA) factors are not distinctly apportioned, considering that a predominant fraction of the organic material is made of modern C in many types of environments in summer, as deduced by ^{14}C studies (Bonvalot et al., 2016; El Haddad et al., 2011; Vlachou et al., 2018).This modern C is part of both the PBOA and the BSOA fractions. It is a strong motivation of this work to define a PBOA factor using molecular tracers to be used in PMF studies.

As not being discriminated in a proper PMF factor, BSOA are somehow redistributed into some of the other factors identified by the PMF method. Hence, our PBOA factor may well be a candidate for such a redistribution.

However, at least four arguments point against a major influence of BSOA into the obtained PBOA factors: the BSOA loadings should be rather variable across our sampling sites (due to spatial-variation in the emission of primary products, variation in climatology and global sunshine duration, etc.), with a temporal evolution different from that of the PBOA fraction. But, in the present study, we observe a stable ratio of polyols / OC_{PBOA} (3.0±1.5 % on average) over the sites, which does not tend in favor of significant contribution from secondary processes that would introduce more variability in the ratio. Second, the mapping of the PBOA factor in the PMF is rather excellent, as presented now in the PMF description. Indeed for all sites, no "swap" between factors is observed during the bootstrap sensitivity analysis. PBOA is always mapped with itself (see Fig. SI-5), indicating a well identified factor at each site. Third, while the PMF deconvolution of sources is mainly based on co-variation of the concentrations of the chemical species within a given factor, the concentrations of molecular tracers of PBOA (i.e. polyols) and those of a large part of BSOA (like pinic acid and 3-MBTCA) present very different seasonal cycles (JL Jaffrezo, unpublished data). The work in progress with these data aiming to investigate whether the PBOA source is mixed with SOA is forthcoming. In such context, Srivastava et al. (2018a) have also recently reported quite different seasonal evolution cycles between BSOA (traced thanks to the oxidation products of isoprene (α-methylglyceric acid, 2-methylerythritol) and of α-pinene (hydroxyglutaric acid)) and PBOA (traced thanks to the polyols). Finally, we further reviewed the literature in order to check if any previous study had investigated the ratio of PBOA tracers to total

OC in the PBOA fraction. Indeed, the OC_{PBOA}-to-arabitol and OC_{PBOA}-to-mannitol ratios in fungal spores were estimated between 7.22–16.25 and 5.20–10.83, respectively (Bauer et al., 2008; Yttri et al., 2011). The OC_{PBOA}-to-polyols ratio in our PMF studies is around 16 on average, which is in the range of what is proposed for fungal spores.

Overall, even if it is not excluded at this stage that some BSOA fraction may be mixed in our PBOA factor, we still believe that a large contribution is rather unlikely, and that the chemical fingerprint produced by the PMF analyses is representative of the average composition of the PBOA fraction obtained over a large range of sites.

We added some text (lines 454-451, page 15) in order to better explain all of this.

*"This result may be nuanced, in particular during summer, since some extent of mixing between PBOA and Biogenic Secondary Organic Aerosols (BSOA) cannot be entirely excluded. However, several evidences tend in favor of a non-significant mixing between BSOA and PBOA. First, the ratio of polyols-to-OC_{PBOA} shows a low variability from site to site, while it is unlikely that such a secondary process led to the same amount of OC for all sites since they present different meteorology, sunshine duration etc. Second, the bootstrap analysis do not show any "swap" between factors for the PBOA profile for all sites, indicative of a well-defined factor (see Fig. SI-5). Finally, the OC_{PBOA}-to-polyols ratio in this work (about 16) is in the range of ratio expected for fungal spores (12 -27, when arabitol and mannitol are considered together) (*Bauer et al., 2008; Yttri et al., 2011).*"*

References:

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