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 However the authors only show the PMF results concerning the source associated to polyols, remitting the reader to an unpublished manuscript for further scrutinizing of the aerosol total source apportionment and this is not acceptable.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).

This result on the general chemical profile of the PBOA factor tends to infirm the hypothesis of an emission process associating PBOA material with mineral dust resuspension. Indeed, our findings rather suggest that a main part of PBOA (and polyols) are most likely associated with biological particle direct emissions. It leaves only a minor fraction that could be linked to the mechanical resuspension of PBOA with crustal elements. Some minor fraction of EC in this factor could come from resuspended EC-containing dust particles being accumulated in topsoil as demonstrated in previous works (Forbes et al., 2006; Hammes et al., 2007; Zhan et al., 2016). Hence, the origin of the larger fraction of the contribution of EC remains unknown. Our conclusions are in good agreement with those made by Jia and Fraser (2011), based on the concentrations of these chemicals in different types of samples: i.e. size-fractionated (equivalent to $PM_{2.5}$ and PM_{10}) soil, plant, fungi, atmospheric $PM_{2.5}$ and PM_{10}. They found that the ambient concentrations of primary saccharide compounds at the suburban site of Higley (USA) are typically dominated by contributions of biological materials rather than resuspension of soil dust particles and associated microbiota."

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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Answer to Anonymous Referee #4 comments

The authors would like to thank Anonymous Referee #4 for his/her review and very useful comments to improve the present paper. We have studied carefully the various comments and tried to answer his/her question point by point in the following discussion.

This is a rich manuscript pooling together datasets from 28 sampling sites across France, focusing on polyols and glucose in the atmosphere. I find the manuscript to fit the scope of the journal, and to be generally well-written. I do have some fairly significant concerns about the analysis and technical comments which should be addressed prior its publication.

General comments:

1. I find the title misleading, as there is not really use of polyols and glucose as tracers of PBOA. To achieve that, both had to be quantified and recommendations provided on how the formers can be used to estimate the latter. Instead, the manuscript is rather descriptive on polyols and glucose, and results from a largely unclear PMF analysis is given, which leads to my next comment.

2. The PMF analysis is overwhelmingly under-reported and under-explained, given that only its main results are presented. The analysis is actually referred to a report on a url which is no longer valid, or refers to publications in preparation, which is not acceptable, given that one cannot first publish the results and later the analysis. If the authors decide to keep PMF analysis for the revised version of this study, further (and complete) details of the analysis must be provided.

We agree with the reviewer that the PMF methodology was too briefly explained in the first version of the manuscript. Since PMF methodology and results are now very common in the literature, we simply referred to the European FAIRMODE guideline and to our previous papers using some of these data (Waked et al., 2014; Weber et al. 2018). We are also working on another manuscript which should described the used PMF methodology in much more details. However, based on reviewer's comments, the revised version is now presenting in a more extended way the PMF methodology used with this large database, and associated general results. Particularly, we included a more detailed explanation of the method both in the text (please see below) and in the SI (extended text, Fig. SI-5 and Tables SI-3 to 5). Further, discussion on the statistical stability of the PBOA factor, using bootstrap analysis, is now included (Fig. SI-5) and the yearly average contribution of each PMF source-factor at each site is now provided (Fig. SI-4).

The url provided for the extended report on the SOURCE program was valid, but pointed to the webpage and not to the pdf. Sorry about that. We changed this reference to point to the pdf instead: report available at https://www.lcsqa.org/system/files/rapport/lcsqa2016-traitement_harmonise_etude_sources_pmf.pdf

Regarding the title accuracy, primary sugar compounds, and in particular polyols (such as arabitol and mannitol) are now commonly recognized as suitable tracers of the PBOA emission sources (Rajput et al., 2018; Zhu et al., 2015, 2016, and therein references). In the present work, we systematically obtained a PBOA profile when concentrations of polyols (defined as the sum of daily arabitol, mannitol and sorbitol concentrations) were included in the datasets used for the PMF analysis. This PBOA profile is characterized by the presence of more than 90% of the total polyols. In this sense, we consider that we use polyols as tracers of the PBOA factor in source apportionment, and that this work is pioneering the definition of a robust chemical profile of such a factor. Further, the chemical profile, thanks to the mass fraction of these tracers, can be used to derive a mass of total PBOA. With all of these, we consider that the title is not misleading and we clarified the main text as follows:

Lines 225-240, page 7:

“The PMF analysis took advantage of the ME-2 algorithm to add constraints to different chemical profiles (see Tables SI-3 and SI-4 for details). Mainly soft constraints were applied in order to add some prior knowledge about the emission sources and “clean” the different profiles without forcing the model toward an explicit solution. In particular, the polyol concentrations were “pulled up maximally”, while levoglucosan and mannosan were set to zero, and EC was “pulled down maximally” in this factor in the PBOA factor. This was achieved to avoid mixing with the biomass burning factor as well as possible influences of unrealistic high contributions of EC to PBOA. Other constraints were added parsimoniously to other factors, targeting specific proxies of sources (Table SI-4).

As for the general results of this large PMF study, we identified some well-known sources for almost all the sites (biomass-burning, road traffic, secondary inorganics, dust and sea salt). Two other less-common factors were identified for all sites: secondary biogenic aerosols (probably from marine origin), traced mainly by the presence of MSA, and PBOA, traced by the presence of more than 90% of the polyols total mass in the factor. Table SI-5 and Fig. SI-4 present more detailed description of the chemical tracers in each factor, together with their yearly average contribution for each site, respectively. Hereafter, only the PBOA chemical profile will be extensively investigated. The uncertainties of this PBOA factor are discussed below and its stability is presented in Fig. SI-5. Bootstrap analysis based on 100 resampling runs evidenced the very high stability of this PBOA factor since the PBOA initial constrained factor was mapped to PBOA bootstrap factor (BF) more than 99% of the time”.

Lines 441-446, page 15:

“*Moreover, the sensitivity of this factor to random noise in the data was investigated thanks to randomly re-sampling the input matrix of observation. In PMF analysis, this is done via the bootstrap method (Paatero et al., 2014) in the constrained run. The PBOA factor was always mapped to itself for 13 of the sites and quasi-always (97%) for the last three ones. It means that the PBOA factor does have a very high statistical stability since it never swaps with another factor (see Fig. SI-5)”.*

3. Please present your results (e.g. Fig. 6) limited only to PM10 sampling, as it is bound to represent more closely the actual atmospheric concentration, instead of being limited by too low sampling cut-off for the species studied. I recommend maintaining though section 3.3 (PM25/PM10 comparison) to report fine vs coarse mode analysis.

We do agree with Anonymous Referee #4. We maintained the section 3.3, reporting and discussing the distribution of ambient polyols (and glucose) concentrations between fine and coarse mode aerosols. Following reviewer’s suggestion, we modified the Figures 6 to 8, now limited to PM_{10} sampling sites only.

4. I find the sampling site denominations used here unsuitable. Urban sites are typically strongly impacted by traffic emissions, so their distinction feels arbitrary. And why rural? Do you mean background? From those denominations it feels like it is lacking filter sampling at forested sites, for example. An improved description of the sampling sites is necessary to better understand its somewhat unexpected results.

All of the monitoring sites (except the site of OPE-ANDRA) used in this study are stations of the air quality monitoring networks in France (AASQA). The AASQAs follow well-defined criteria for the classification (typology) of all sites in France. This methodological guide of air quality monitoring is part of the national technical reference. We kept the same classification. Table SI-1 is also now including a web link for the description of each sampling station as provided by the respective AASQA.

In this regard, it should be emphasized that urban sites presented in this study are in fact urban background sites, thus not impacted solely by traffic (in contrast to the roadside sites of Roubaix, Strasbourg, and partly Chamonix). Additionally, the rural sites are localized in rural environments, far enough from any anthropogenic sources (such as traffic, industry, etc.). This information has been added, page 5, lines 145-148.

5. There is certainly a lot to gain from combining several sampling sites, but I find that the analysis has become too shallow, unfortunately. Could you also focus on one sampling site and add more analysis (e.g. comparison with FBAP, total number, other species, wind direction/speed, backtrajectory, etc.) to try to better understand what is driving polyols and glucose atmospheric concentration? The manuscript seems to bring more questions than to answer at this point. Especially when it is kept fairly general (unclear PMF, unclear sampling periods, unclear site characterizations, etc.).

We also agree with Anonymous Referee #4 that this paper is only presenting one side of a very large study, the one dealing with average concentrations of a limited number of chemical species for a large number of sites, their seasonal variations, comparison of size distributions, and chemical profile of PBOA factors obtained by source apportionment (SA) studies. This is performed by an ensemble-like study that brings, as mentioned by the reviewer, a different and robust view of the PBOA factor in the atmosphere. We found the term “shallow” a bit restrictive considering the wealth of information that is unearthed and settled by this study. We made the choice of a very different approach than that proposed by the reviewer, who is asking for more classical single site studies.

It is clear that the present paper is intended to 1) settle the importance of the PBOA fraction in total PM over a large area, and 2) provide a robust chemical profile of this factor to be used in SA studies. As such, we believe that it can stand alone. However, as now mentioned at the end of the introduction, a second paper in progress will partly address the wishes of the reviewer on the processes behind the introduction of polyols into the atmosphere. And a third one will present some results of covariation of polyols concentrations and microbial fingerprints in air, soil, and plants at a local scale.

We also agree with the reviewer that the source apportionment study was lacking description in the submitted version of this paper, and it is now much more described in this updated version. We do not agree with him / her on the “unclear sampling periods” as Table S1 and Fig. S1 (already present in the submitted version) are clearly giving the dates for the sampling period at each site. We partially agree with him / her on the unclear site description. We updated the sites description table (Table S1) with web links describing each of the station, and now give a reference for the site nomenclature used for French Air Quality network. However, one should keep in mind that the characteristics of the immediate surroundings of the sites are of little importance for the atmospheric concentrations of polyols: this will be described in the second paper, showing for example that the time series of concentrations, for polyols and glucose, are within 10% of each other for 3 sites in the Grenoble area 15 km apart (one downtown in a pedestrian area, one in a park about 2.5 km away, and one in a suburban area 15 km away).

Specific/technical comments:

Abstract: Unclear why dust ressuspension would be linked to PBOA factor.

We do agree with Anonymous Referee #4 and have rephrased more precisely why dust resuspension could be linked to the PBOA factor. From the current literature, it is not clear if the ambient particulate polyols (tracers of PBOA) enter the atmosphere mainly through biological direct emissions or if they are associated to other materials such as the soil dust particles during resuspension processes. The contribution of crustal materials in PBOA chemical profile can give a good indication of the potential relationships between PBOA factors (polyols) and resuspension of soil dust particles.

