Author's response:

We thank the Referees for the careful revision and comments which helped improving the overall quality of the manuscript.
A point-by-point answer (in regular typeset) to the referees' remarks (in the *italic typeset*) follows, while changes to the manuscript are indicated in blue font.
In the following page and lines references refer to the manuscript version reviewed by the anonymous referees.

Anonymous Referee #2

Received and published: 28th February 2017

Bozzetti et al. describe year-long, offline AMS measurements of filters collected in Marseille. The authors perform source apportionment analysis to the filters to demonstrate changing contributions of BBOA, OOA, HOA, and INDOA. The authors compare this analysis to previous studies (e.g. El Haddad et al. 2013) and winter-time measurements conducted using a high resolution aerosol mass spectrometer. The authors find good agreement between the online and offline methods, and observe significant contributions from residential biomass burning during winter months. The authors provide additional analysis of the biomass burning factor and attribute changes in burning markers to differences in burning activities throughout the year. The authors also observe enhancements in methyl-nitrocatechol, which suggests secondary processing of the biomass burning emissions.
Overall, the paper is very well written, the methods are clear, and the interpretations of the data are reasonable. The PMF solutions, in particular, are incredibly detailed and thoroughly rationalized. The paper provides another example of the utility of off-line AMS analysis, which may serve as a useful low(er)-cost means for monitoring aerosol composition. While the study tends to confirm results previously observed in Marseille, it provides useful observations related to the seasonal changes in biomass burning markers. My biggest concerns relate to the over simplification of biomass burning sources, particularly to the assignment of periods described as lignin and cellulose burning. Upon addressing my comments, I recommend the manuscript for publication.

We thank Anonymous Referee #2 for his thorough review, which helped improving the overall quality of our work. We have inserted a more careful discussion of the complexity of BBOA emissions following the suggestions in the comments below.

Major comments

Page 25, Lines 3 – 10: I'm persuaded by the argument that differences in biomass burning markers could be related to changing fuel types; however, I would recommend that the authors refrain from suggesting that the differences are strictly related to

cellulose vs. lignin combustion. This also pertains to Fig. 11, which highlights periods of "lignin-combustion" and "cellulose-combustion." In reality, agricultural waste burning, open burning, prescribed burning, etc is the combustion of mixtures of lignin and cellulose-rich fuels; therefore, attributing changes in tracers to one plant structure or another downplays the complexity of biomass burning. I recommend the authors reframe the discussion to focus on changes in human activity, i.e. periods of increased prescribed burning, periods of increased residential heating, etc. Within that discussion, the authors may describe the differences in fuel composition, keeping in mind that mixed fuels (as well as burning conditions, fuel moisture content, etc) will contribute to the variability of biomass burning tracers.

While we do agree with the reviewer that the two periods would relate to open agricultural burning and residential heating, referring to these periods as such would imply that we know with certainty the patterns of biomass combustion in the region. However this is not the case and in France domestic green waste burning, with the exception of agricultural burning, is prohibited. Aerosol from agricultural burning was previously modelled for southern France (Dernier van der Gon et al., 2015, Fountoukis et al., 2014) and we suspect that this practice occurs in this region, without knowing the extent of it or the contribution of prohibited domestic green waste combustions. Our results indicate the importance of green waste combustion and provide means for tracing it. By referring to the periods in the manuscript as cellulose rich and lignin rich biomass combustion, we did not intend to oversimplify the biomass burning processes, and we do agree that all biomass contain both cellulose and lignin. Instead, we have carefully chosen these designations as they reflect most our observations, increase of lignin pyrolysis products over cellulose pyrolysis products during coldest days. Based on these observations we could only speculate that these differences are due to a change in the biomass burning pattern. Therefore, we prefer keeping the same designations purely based on the observations and not to use the nomenclature proposed by the reviewer which would be based on the further interpretation of the data. Nevertheless, we added additional explanation for using these terms at P25, L3-10.

In this study we related the evolution of the BB composition over the cold season to the combustion of cellulose-rich and lignin-rich fuels, considering that lignin and cellulose are contained in different ratios in different biomass fuels. This designation should not be considered as an oversimplification of the combustion processes or of the fuel complexity, but rather as a classification of the BB aerosol based on our observations of increasing lignin pyrolysis products over cellulose pyrolysis products during the coldest days.