Our findings evidenced that the mean PBOA chemical profile is clearly dominated by contribution from OM (78±9 % of the mass of the PBOA PMF factor on average), with only a minor contribution from the dust class (3±4 %), suggesting that ambient polyols are most likely associated with direct biological particle emissions (e.g. active spore discharge) rather than soil dust resuspension. Our conclusions are in good agreement with those made by Jia and Fraser (2011), based on characterizing the concentrations of these chemicals in different type of samples: i.e. size-fractionated (equivalent to $PM_{2.5}$ and PM_{10}) soil, plant, fungi, $PM_{2.5}$/ PM_{10}. They found that the ambient concentrations of primary saccharide compounds at Higley (USA) are typically dominated by contributions of biological materials rather than resuspension of soil dust particles and associated microbiota.

L.53: PM affects climate, not necessarily negatively.

We do agree with Anonymous Referee #4 and have rephrased this sentence (lines 53-54, page 2)

L.57: please refer to a more recent reference for carbonaceous matter.

More recent references have been added (line 58, page 2).

L.57-L.66 I suggest focusing on OM on the introduction, rather than OC, an artificial species from analytical limitations.

L.63: a significant fraction of OM can be associated with . . .

We do agree with Anonymous Referee #4 and we focused on OM (lines 58-65, page 2).

L.72: Please specify in which environments you are referring this figure, including atmospheric layer and aerosol sizes.

We rephrased this sentence and information on environment type, aerosol sizes, etc. have been added (lines 73-74, page 3).

L.74-76: And fluorescent techniques?

Fluorescent techniques, in particular fluorescent microcopy methods have been previously employed to analyze airborne biological particles. This former technic has the drawback to be laborious and time consuming when it comes to analyze many samples (Bozzetti et al., 2016; Heald and Spracklen, 2009). However, it is worth mentioning that recent fluorescent techniques (e.g. UV-APS, WIBS, etc.) have considerably improve our knowledge about the abundance of airborne biological particles (Fröhlich-Nowoisky et al., 2016; Gosselin et al., 2016; Rajput et al., 2018).

L.79: Unclear how atmospheric transport complements sources and abundances

The term "atmospheric transport pathways" has been removed as it can be confusing.

L.101: Datasets

Large sets of data have been modified into "datasets" (line 114, page 4).

L.104: Please define atmospheric emission pathway. Do you mean the processes the plant underwent to emit polyols?

More precise definition has been added. The term atmospheric "emission pathways" was used to specify how particulate polyols and glucose enter the atmosphere (line 117, page 4).

L.132: Please define "very rural".

The OPE-ANDRA site is a rural background site, which lies in the North-East of France, in a crop field area. The term "very rural" has therefore been replaced by a more precise description of OPE-ANDRA site (lines 149-150, page 5).

L.152: Please state that this number typically ranges from 1.2 to 2, so the estimates here represent an upper value of OM, thus a lower estimate of the contribution of PBOA.

We do agree with Anonymous Referee #4 and this information has been added (lines 170-172, page 6).

L.185: extra space before comma.

The extra space before comma has been removed.

L.186. Define JRC

JRC was used to specify the European Joint Research Centre. This definition has been added in the main text (line 206, page 7).

L.194: It is unclear why mix up filter-based BC with already quantified thermo-optical EC. Or there was no EC from DECOMBIO project? Please clarify.

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.

We clarified the main text as follows (lines 211-215, page 7):

"*The PMF conducted within the DECOMBIO project, for the sites of Marnaz, Chamonix, and Passy, used aethalometer (AE 33) measurements instead of EC (Chevrier, 2016). This complementary measure gives the total black carbon (BC), thus enabling the deconvolution of BC concentrations into its two main constituents: wood-burning BC (BCwb) and fossil-fuel BC (BCff) (Sandradewi et al., 2008). For graphical simplicity, BC_{wb} and BC_{ff} were summed up and labeled as EC in the following figures*".

L.200: See comment #2

Please see answer at comment #2

L.211: Range values refer to min/max? In terms of readability I prefer you remove this info and present only avg±std.

For readability, data has been presented as average ± standard deviation in the revised manuscript, as suggested by reviewers.

L.212: Please define Primary Sugar Compound (SC).

The term Primary Sugar Compound (SC) was used to specify polyols together with primary saccharide species. The definition has been added (lines 101-102, page 3).

L.228: Please increase axis font sizes.

The axis font sizes have been increased (Fig.2, page 8).

L.233: The asterisk is hard to readily identify. Please show only PM10 cutoff filters on this figure.

As explained in comments #3, Fig. 6 to 8 (Fig. S5 as well) are now limited to only PM10 cutoff filters.

L.233: The selected period feels somewhat arbitrary, thus lacking a clear definition of what is shown. Please be more direct on the chosen periods (dd-mm-yyyy) and criteria applied.

Selecting a specific date season could indeed be arbitrary. For simplicity, it is quite common to use months rather than the days to calculate seasonal concentration values (Verma et al., 2018). In the present work, seasons were defined as follows: Winter = December to February, Spring = March to May, Summer = June to August, and Autumn = September to November (see lines 368-370, page 12).

Comments

L.255: Please add the information of their estimated atmospheric lifetime.

The primary sugar compounds (including polyols and primary saccharide compounds) are actually thought to be relatively stable in the atmosphere (Wang et al., 2018). However, studies investigating their atmospheric lifetime are quite limited. One previous laboratory study has been conducted by the US-EPA to evaluate the stability of these chemicals on filter material exposed to gaseous oxidants as well as in aqueous solutions (simulating clouds and fog droplet chemistry). Findings of this former study have shown that primary sugar compounds remain quite stable up to 7 days (the extent of the testing period), pointing out their suitability for use as tracers of atmospheric transport (Fraser, 2010).

This information has added in the updated manuscript version (lines 101-109, page 3)

L.256: It feels like a weak hypothesis to me, from the PBOA perspective, could it be emission ratios change with wind speed, temperature, RH? If focusing on comparable season/meteorology, could the correlation be improved, given distinct emission pathways? And how about interferences from other sources? Is it mixing PM2.5 samples?

The reviewer is right that this is a weak hypothesis, but there is very few literature on the subject (and so far no PMF study using glucose concentrations). We removed this sentence and keep working on the topic in order to figure out the sources of atmospheric glucose and its potential relation with the PBOA factor.

L.267: To improve readability, please remove SD and describe only the four average values of both sampling sites, given the interest is the distribution of fine vs coarse mode.

Presenting “only” average values may certainly improve the readability. Nonetheless, average ± standard deviation give an in-depth overview of the statistical size distribution of ambient particulate polyols and glucose concentrations. In this regard, we think that it is preferable to keep these concentration values as Mean ± SD.

L.290: Please remove “compartment”.

The term compartment has been removed

L.282: Please indicate the number of samples used on this analysis.

The number of samples has been specified (lines 327-328, page 11).

L.301: Does it make sense that PBOA-related polyols are “only” 2-3 times higher in summer in comparison to winter time? The trend behind concentrations in “rural”, “urban” or “traffic” feels inconsistent with PBOA interpretation.

The seasonal concentrations of polyols presented in this section correspond to the average values over all studied sites. When focusing on one site, the summer concentrations can be 5-8 times higher than those observed in winter, which is consistent with an emission process more likely associated with increased biological activities in summertime. This observation is in good agreement with previous works (Jia et al., 2010a, 2010b; Liang et al., 2016; Verma et al., 2018). Furthermore, one should keep in mind that the values presented are seasonal averages and that daily average concentrations can be much higher in summer.

Concerning the second part of the remark (about the trend according to site typology), and to the best of our knowledge, there is no observation in the literature that could support the existence of such an intuitive trend. Conversely, and as mentioned above, our measurements indicate that concentrations are nearly identical for the 3 sites of the Grenoble area, at a scale of c.a. 15 km encompassing several types of sites.

L.404: In which time series?

These time series refer to a data in the study conducted by Bonvalot et al., (2016). This sentence has been removed, as the whole paragraph has been modified in the updated manuscript version.

L.440 Please correct sea-salt and not " sea minus salt".

This correction has been added

L.445: Unclear sentence.

This sentence has been rephrased more precisely (lines 507-524, page 17).

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Polyols and glucose particulate species as tracers of primary biogenic organic aerosols at 28 F~~f~~rench sites

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Abstract. A growing number of studies are using specific primary sugar species, such as sugar alcohols or primary saccharides, as marker compounds to characterize and apportion primary biogenic organic aerosols (PBOA) in the atmosphere. To better understand their annual cycles, as well as their spatio-temporal abundance in terms of concentrations and sources, we conducted a large study focusing on three major atmospheric primary sugar compounds (i.e. arabitol, mannitol and glucose) measured in various environmental conditions on about 5,300 filter samples collected at 28 sites in France. Our results show significant atmospheric concentrations of polyols (defined here as the sum of arabitol and mannitol) and glucose at each sampling location, highlighting their ubiquity. Results also confirm that polyols and glucose are mainly associated with the coarse rather than the fine aerosol mode. At nearly all sites, atmospheric concentrations of polyols and glucose display a well-marked seasonal pattern, with maximum concentrations from late spring to early autumn, followed by an abrupt decrease in late autumn, and a minimum concentration during wintertime. Such seasonal patterns support biogenic emissions associated with higher biological metabolic activities (e.g. sporulation, growth, etc.) during warmer periods. Results from a previous comprehensive study using Positive Matrix Factorization (PMF) based on an extended aerosol chemical composition dataset of up to 130 species for 16 of the same sample series has also been used in the present work. Results show that PBOA are significant sources of total OM in PM_{10} (13±4 % on a yearly average, and up to 40 % in some environments in summer) at most of the investigated sites. The mean PBOA chemical profile is clearly dominated by contribution from OM (78±9 % of the mass of the PBOA PMF factor on average), and~~,~~ only a minor contribution from dust class (3±4 %), suggesting that ambient polyols are most likely associated with biological particle emissions (e.g. active spore discharge) rather than soil dust resuspension.

1. Introduction

Airborne particles (or particulate matter, PM) are of major concern due to their multiple ~~deleterious~~ effects on climate ~~on both~~and adverse human health impacts~~and climate~~ (Boucher et al., 2013; Cho et al., 2005; Ntziachristos et al., 2007). The diversity of PM impacts is closely linked to their complex and highly variable nature: size distribution, concentration and chemical composition, or specific surface properties. PM consists of inorganic and elemental substances, and a large fraction made of carbonaceous matter (organic carbon (OC) and elemental carbon (EC)) (Franke et al., 2017; Putaud et al., 2004a; Yttri et al., 2007a). Substantial amounts of atmospheric organic matter (OM) remain unidentified and uncharacterized at the molecular level. In most studies, a maximum of only 20 % of particulate OM mass ~~of PM~~ can generally be speciated and quantified (Alfarra et al., 2007; Fortenberry et al., 2018; Liang et al., 2017; Nozière et al., 2015). This detailed composition of OM and its spatial and seasonal distribution can give important insights on the adverse effects of PM. So far, the majority of air pollution studies have focused on organic atmospheric particles associated with anthropogenic and secondary sources, whereas a significant fraction of OM~~C~~ is also associated with primary emissions from biogenic sources (Bauer et al., 2008a; Jaenicke, 2005; Liang et al., 2016). Therefore, the characterization of primary OM~~C~~ biogenic sources at the molecular level is still limited (Fuzzi et al., 2006; Liang et al., 2017; Zhu et al., 2015), and should be further investigated for a better understanding of aerosol sources and formation processes.

Primary biogenic organic aerosols (PBOA) are emitted directly from the biosphere to the atmosphere where they are ubiquitous and participate in many atmospheric processes (Elbert et al., 2007; Fröhlich-Nowoisky et al., 2016). Additionally, their inhalation has long been associated with human respiratory impairments (e.g. asthma, aspergillosis, etc.) (Després et al., 2012; Morris et al., 2011). PBOA comprises living and dead microorganisms such as bacteria, fungi, viruses, bacterial and fungal spores, and microbial fragments, endotoxins, mycotoxins, or pollens (Elbert et al., 2007; Jaenicke, 2005; Morris et al., 2011). In most semi-urban European site, PBOA can account for up to 25 % of the atmospheric aerosol mass, in the size range of 0.2 to 50 µm (Fröhlich-Nowoisky et al., 2016; Jaenicke, 2005; Huffman et al., 2012; Manninen et al., 2014; Morris et al., 2011). However, their sources and contribution to total airborne particles are still poorly documented, partly because of the difficulty to recognize them by conventional microbiological methods (cells culture, microscopic examination, etc.) (Di Filippo et al., 2013; Heald and Spracklen, 2009; Jia et al., 2010a).

Several specific chemical components, such as primary sugar compounds (i.e. primary saccharides and sugar alcohols) emitted persistently from biogenic sources, have long been suggested as powerful and unique biomarkers in tracing sources, and abundances ~~, as well as atmospheric transport pathways~~ of PBOA as well. For instance, ambient concentrations of glucose have been used as markers for plant materials (such as pollen, leaves, and their fragments) or soil emissions from several areas in the world (Fu et al., 2012; Jia et al., 2010a, 2010b; Pietrogrande et al., 2014; Rathnayake et al., 2017). Many studies indicated that glucose is the most abundant monosaccharide in vascular plants, where it serves as the common energy materials, and an important source of carbon for soil active microorganisms (such as bacteria or fungi) (Jia et al., 2010a; Medeiros et al., 2006; Pietrogrande et al., 2014; Zhu et al., 2015). Additionally, sugar alcohols (also called polyols) including arabitol and mannitol have been proposed as markers for airborne fungi, and are widely used to quantify their contributions to PBOA ~~PM~~ mass (Bauer et al., 2008a, 2008b; Golly et al., 2018; Srivastava et al., 2018; Zhang et al., 2010). ~~These sugar alcohols also correlate very well with a factor identified as PBOA in AMS off-line studies (Vlachou et al., 2018b).~~ These sugar alcohols have also been found to correlate very well with fluorescent PBOA in UV-APS and WIBS-3 online studies, particularly in rainy periods (Gosselin et al., 2016), favoring microbial sporulation (such as fungi belonging to Ascomycota and Basidiomycota phyla) (China et al., 2016; Elbert et al., 2007; Jones and Harrison, 2004). Polyols are produced in large amounts by many fungi and bacteria, and several functions have been described for these compounds, such as common energy storage materials, intracellular protectants against stressful conditions (e.g. heat or drought), storage or transport of carbohydrates, quencher of oxygenated reactive species, or regulators of intracellular pH by acting as a sink or source of protons (Jennings et al., 1998; Medeiros et al., 2006; Vélëz et al., 2007). Hence, polyols, especially arabitol and mannitol, may represent a significant fraction of the dry weight of fungi, and mannitol can contribute between 20 to 50 % of the mycelium dry weight (Ruijter et al., 2003; Vélëz et al., 2007). However, polyols are also often identified in the lower plants (leaves, pollens) and green algal lichens (Medeiros et al., 2006; Vélëz et al., 2007; Yang et al., 2012). The primary sugar compounds (defined as polyols and primary saccharide species) are actually thought to be relatively stable in the atmosphere (Wang et al., 2018). However, studies investigating their atmospheric lifetime are quite limited. One previous laboratory study has been conducted by the US-EPA to evaluate the stability of these chemicals on filter material exposed to gaseous oxidants as well as in aqueous solutions (simulating clouds and fog droplet chemistry). Findings of this former study have shown that primary sugar compounds remain quite stable up to 7 days (the extent of the testing period), pointing out their suitability for use as tracers of atmospheric transport (Fraser, 2010). With all of this information, the use of primary sugar compounds (such as mannitol, arabitol, glucose, etc.) as suitable tracers of PBOA is generally acknowledged (Jia and Fraser, 2011; Zhu et al., 2015, 2016).

Although atmospheric concentrations of polyols, including arabitol and mannitol, as well as that of some primary monosaccharides (e.g. glucose), have been previously quantified as part of several studies in various environments including urban/suburban, rural, rainforest, mountain, and marine areas (Fu et al., 2012; Graham et al., 2003; Jia et al., 2010a, 2010b; Liang et al., 2016; Pietrogrande et al., 2014; Simoneit, 2004; Verma et al., 2018; Yttri et al., 2007b; Zhu et al., 2015), large ~~sets of d~~d~~D~~atasets investigating their annual cycles and spatial distributions are still limited. Such information could give important insights on environmental factors influencing their atmospheric levels such as climate and biotope, and therefore help to elucidate patterns regarding their major sources and atmospheric emission pathways (i.e. atmospheric input process). Even if numerous sources and emission mechanisms have been widely proposed, including among others, metabolic active microbial wet emissions, entrainment of farmland or natural soils and associated microbiota (Elbert et al., 2007; Fu et al., 2013; Gosselin et al., 2016; Jia et al., 2010a, 2010b; Medeiros et al., 2006; Pietrogrande et al., 2014; Simoneit et al., 2004; Verma et al., 2018; Yttri et al., 2007b), the dominant atmospheric input processes have not been yet sufficiently elucidated.

In this context, the present study was designed to provide a large overview of the spatial and seasonal variations of polyols and glucose mass concentrations, as well as their contribution to the aerosol organic mass fraction, in France. To do so, data was collected at many sites in different environments (rural, traffic, urban), in order to represent various sampling conditions in terms of site typologies and meteorological conditions. Thanks to the availability of results from an extended Positive Matrix Factorization (PMF) analysis performed for the corresponding datasets, the overall contributions of the main polyols and glucose emission sources could also be investigated in light of their spatial patterns. To the best of our knowledge, this is the first study providing such an extended phenomenology of these compounds over multiple sites with different typologies. This paper is the first part of on-going work on the concentrations of ambient particulate polyols and glucose in France. A second part will examine the short-term (daily) variations of these chemicals at multiple spatial scale (local to nation-wide) and their potential processes for entering the atmosphere. A third part will investigate the links between the atmospheric concentrations of polyols and glucose and airborne microbial fingerprint up to the genus level.

2. Material and methods

2.1 Aerosol sampling

Ambient aerosol samples considered in the present work come from different research and monitoring programs, conducted over the last 5 years in France (Figure 1~~Figure 1~~). Each program includes at least one-year of field sampling, providing a total number of 5,343 daily filter samples available for the sake of the present study. These sites offer diverse conditions in terms of typologies (i.e. rural, traffic, urban sites, Alpine valley environments, etc.), local climate and vegetation types and were selected in order to cover the complex and variable national environmental conditions. These sites are assumed to represent typical environmental conditions in France, and our observations/and general tendency could therefore be extrapolated to neighboring western European countries presenting quite homogeneous environmental conditions.

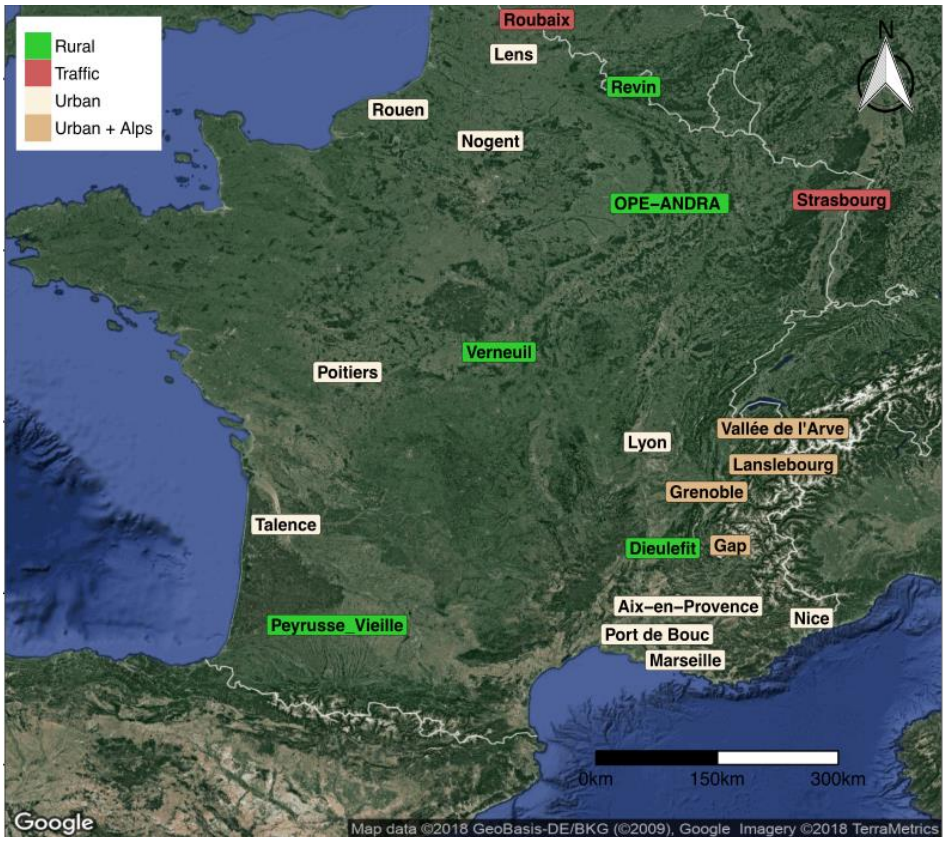


Figure 1: Map of sampling site locations in France. Green: rural background, red: traffic, wheat: urban background and dark wheat: u~~U~~rban background in Alpine~~s~~ valley~~ environment~~ sites. The area~~Stations~~ of Grenoble (Grenoble_LF, Grenoble_CB and Grenoble_VIF) and Vallée de L'Arve (Marnaz, Passy and Chamonix) include~~ each~~ 3 sites each. The area~~Station~~ of Marseille includes four sites: Marseille, Mallet, Meyreuil and Gardanne.

The site of OPE-ANDRA is a specific monitoring observatory in a~~ very~~ rural environment, without any village or industry within several kilometers (description available from: http://www.andra.fr). All other sites correspond to stations of regional air quality monitoring networks (AASQA). The availability of filter samples was variable from one site to the other one, depending on the sampling frequency (typically every third or sixth day). Filter collection was conducted within the PM_{10} or the $PM_{2.5}$ aerosol size fraction, depending on the investigated site (Table SI-1). Moreover, co-located and simultaneous PM_{10} and $PM_{2.5}$ samplings were conducted at OPE-ANDRA and Revin, allowing to investigate the distribution of primary sugar compounds between the fine and the coarse aerosol size fractions at these two sites.