The Fig. 11 legend was modified as follows:

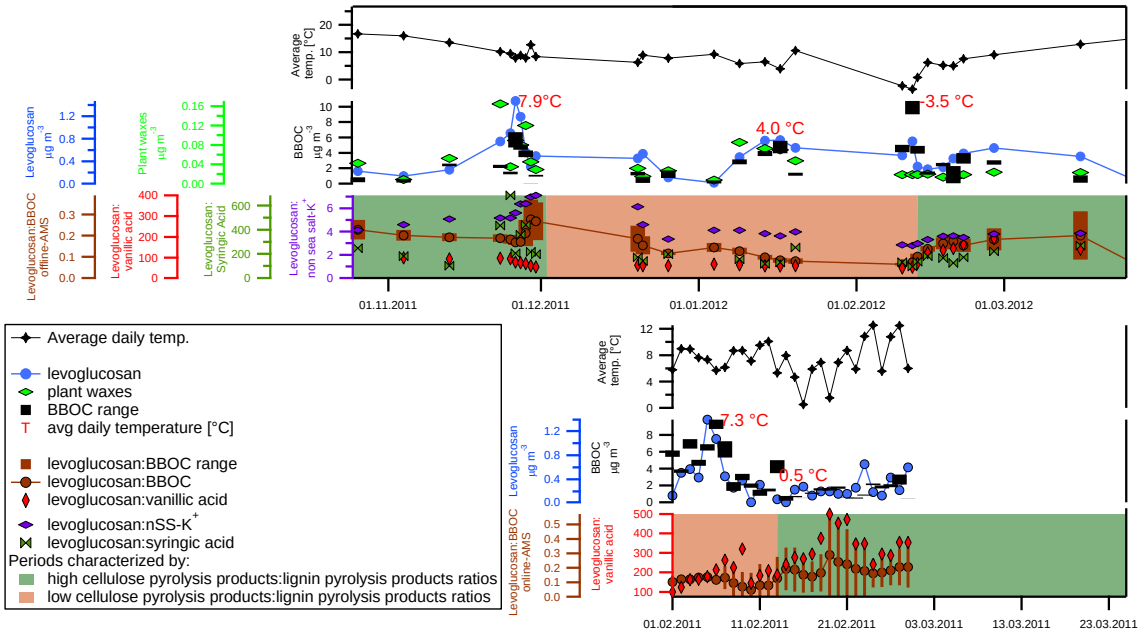
Periods characterized by:

-high cellulose pyrolysis products:lignin pyrolysis products ratios

-low cellulose pyrolysis products:lignin pyrolysis products ratios

Page 24, Lines 20-32: The authors discuss plant waxes, but do not provide any figures or correlations with other BBOA tracers. Are these supposed to be incorporated into Fig 11 (suggested at page 25, line 1)? I believe these traces need to be shown in the figure if they are to be discussed and attributed to different fuels

Following anonymous reviewer #2's suggestion, we added the plant waxes trace in Fig. 11 and modified the figure to make it clearer.



The following text was added to Fig. 11 caption:

The plant waxes concentrations were determined from GC-MS measurements of alkanes with an odd number of carbons (Li et al., 2010). As discussed in the main text the spike observed in late autumn could be related to incomplete green waste combustion.

Page 10, line 4: The source apportionment performed on AMS data is very detailed; however, at times, I had difficulty following the progression due to the amount of detail provided. This discussion should be included in the main text, however I think it would be useful if the authors could provide a brief listing of the steps taken to perform this analysis at the beginning of this section. For example, one could add "… In order to optimize the source separation, we performed sensitivity analyses on PMF solutions by (1) selecting number of factors, (2) constraining HOA and COA, (3) cluster anlaysis, (4)…. ". As the reader continues reading your method, they could reference this listing and follow the logical progression more easily.

Following the suggestion of anonymous reviewers #1 and #2 we introduced in the main text a summary of the online-AMS optimization procedure (P10 L11).

In order to optimize the source separation, we performed sensitivity analyses on PMF solutions according to the following scheme:

I) Selection of the number of factors based on residual analysis.

II) Qualitative evaluation of the unconstrained PMF solution in comparison with the constrained PMF solutions (*a*-value approach: COA and/or HOA constraints)
III) Constrain of both the HOA and COA factors profiles adopting an *a*-value approach. *a*-value sensitivity analysis (121 PMF runs performed scanning all the COA and HOA *a*-value combinations, a-value scanning steps: 0.1).
IV) Classification of the 121 PMF runs based on the cluster analysis of the COA diurnal cycles. Selection of the best clusters, and corresponding PMF solutions. Best clusters were selected based on the analyses of the average cluster spectra of COA, HOA and BBOA. In other words, clusters characterized by average factor mass spectra (and corresponding clusters) not statistically different from the corresponding average literature profiles were retained.
V) PMF rotational ambiguity exploration. 100 bootstrap (Davison and Hinkley, 1997; Brown et al., 2015) PMF runs were performed by simultaneously varying the COA and HOA *a*-value combinations (using only the optimal *a*-value combinations identified from step IV). The average of the 100 bootstrap runs represented the online-AMS source apportionment average solution. The corresponding standard deviation represents the source apportionment uncertainty.