Ambient aerosols were collected onto quartz fiber filters (Tissu-quartz PALL QAT-UP 2500 150 mm diameter), preheated at 500 °C for 4 h minimum before use. After collection, all filter samples were wrapped in aluminum foils, sealed in zipper plastic bags and stored at <4°C until further chemical analysis. Field blank filters were also collected, at least once a month, using the same handling procedure than for PM samples. More detailed information on the sampling periods, air sampler, number of filters and nature of PM samples are provided in Table S1 and Fig. S1.

2.2 Chemical analyses

PM samples were analyzed for various chemical species using sub-sampled fractions of the collection filters. In the frame of the present study, the carbonaceous matter (organic carbon (OC) and elementary carbon (EC)) was analyzed using a thermo-optical method on a Sunset Lab analyzer (Birch and Cary, 1996) as described by Aymoz et al. (2007), using the EUSAAR2 temperature program (Cavalli et al., 2010), except for the five sites of Northern France where the NIOSH870 protocol was employed (Birch and Cary, 1996). Particulate organic matter (OM) contents were then estimated by multiplying the organic carbon mass concentrations by a fixed factor, with $OM = 1.8 \times OC$. This OM-to-OC ratio value of 1.8 was chosen based on previous studies performed in France (Favez et al., 2010; Petit et al., 2015 and reference therein) and around the world. (e.g., Aiken et al., 2008; Li et al., 2018; Ruthenburg et al., 2014; Vlachou et al., 2018~~a~~), with a typical range of 1.2-2.4 values.

For the analysis of anhydrosugars, sugar alcohols, and primary saccharides, filter punches (typically of about 10 cm^2) were first extracted into ultrapure water, then filtered using a 0.22 µm Acrodisc filter. Depending on the site, analyses were conducted either by IGE (Institut des Géosciences de l'Environnement) or by LSCE (Laboratoire des Sciences du Climat et de l'Environnement) (Table SI-1). At IGE, extraction was performed during 20 min in a vortex shaker and analyses were achieved using an HPLC with Pulsed Amperometric Detection. A first set of equipment was used until March 2016, consisting of a Dionex DX500 equipped with three columns Metrosep (Carb 1-Guard + A Supp 15-150 + Carb 1-150), the analytical run being isocratic with 70 mM sodium hydroxide eluent, followed by a gradient cleaning step with a 120 mM NaOH eluent. This analytical technique enables to detect anhydrous saccharides (levoglucosan, mannosan, galactosan), polyols (arabitol, sorbitol, mannitol), and glucose (Waked et al., 2014). A second set of equipment was used after this date, with a Thermo-Fisher ICS 5000^+ HPLC equipped with 4 mm diameter Metrosep Carb 2 × 150 mm column and 50 mm pre-column. The analytical run is isocratic with 15 % of an eluent of sodium hydroxide (200 mM) and sodium acetate (4 mM) and 85 % water, at 1 mL min^{-1}. This method allows for additional separation and quantification of erythritol, xylitol, and threalose. At LSCE, extraction was performed during 45 min by sonication and analyses were achieved using an IC (DX600, Dionex) with Pulsed Amperometric Detection (ICS3000, Dionex). A CarboPAC MA1 columns has be used (4 × 250 mm, Dionex), the analytical run being isocratic with 480 mM sodium hydroxide eluent. This analytical technique enable to detect anhydrous saccharides (levoglucosan, mannosan, galactosan), polyols (arabitol, mannitol), and glucose.

Field blank filters were handled as real samples for quality assurance. The present data were corrected with field blanks. The reproducibility of the analysis of primary sugar species (polyols, glucose), estimated from the analysis of extracts of 10 punches from the same filters are generally in the range of 10-15 %.

Additional chemical analyses were conducted for most of the sites, allowing to quantify up to 130 different chemical species (Calas et al., 2018). 30- 35 chemical species were then selected ~~-~~in order to achieve PMF analyses as discussed hereafter.~~, as will be presented in a forthcoming paper (Salameh et al., in prep.).~~

2.3 Statistical analysis

Species concentration measurements were first analyzed for normality using Shapiro-Wilk's method with the statistical program *R studio interface* (version 3.4.1). Since data were generally not distributed normally, we used non-parametric statistical methods. The strength of the relationship between species concentrations was investigated using the non-parametric Spearman rank correlation method. Multiple mean comparison analyses were performed with the Kruskall-Wallis test method. Statistical significance was set at $p < 0.05$.

Positive Matrix Factorization for the source apportionment of the PM was previously performed at several sites of this study, as part of the SOURCES (Favez et al., 2016; Salameh et al., in prep.) and DECOMBIO (Chevrier, 2017) projects. We used the US EPA PMF 5.0 software (US EPA, 2015)~~–~~, following the general recommendation guidelines of the European Joint Research Centre (JRC) (Belis et al., 2014). Briefly, the SOURCES program aimed at performing source apportionment at 15 sites using a harmonized methodology, i.e. using the same chemical species, uncertainties, constraints, and criteria for factor identification. The PMF conducted within SOURCES project uses about 30 different species (Table S6), including carbonaceous fraction (OC, EC), ions (Cl^-, NO_3^- SO_4^{2-}, NH_4^+ K^+, Mg^{2+}, Ca^{2+}), organic markers (polyols i.e. sum of arabitol, mannitol and sorbitol; levoglucosan; mannosan) and metals (Al, As, Ba, Cd, Co, Cs, Cu, Fe, La, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, V, Zn). The PMF conducted within the DECOMBIO project, for the sites of Marnaz, Chamonix, and Passy, used aethalometer (AE 33) measurements instead of EC (Chevrier, 2016). This complementary measure gives the total black carbon (BC), thus enabling the deconvolution of BC concentrations into its two main constituents: wood-burning BC (BC_{wb}) and fossil-fuel BC (BC_{ff}) (Sandradewi et al., 2008). For graphical simplicity, BC_{wb} and BC_{ff} were summed up and labeled as EC in the following Figures. ~~stead of EC The PMF conducted within the DECOMBIO project, for the sites of Marnaz, Chamonix, and Passy, used in addition to the 30 different species, aethalometer (AE 33) measurements for the separation between BC_{wb} and BC_{ff} (black carbon from wood burning and fossil fuel, respectively). For simplicity, BC_{wb} and BC_{ff} were summed up and labeled as EC in the present study.~~ PMF modelling was performed separately for each site. Statistical significance was validated with bootstrap higher than 80 % for each factor. Detailed methodology and results about these studies are given in their respective papers (Chevrier, 2017; Favez et al., 2016; Salameh et al., in prep.). It should be noted that glucose was not included in the final solution for any of these PMF, since it generally produced statistical instability of the solutions (this point is further discussed in Sect. 3.2).

The PMF analysis took advantage of the ME-2 algorithm to add constraints to different chemical profiles (see Tables SI-3 and SI-4 for details). Mainly soft constraints were applied in order to add some prior knowledge about the emission sources and “clean” the different profiles without forcing the model toward an explicit solution. In particular, the polyol concentrations were “pulled up maximally”, while levoglucosan and mannosan were set to zero, and EC was “pulled down maximally” in this factor in the PBOA factor. This was achieved to avoid mixing with the biomass burning factor as well as possible influences of unrealistic high contributions of EC to PBOA. Other constraints were added parsimoniously to other factors, targeting specific proxies of sources (Table SI-4).

As for the general results of this large PMF study, we identified some well-known sources for almost all the sites (biomass-burning, road traffic, secondary inorganics, dust and sea salt). Two other less-common factors were identified for all sites: secondary biogenic aerosols (probably from marine origin), traced mainly by the presence of MSA, and PBOA, traced by the presence of more than 90% of the polyols total mass in the factor. Table SI-5 and Fig. SI-4 present more detailed description of the chemical tracers in each factor, together with their yearly average contribution for each site, respectively. Hereafter, only the PBOA chemical profile will be extensively investigated. The uncertainties of this PBOA factor are discussed below and its stability is presented in Fig. SI-5. Bootstrap analysis based on 100 resampling runs evidenced the very high stability of this PBOA factor since the PBOA initial constrained factor was mapped to PBOA bootstrap factor (BF) more than 99% of the time.

~~Also, the PMF in the SOURCES project took advantage of the possibility to add constraints in the solution chemical profiles. In the PBOA profiles that are systematically obtained when polyols are included in the initial datasets, we “pulled up maximally” their concentrations, while levoglucosan and mannosan were set to zero and EC was “pulled down” maximally. It means that the PMF model tried to enrich the polyols mass in the PBOA~~

~~factor and deplete EC. Other constraints were added parsimoniously, targeting specific proxies of sources and are further discussed in the respective papers.~~

3. Results and discussion

3.1 Relative distribution between sugar alcohols and glucose

Figure 2 presents an overview of the relative mass concentration distributions of individual chemical species quantified at two sites with very different characteristics, an urban site in Grenoble and the rural site of OPE-ANDRA. Data are presented for the warmer season (e.g. during summer and fall), when concentrations were at their maximum (see Sect. 3.4). Glucose is the most abundant species measured (~~range 3.2–297.2 ng m^{-3};~~ average 37.6±26.4 ng m^{-3}), accounting on average for 25 % of primary sugar compounds (SC) total mass at both sites. Mannitol (~~1.4–199.1 ng m^{-3};~~ 37.3±24.6 ng m^{-3}) and arabitol (~~0.2–133.9 ng m^{-3};~~ 32.0±22.2 ng m^{-3},) are the second and third most abundant species, accounting respectively for 25 and 23 % of SC mass. Threalose is relatively abundant in samples from these two sites (~~4.3–104.1 ng m^{-3};~~ 20.1±16.2 ng m^{-3}), accounting for 14 % of SC mass, but in general its concentration is frequently below the limit of quantification for samples from other sites in France~~(Fig. SI-3)~~. The other identified polyols (i.e. erythritol, inositol, glycerol, sorbitol, and xylitol) present lower concentration levels (~~0.01–33.8 ng m^{-3},~~ 4.9±2.1 ng m^{-3}), corresponding altogether to 13 % of SC total mass.

Such ambient mass concentration distribution patterns are similar (but with variable intensities) to those previously reported for aerosol samples collected at various locations around the world. For example, Verma et al. (2018) found that glucose, and arabitol together with mannitol, contributed to 16.7 and 48.1 %, respectively, of total primary sugar compounds in aerosols from Chichijima Island. Similarly, Yttri et al. (2007b) showed that glucose and the pair arabitol-mannitol were the main contributors of total primary monosaccharides and sugar alcohols in aerosols collected from four various background sites in Norway. In addition, Carvalho et al. (2003) reported that arabitol, mannitol and glucose as the most dominant primary sugar compounds in aerosols from rural background and boreal forest sites in Germany and Finland, respectively.

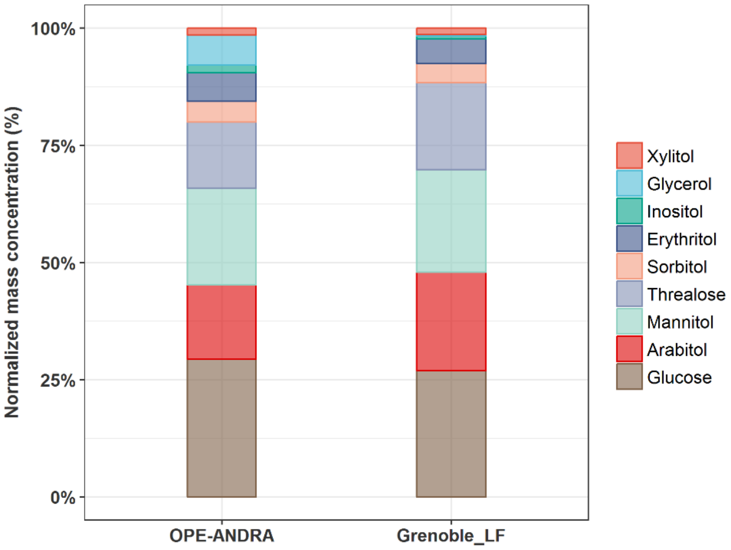


Figure 2: Overview of relative mass distributions of individual primary sugar alcohols and saccharide compounds quantified in PM$_{10}$ samples at two sites over summer and autumn periods (June to November) corresponding to maximal atmospheric concentrations of sugar alcohols/saccharide compounds.

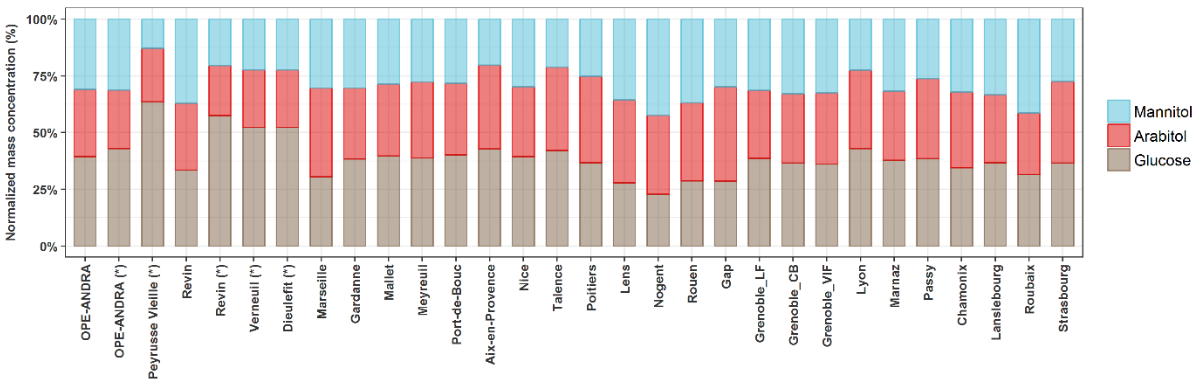


Figure 3: Average ~~M~~mass concentration distributions of arabitol, mannitol, and glucose. Symbol (*) indicates $PM_{2.5}$ aerosol samples. Only data for warmer season (June to November~~e.g. during summer and fall~~), corresponding to maximal atmospheric concentration of polyols and glucose are shown.

Although various primary sugar alcohols and saccharides have been detected and quantified for most of the investigated sites, the following study focuses only on the three major and ubiquitous species, namely arabitol, mannitol and glucose. Figure 3 presents their average relative contributions at all sites, for the warmer period, displaying very similar features at a first glance. However, discrepancies could be observed from site to site, as discussed in following sections.

3.2 Relationships between selected primary sugar compounds

Figure 4 summarizes linear correlations obtained between arabitol and mannitol concentrations at each site during the warmer period. Medium to very high correlation coefficients could be observed ($0.58 \leq R^2 \leq 0.93$; $30 \leq n \leq 143$ or $45 \leq n \leq 341$ for $PM_{2.5}$ and PM_{10} series, respectively), with slopes in a rather narrow range (between 0.59 and 1.10), and quite low intercepts (always below 9 ng m^{-3}). Such covariations indicate that both species are most probably co-emitted, by one or several type(s) of sources, at each site during the summer-autumn period. These observations are in agreement with previous studies also showing strong covariations between arabitol and mannitol (Kang et al., 2018; Verma et al., 2018; Zhu et al., 2015). Therefore, it seemed reasonable to consider both species together, so that their concentrations are summed up and labelled as "polyols" in the following sections.

Conversely, linear correlations between glucose and polyols concentrations are generally weaker ($0.10 < R^2 \leq 0.78$), with slopes varying over a much larger range (between 0.12 and 0.94), and variable intercepts (between -5.6 and 16.4 ng m^{-3}). This suggests that glucose concentrations might follow a different pattern compared to that of polyols, either due to different emission sources, or different chemical stability in the atmosphere. It is therefore reasonable to keep glucose as a separate chemical species in the following discussion. ~~Also, this distinct behavior is most probably one reason why we were not able to obtain stable solutions when including glucose in the PMF studies described in Sect. 3.5.~~

It should be emphasized that the~~-~~ variability in the slope of the regressions between the chemical concentrations are most probably related to the emissions and atmospheric processing. Particularly in the case of mannitol and arabitol, they may be influenced by biogenic or biotope characteristics. Nevertheless, no evident relationship between the slope values and the typology or the geographical location of the sites could be observed (Figure 4~~Figure 4~~).

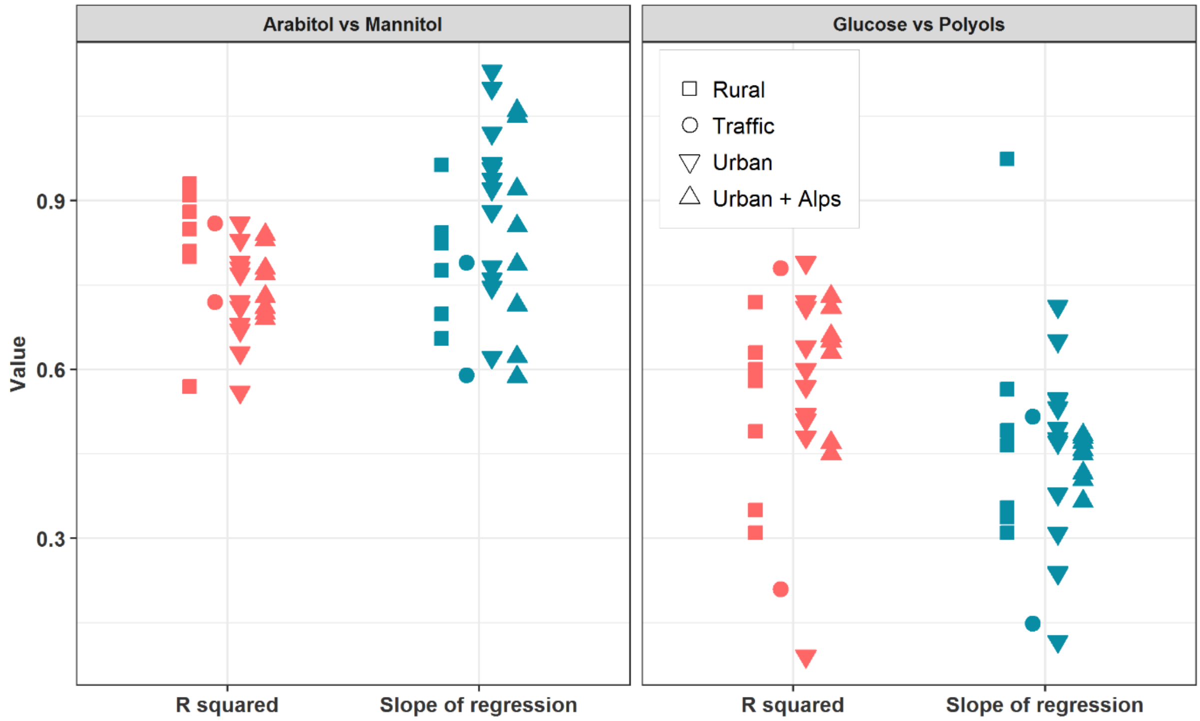


Figure 4: Linear regression analysis between selected primary sugar compounds mass concentrations (i.e. arabitol, mannitol and glucose) during summer and autumn seasons (June to November), for all the sites considered in this study.

3.3 Relative distributions between PM$_{10}$ and PM$_{2.5}$

Figure 5~~Figure 5~~ shows the average PM$_{10}$ and PM$_{2.5}$ concentrations of polyols and glucose at OPE-ANDRA and Revin during the summer and autumn seasons. The polyols mass concentrations ranged from 7.5±10.9 to 27.8±33.3 ng m^{-3} in PM$_{2.5}$, and from 48.9±38.2 to 73.5±61.8 ng m^{-3} in PM$_{10}$, in Revin and OPE-ANDRA sites, respectively. PM$_{10}$-to-PM$_{2.5}$ ratios were then on average of about 3 to 5. Similar size distribution patterns, with variable intensity, were observed for glucose (Fig. 5). These results indicate that polyols and glucose are mainly associated with the coarse PM fraction. This observation is in good agreement with several previous investigations where polyols (especially arabitol and mannitol), together with glucose, were prevalent in the coarse fraction (Fu et al., 2012; Fuzzi et al., 2007; Pio et al., 2008; Yttri et al., 2007b). However, Carvalho et al. (2003) reported different size distributions for polyols and glucose, with variable fine or coarse mode maxima depending upon sampling location. For instance, maximum atmospheric concentrations of mannitol were associated to fine and coarse aerosols from boreal forest (Finland) and rural background sites (Germany), respectively. The authors hypothesized that these observations are due to different assemblages of dominant fungal biota (with variable aerodynamic characteristics) at different sites. Some other previous studies showed aerodynamic diameters typically ranging from 2 to 10 µm, even though a few airborne bacterial/fungal spores could exceed that size (Bauer et al., 2008a; Elbert et al., 2007; Huffman et al., 2012; Zhang et al., 2015).

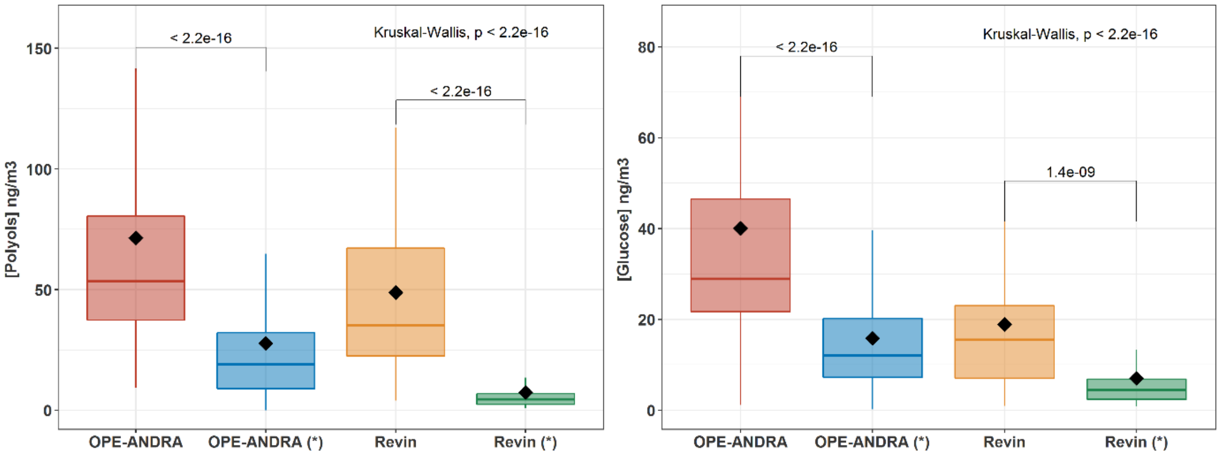


Figure 5: Box plots of mass concentrations of polyols (left) and glucose (right) in PM$_{10}$ and PM$_{2.5}$ (with symbol (*) samples). Black markers inside each boxplot indicate the mean concentration value, while the top, middle and bottom lines of the box represent the 75th, median and 25th percentile, respectively. The whiskers at the top and bottom of the box extend from the 95th to the 5th percentile. Number of samples were N = 123 for OPE-ANDRA and N = 87 for Revin ~~sites~~, respectively. Statistical differences between average mass concentrations were analyzed with the Kruskall-Wallis methods ($p < 0.05$).

Hence, although if the precise mechanisms of atmospheric emission of particulate polyols and glucose are not fully resolved, our observations are in good agreement with ambient mass concentrations of polyols and glucose being likely associated with biological particles, as already suggested elsewhere (Fu et al., 2012; Verma et al., 2018; Zhang et al., 2015). These species could enter into the atmosphere~~ic~~ ~~compartment~~ through either natural or anthropogenic resuspension of surface soils and associated bacterial/fungal spores (containing polyols and primary sugar compounds), or via a direct input resulting from microbial activities (e.g. sporulation). Another hypothesis would be the abrasion of leaves and the subsequent release of microbial organisms and plant debris (Fu et al., 2012; Medeiros et al., 2006; Simoneit et al., 2004).

3.4 Spatial and seasonal distribution of atmospheric concentrations

3.4.1 Spatial and seasonal patterns of polyol concentrations

As illustrated in Fig. 6, significant concentrations of polyols were measured at each investigated site, evidencing the ubiquity of these organic compounds. The annual average concentration levels of polyols measured in PM$_{10}$ aerosols at all sites (33.2±33.5 ng m^{-3}; see Table SI-2) are within the range previously reported for urban and rural sites across Europe (Burshtein et al., 2011; Di Filippo et al., 2013; Pietrogrande et al., 2014; Yttri et al., 2007, 2011). Additionally, p~~P~~olyols mass concentrations clearly exhibit seasonal trends, with variable intensity according to the sampling sites. On a seasonal average, polyols are more abundant in summer (46.8±43.6 ng m^{-3}) and autumn (43.0±36.7 ng m^{-3}), followed by spring (19.0±13.6 ng m^{-3}) and winter (16.2±11.5 ng m^{-3}). The average concentrations of polyols are then at least 2 to 3 times higher during summer or autumn months than during the cold months, with a ratio that can be as high as 8 to 10.

Previous studies also reported similar seasonal variation pattern for urban and rural aerosol samples collected at various locations. For example, Pashynska et al. (2002) measured higher atmospheric polyol (arabitol, mannitol) contents during late summer and autumn, in Belgium. Several other studies reported higher concentrations of polyols in summer than spring and winter time, in aerosols collected from Texas, USA and Jeju Island, respectively

(Fu et al., 2012; Jia et al., 2010a, 2010b). More recently, Liang et al. (2016) and Verma et al. (2018) also reported similar seasonal distributions for aerosols sampled at Beijing, China and north-western Pacific, respectively.

The higher atmospheric polyols concentrations observed are likely due to the increased contribution from metabolically active microbial derived sources (fungi, bacteria, green algal lichens) as a result of external stressors such as heat, drought and relative moisture. Indeed, fungal and prokaryotic cells activities, including their growth and sporulation, are promoted by high temperature and humid conditions occurring in summer and autumn (China et al., 2016; Elbert et al., 2007; Jones and Harrison, 2004; Rathnayake et al., 2017).

As also evidenced from Fig. 6, atmospheric polyols concentrations do not present any significant seasonal differences related to the site typology (rural, traffic, urban sites with/without Alpine influences), or latitude. There is some tendency toward higher concentrations in summer in Alpine environments, but some other sites (like the rural site of OPE-ANDRA, in the North-East of France) can reach the same levels of concentrations. We tested several types of hierarchical classifications, including variables like monthly or seasonal mean polyols concentrations, the ratio arabitol-to-mannitol, or linear regression parameters (slope, R square) but none of them led to a simple clustering of the sites that would explain the variability of the concentrations.

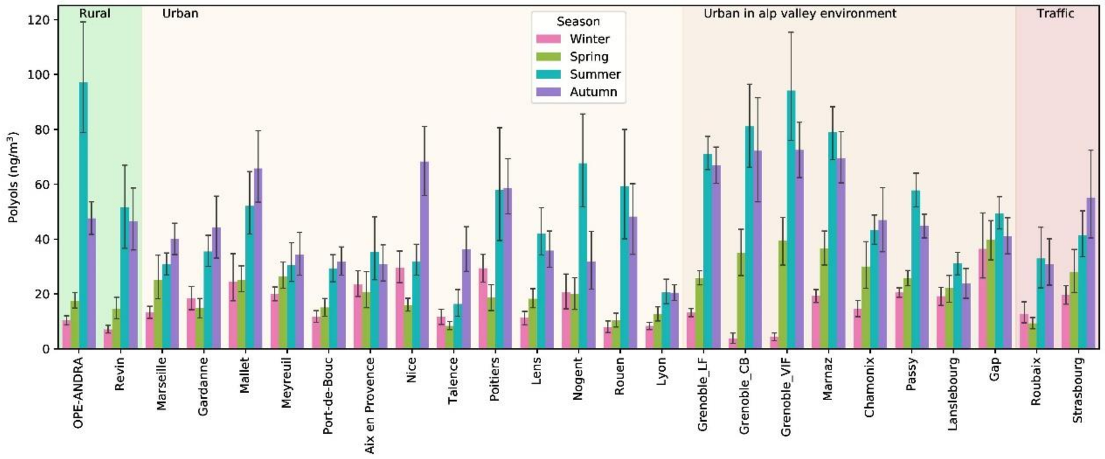


Figure 6: Spatial and seasonal distributions of atmospheric polyol average concentrations (ng m^{-3}) for various types of sites in France. Error bars correspond to standard deviations calculated with seasonal concentrations. The seasons were defined as follows: Winter = December to February, Spring = March to May, Summer = June to August, and Autumn = September to November. ~~Symbol (*) indicates $PM_{2.5}$ aerosol samples.~~

3.4.2 Spatial and seasonal patterns of glucose concentrations

The annual average concentrations of glucose measured in PM_{10} aerosols at all sites (20.4±15.6 ng m^{-3}; see Table SI-2) are comparable to those previously reported for various sites across Europe (Alves et al., 2006; Theodosi et al., 2018; Yttri et al., 2007, 2011). Likewise polyols, the atmospheric concentrations of glucose also display seasonal and site-to-site variations (Fig. 7). The~~Except for Peyrusse Vieille and Dieulefit, both rural sites with $PM_{2.5}$ sampling,~~ ambient seasonal mean concentrations (with standard deviations) of glucose are maximum in summer (25.0±24.2 ng m^{-3}) and autumn (24.6±19.8 ng m^{-3}), followed by spring (15.8±12.4 ng m^{-3}) and winter (12.6±10.2 ng m^{-3}). The summer / winter ratio for glucose seems generally lower than that of polyols, with higher ratios in the Alpine areas than in other parts of France. However, as for polyols, it remains difficult to classify the sites according to any criteria linked to site typology or latitude.

The seasonal trend of glucose concentrations in the present work is similar to that recently observed for aerosols (PM$_{10}$ or total suspended particles) collected at various environmental background (suburban, urban and coastal) sites around the world (Liang et al., 2016; Srithawirat and Brimblecombe, 2015; Verma et al., 2018). On average, a wide range of daily glucose concentrations (expressed as min-max, mean) in ~~PM$_{2.5}$ (0.02-162.0 ng m^{-3}, 10.5±15.1 ng m^{-3}) and~~ PM$_{10}$ (0.1-297.2 ng m^{-3}, 20.6±18.7 ng m^{-3}) were observed in the present study. These values are comparable to those in ~~PM$_{2.5}$ (4.3-12.0, 7.2 ng m^{-3}) and~~ PM$_{10}$ (8.4-93.0, 47.0 ng m^{-3}) reported from an urban site in Belgium (Yttri et al., 2007b). More recently, Liang et al. (2016) also reported similar concentrations in ~~PM$_{2.5}$ (7.1-202.8, 22.1±15.7 ng m^{-3}) and~~ PM$_{10}$ (3.1-343.6, 46.2±27.5 ng m^{-3}) from Beijing (China).

The sources and formation processes of glucose in the atmosphere are not currently well known and are rarely discussed. Glucose is an important carbon source for soil metabolic active microbiota, and it is commonly present in vascular plants. Additionally, cellulose (a linear polymer made of glucose subunits linked by β-1,4 bonds) is one of the most important form of organic compounds in terrestrial ecosystems and a major plant structural polymer (Boex-Fontvieille et al., 2014). It can also be quite abundant in the atmosphere (Puxbaum and Tenze-Kunit, 2003). Hence, it is hypothesized that ambient glucose could be formed through active microbial (i.e. bacteria, fungi etc.) enzymatic hydrolysis of cellulose in plant debris. Consistent with these observations, glucose could be released into the atmosphere from both vascular plant materials (e.g. leaves, fruits, pollens, etc.) growing in spring and decomposing in autumn/summer, and soil microbiota, as already suggested elsewhere (Di Filippo et al., 2013; Jia et al., 2010a; Medeiros et al., 2006; Verma et al., 2018; Zhu et al., 2015).

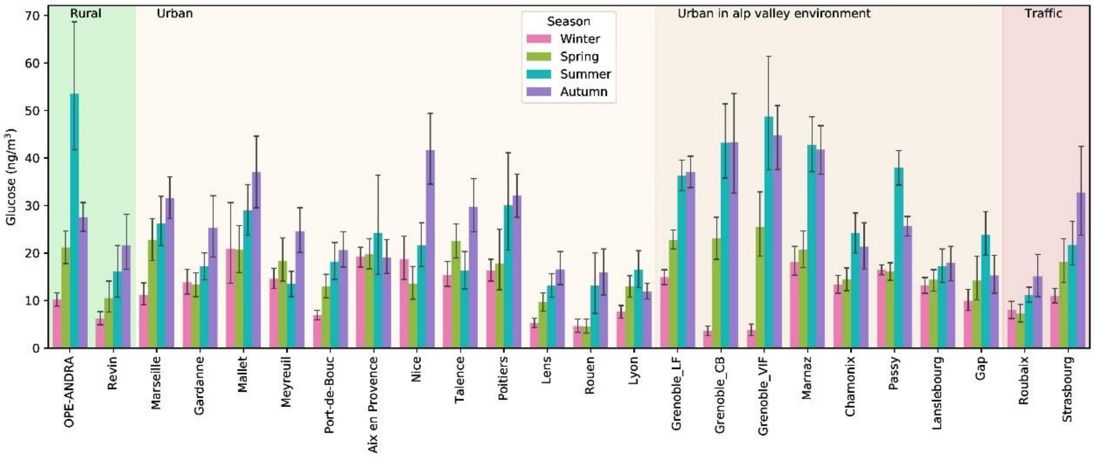


Figure 7: Spatial and seasonal distributions of atmospheric glucose levels (ng m^{-3}) for various types of sites in France (except the site of Nogent, which presented too many missing values. Error bars correspond to standard deviations calculated with seasonal concentrations.

3.4.3 Relative contributions to aerosol organic matter concentrations

The average contribution of polyols to the organic matter content (OM) of PM clearly displayed a seasonal behavior, as shown in Fig. 8. Here again, contributions are 2 to 10 times higher during summer and autumn compared to winter and spring, consistent with the assumption of higher emissions during these periods. The seasonal mean contribution of polyols to OM fluctuates from site to site, and accounts for 0.1 to 2.1 % of overall OM for these French sites (Fig. 8). Similarly, the seasonal mean concentrations of polyols together with glucose represent between 0.2 to 3.1 % of total OM at these sites (Fig. S2). However, on a daily basis (Samake et al., in prep.), atmospheric polyols mass concentrations can represent up to 6.3 % of total OM in PM$_{10}$, indicating that polyols can be amongst the major molecular species identified in aerosol organic matter (Fig. S3). Again, we could not find any simple way to group the sites according to their characteristics (typology or latitude, or climatic region), in order to better understand the drivers behind the variability of this mass fraction. Further studies are currently conducted using multi criterion examinations.

The seasonal polyols-to-OM distribution patterns in this study are comparable to those found for different urban or rural sites in Europe (around 0.2 to 2.5 % of OM) (Pashynska et al., 2002; Yttri et al., 2007b). Zhu et al. (2015) also reported similar seasonal polyols-to-OM contribution trend for aerosols sampled at Cape Hedo (coastal site, Japan).

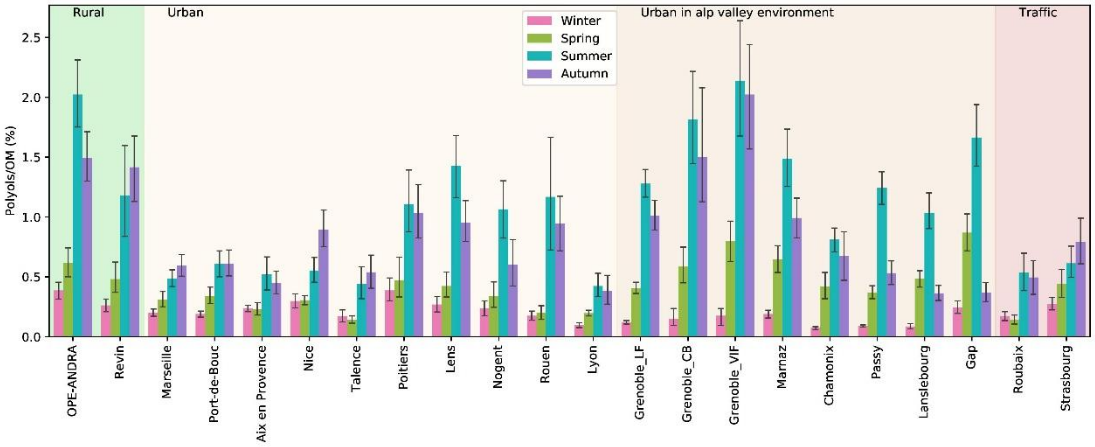


Figure 8: Spatial and seasonal distributions of mean contributions (in %) of polyols to the organic matter content of PM for various types of sites in France. Daily time-series of organic carbon (OC) were not available for the following sites: Gardanne, Mallet, and Meyreuil. Error bars correspond to standard deviations calculated with seasonal concentrations.

3.5 Primary biogenic factor in PMF studies

The sum of polyols (arabitol + mannitol) represent only a small fraction of the total OM. However, as proxies of PBOA, they are most probably emitted with other chemical species. Emission from biological particles is a complex topic since it may include a wide variety of compounds, both organic and inorganic (Elbert et al., 2007; Zhang et al., 2015). Moreover, it is not clear if polyols are mainly emitted directly in the atmosphere or are linked to other materials, for example with soil dust during resuspension processes. To investigate the relationship between polyols and other species, it would have been possible to perform simple correlation analysis with individual chemical species. This approach has the disadvantage of being a one-to-one relation and thus highly sensitive to the dynamics of all PM emission sources, not only the one we are interested in. Alternatively, another way is to use a PMF approach, also based on correlations but including much more information on the temporal variations of the different sources influencing the PM chemistry at a given receptor site.

As mentioned in Sect. 2.3, the PMF results used in this study ~~come from two different programs (SOURCES and DECOMBIO) (Chevrier, 2017; Favez et al., 2016; Salameh et al., in prep.) and~~ include sites of different typologies (rural, traffic, urban sites in Alpine valley environments, etc.) for 16 different locations spread over France and part of the current dataset. At each site, the PMF studies allowed to identify a PBOA factor, characterized by the presence of more than 90 % of the total polyols content (sum of arabitol, mannitol and sorbitol), as presented in table SI-5 and Fig. SI-6. Moreover, the sensitivity of this factor to random noise in the data was investigated thanks to randomly re-sampling the input matrix of observation. In PMF analysis, this is done via the bootstrap method

(Paatero et al., 2014) in the constrained run. The PBOA factor was always mapped to itself for 13 of the sites and quasi-always (97%) for the last three ones. It means that the PBOA factor does have a very high statistical stability since it never swaps with another factor (see Fig. SI-5). Hence, the chemical composition of this factor may be informative to investigate the PBOA source components (Table S6), and to evaluate the importance of PBOA emissions in term of OM mass apportionment.

3.5.1. Contributions of PBOA to OM and polyols to PBOA

Altogether, the results from these 16 sites highlight the importance of the PBOA source contribution to total OM. As shown in Fig. 9, the OM apportioned by the PBOA factor represents a significant fraction of the total OM mass on a yearly average (range 6–28 %; average 13±6 %). When considering only the summer period (June-July-August), this contribution is even larger and can exceed 40 % of the total OM at sites in the Alpine area (Marnaz, Passy, Chamonix, Grenoble_LF) which are partially protected from large regional influences due to the local topography. 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).

Interestingly, some previous work using the same samples from the sites in the Arve valley (Passy, Chamonix) showed that about 90 % of the OM is from modern origin (using ^{14}C measurements) during summer, with no apparent correlation between this modern carbon and polyols concentrations (Bonvalot et al., 2016). Hence, despite being an important contributing source, PBOA is not the major biogenic source in this type of environment. ~~Tracers of secondary biogenic formation processes (like pinic acid or 3-MBTCA) were measured in these series.~~

Interestingly, opposite to the case of the Alpine valleys where this proportion is the highest, the ratios OM_{PBOA}-to-OM_{total} are amongst the lowest for coastal environments (Talence, Marseille, Nice), a possible indication that the marine environment is not a large emitter for these species. Recently, much lower concentrations of polyols in aerosols from marine environments than those in terrestrially influenced sites were also reported off the coast of Japan, also suggesting a higher contribution from terrestrial sources (Kang et al., 2018).

As illustrated in Fig. 9, polyols represent only a small fraction of the OM apportioned in the PBOA factor (1.2 %–6.0 %; average 3.0±1.5 %) for the 16 studied sites. This variability is indeed rather small, considering the wide range of sites and the diversity of other potential sources (on average 8 to 10 PMF factors were obtained for the different sites). Indeed, this narrow range of the polyols fraction to the OM_{PBOA} highlights the stability of the chemical profile of this source over a large regional scale. It indicates also that, if polyols are good proxies of the PBOA sources, a large amount of other organic species are co-emitted, that still remain unknown.

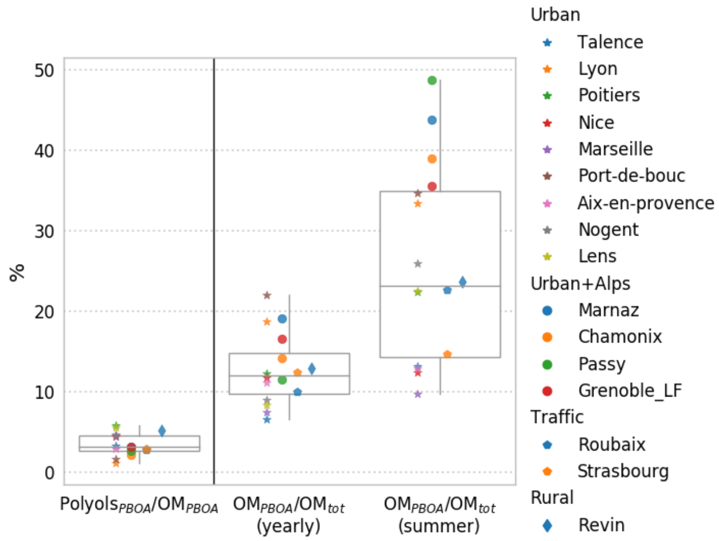


Figure 9: Mass contribution of polyols to OM in the PBOA factor, and relative contributions of the OM$_{PBOA}$ factor to the total OM in PM for the 16 studied sites where PMF model was run, over the year and summertime only. Stars and circle refer to urban sites without/and with Alpine valley influence, respectively. Pentagon corresponds to traffic sites and diamond to rural sites.

3.5.2 PBOA profile constituents and emission process

Figure 10 shows the contribution (in µg of species per µg of PM in the PBOA factor profile) of each chemical species included in the averaged PBOA factor from the 16 PMF studies. The principal contributors are OC and EC, and significant fractions of crustal material also appear (Na^+, K^+, Ca^{2+}, Al, Ba, Cu, Fe, Mn, Ti, Zn) as well as secondary elements such as nitrate and sulfate. However, EC appears to be highly variable both within and between sites under consideration. The reader may refer to figure SI-7 for an estimation of the EC mass uncertainties in the different sites. On average, the PBOA factor does not comprise a large fraction of metals and trace elements, most of them being below 1 pg µg^{-1}. Here again, the low variability of the PBOA chemical profile encountered across a large array of sites is remarkable.

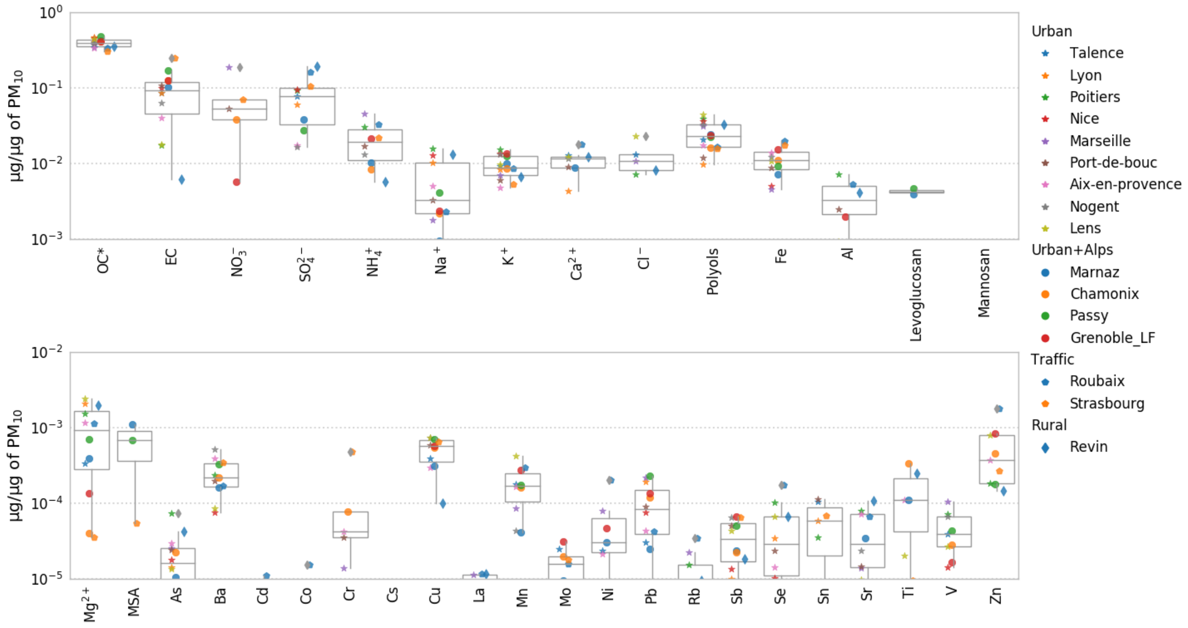


Figure 10: PMF chemical profile of the PBOA factor in the DECOMBIO and SOURCES programs expressed as a fraction of the PM mass. Values lower than a few pg µg^{-1} are not displayed on purpose. For each boxplot, the top, middle

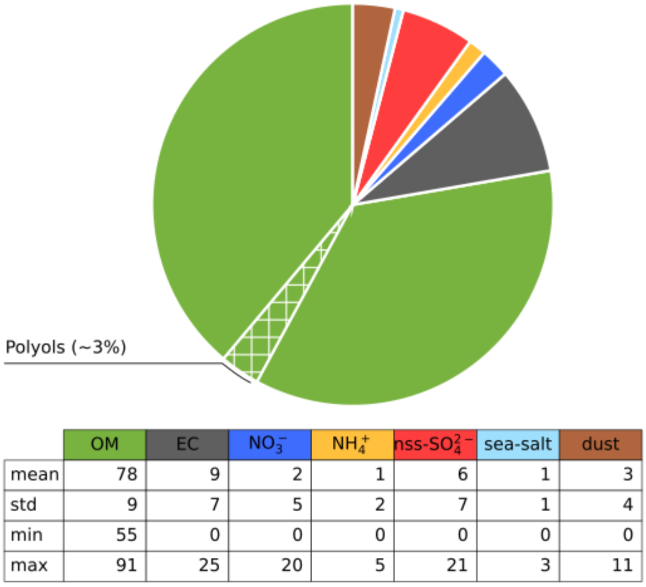
and bottom lines represent the 75th, median and 25th percentile, respectively. The whiskers at the top and bottom of the box extend from the maximum to the minimum. OC* corresponds to the bulk organic carbon fraction minus individual molecular weight of characterized organic species.

The contribution from some crustal material could agree with the coarse mode distributions of polyols (Sect. 3.3) and could be indicative of an emission process with the entrainment of spores with soil dust resuspension. To investigate the importance of mineral dust in the PBOA factor, we clustered the chemical components of PM from PBOA into 7 classes: OM (= 1.8 × OC), EC, NO_3^-, NH_4^+, non-sea-salt sulfate (nss-SO_4), sea-salt, and dust. nss-SO_4^{2-} is calculated from the measured SO_4^{2-} minus the sea-salt fraction of SO_4^{2-} ($nssSO_4{}^{2-} = SO_4{}^{2-} - ssSO_4{}^{2-}$ where $ssSO_4{}^{2-} = 0.252 \times Na^+$) according to Seinfeld and Pandis (1997). The sea-salt fraction is calculated according to Putaud et al. (2010): $sea -$ ~~$minus -$~~ $salt = Cl^- + 1.47 \times Na^+$. Finally the dust fraction is estimated from Putaud et al. (2004b) as: $dust = (nss - Ca^{2+}) \times 5.6$ with nss-Ca^{2+} stands for non-sea salt Ca^{2+} and is computed thanks to $nss - Ca^{2+} = Ca^{2+} - Na^+/26$.

Figure 11 presents the normalized average contributions of these 7 classes to the PBOA mass for the 16 sites with PMF modelling. It clearly revealed that the PBOA factor is dominated by contributions from OM (78±9 %), followed by EC (9±7 %), and only a minor contribution from~~fraction~~ ~~of~~ the dust class (3±4 %).

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).

This result on the general chemical profile of the PBOA factor tends to infirm the hypothesis of an emission process associating PBOA material with mineral dust resuspension. Indeed, our findings rather suggest that a main part of PBOA (and polyols) are most likely associated with biological particle direct emissions. It leaves only a minor fraction that could be linked to the mechanical resuspension of PBOA with crustal elements. Some minor fraction of EC in this factor could come from resuspended EC-containing dust particles being accumulated in topsoil as demonstrated in previous works (Forbes et al., 2006; Hammes et al., 2007; Zhan et al., 2016). Hence, the origin of the larger fraction of the contribution of EC remains unknown. Our conclusions are in good agreement with those made by Jia and Fraser (2011), based on the concentrations of these chemicals in different types of samples: i.e. size-fractionated (equivalent to $PM_{2.5}$ and PM_{10}) soil, plant, fungi, atmospheric $PM_{2.5}$ and PM_{10}. They found that the ambient concentrations of primary saccharide compounds at the suburban site of Higley (USA) are typically dominated by contributions of biological materials rather than resuspension of soil dust particles and associated microbiota.



	OM	EC	NO_3^-	NH_4^+	nss-SO_4^{2-}	sea-salt	dust
mean	78	9	2	1	6	1	3
std	9	7	5	2	7	1	4
min	55	0	0	0	0	0	0
max	91	25	20	5	21	3	11

Figure 11: Average contribution (%) of species in the PBOA factor for the sites in SOURCES and DECOMBIO. The hatched area represents the proportion of the OM apportioned by the polyols (see text for reconstruction method).

4. Conclusion

The contribution of primary biogenic organic aerosols to PM is barely documented in the scientific literature. The present study aimed at providing a large overview of the spatial and temporal evolution of concentrations and contributions to aerosol organic matter of dominant primary sugar alcohols and saccharide compounds, for a large selection of environmental conditions in France. With 28 sites and more than 5,340 samples, it is to our knowledge the most comprehensive dataset for these compounds. The main results obtained indicate that:

- among the identified polyols, arabitol together with mannitol are the major species by mass, with lesser amounts of others polyols (e.g., erythritol, inositol, glycerol, sorbitol, and xylitol). Glucose is the dominant primary monosaccharide and its relative abundance is comparable to the sum of arabitol and mannitol;
- the two main polyols (arabitol and mannitol) together with glucose are mainly present within the coarse aerosol mode;
- at nearly all sites, ambient levels of the main polyols and glucose displayed clear seasonal variation cycles, with a gradual increase from spring and maximum in summer and autumn aerosols, followed by a sudden decrease in late autumn, and a winter minimum;
- atmospheric concentrations of the main polyols and glucose fluctuate according to site and season, and account each for between 0.1 to 2.1 % of OM on a seasonal average basis at these French sites;
- ambient mass concentrations of arabitol and mannitol are comparable. Meanwhile, they display very good temporal covariation, with ratios varying between sites. Conversely, linear correlations between the main polyols and glucose concentrations are much lower, suggesting different atmospheric sources, or atmospheric processes;

- a~~A~~rabitol and mannitol are efficient organic markers for PBOA. PMF studies of the yearly series from 16 sites give contributions of the primary biogenic emission (traced with the main polyols) to the total OM around 13±6 % on a yearly average and 26±12 % during summer, thereby showing that PBOA is an important source of total OM in PM_{10} for all sites across France. Furthermore, the average PBOA chemical source profile is made out of a very large fraction of OM (78±9 % of the total PBOA mass on average), suggesting it is mainly related to direct biogenic emissions from biological particles. Noteworthy, the presence of BSOA within the PBOA factor, particularly during summer could not be fully ruled out and further works using additional organic tracers (such as 3-MBTCA, pinic acid, and/or cellulose) are still needed to solve this issue. Additionally, the low crustal fraction indicates that this factor is weakly linked to soil dust resuspension associated with biological material;
- however, the PBOA source remains chemically poorly characterized as the main polyols represent only a small fraction of its total OM mass (3.0±1.5 % on average);
- despite comparable high concentrations in the atmosphere, the sources and processes leading to glucose concentrations and seasonal evolutions are still elusive. Indeed, the different PMF performed with glucose in input variable do not lead to statistically stable solution;

Further investigations of the emission pathways and chemical characterization of the PBOA source associated with polyols are on-going, which may improve our understanding of its dynamic at various geographical scales, for a potential implementation in emission models in the future.

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Author contributions: JLJ was the supervisor for the PhD for AS, FC, SW, and for the post-doc of DS. He directed all the personnel who performed the analysis at IGE. He was coordinator or PI for the programs that generated the data for 18 of the 28 sites in this study (OPE-ANDRA, Part'Aera, CAMERA, SRN 2013, 3 Villes PACA, DECOMBIO, QAMECS) and co-PI for programs for 5 other sites. He is the coordinator for the CNRS LEFE-EC2CO CAREMBIOS program that is funding the work of AS. GU was the co-supervisor for the PhD of AS and SW. OF is the coordinator of the CARA program, (co-)funding and supervising the filter sampling and chemical analyses at 12 of the 28 sites. EP, OF, and VR supervised the PhD of DMO who investigated the 5 sites in northern France. Finally, JLB was the coordinator (program Lanslebourg) or partner of several programs whose

data were used in this study (OPE-ANDRA, Part'Aera, 3 Villes PACA, DECOMBIO), and OF was the coordinator of the SOURCES program, which includes the work of DS as a post-doctoral fellow under the supervision of JLJ to gather and prepare most of the datasets used in the present studies.

All authors from the ANDRA (#5) and AASQA (#6 to 13) are representatives for each network that conducted the sample collection and the general supervision of the sampling sites.

FC and DS ran the PMF analysis. AS, SW and JLJ processed the data and wrote up the manuscript. All authors reviewed and commented on the manuscript.

Competing interests: The authors declare that they have no conflict of interest.

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