In a similar way we introduced a summary of the offline-PMF source apportionment optimization (P12 L13):

In order to optimize the source separation, we performed sensitivity analyses on PMF solutions according to the following scheme:
I) Selection of the number of factors based on residual analysis.
II) Qualitative evaluation of the unconstrained PMF solution in comparison with the constrained PMF solutions (*a*-value approach: COA and/or HOA constraints)
III) PMF rotational ambiguity exploration. 1080 bootstrap (Davison and Hinkley, 1997; Brown et al., 2015) PMF runs were performed by simultaneously varying the COA and HOA *a*-value combinations. PMF solutions were retained based on the correlation of the PMF factors with external tracers. The PMF solutions retrieved from this step are relative to the water-soluble fraction.
IV) Retained water-soluble PMF solutions from step (III) were rescaled to the total OM concentrations by applying factor recoveries. Factor recoveries were fitted (using *a*-priori information) to match total OC. Only PMF solutions and factor recoveries fitting OC with yearly and seasonally homogenous residuals were retained. The average of the retained PMF solutions represented the average source apportionment results. The corresponding standard deviation represented the source apportionment uncertainty.

Page 10, lines 24-26: For readers who may be unfamiliar with the a-value sensitivity analysis, it would be useful to explain here why one might apply this analysis to HOA and COA components. The authors mention that lack of acceptable tracers for COA emissions (line 31), but it may also be helpful to discuss that other studies have observed improved resolution of HOA after constraining these factors (e.g. Canonaco et al. (2013)), or that these two factors may exhibit similarities in the mass spectrum and/or diurnal profile, as demonstrated in the cluster analysis described in the SI.

We thank reviewer #2 for the suggestion. Since a similar argument was raised also by anonymous reviewer #1, we introduced a paragraph elucidating the improvements of the constrained PMF solution in comparison to the unconstrained approach (see 3rd comment, subsection I).

> *Page 11, Lines 24 – 28 and Page SI 13, Lines 18-22: My understanding from reading this section is that the authors rejected clusters 4 and 5 primarily based on mass spectrum similarities with reference spectra, or by similarities with other factors (e.g. COA with HOA). From my untrained eye, it also appears that cluster 3 exhibits a strong correlation with cluster 4 (Fig S7 and Table S3, R = 0.93). Similarly, the correlation between Cluster 3 and NOx (R=0.57) is not substantially different from that of Cluster 4 and NOx (0.64). Would this also be grounds to reject cluster 3? Or, are the authors placing more weight on similarities mass spectra as opposed to similarities in temporal profiles? Personally, I believe similarities in mass spectra is a more important criterion, but other readers may disagree.*

As anonymous reviewer #2 correctly mentioned, the cluster selection was based on mass spectral similarities. In absence of a reliable COA tracer, retaining a cluster based on the COA diurnal cycles was more subjective than accepting/rejecting a cluster based on the resemblance of the mass spectra with literature profiles. For these reasons we opted for the selection of the clusters based on mass spectral analyses. Indeed the average COA diurnal of cluster 3 and 4 are quite well correlated, however the COA diurnal cycle for cluster #3 showed lower background values at night and a more pronounced peak at noon, while for cluster #4 this peak was almost not visible. Overall, after applying the last selection step (Fig. S8), almost no solution from cluster #3 was retained, i.e. most of the solutions associated to cluster #3, were attributed to cluster #4 for more than 5% of the *k*-means initiations, confirming the resemblance between the two clusters.

> *Page 14, lines 10-12: The authors indicate that a 5th factor was resolved by source apportionment of the offline measurements, but not by online measurements. The authors note later in the manuscript (page 22, lines 4-5) that this was previously discussed, however I can't find this discussion in the PMF description. Please clarify.*

The authors referred to section 3.1: P16, L18-29. This reference was added for clarity (P22 L4).

> *Page 20, Lines 3-4: Since online and offline AMS measurements were not conducted simultaneously, I don't agree that you can make a direct comparison. Please revise.*

We rephrased P20 L 3-6 as follows:

In this study, we present one of the first OA source apportionments conducted over an entire year in the Mediterranean region. This work represents also the first comparison between HR online-AMS and HR offline-AMS source apportionments conducted at the same location, despite in two different periods. Previous studies (Daellenbach et al., 2016) reported a comparison between offline-AMS and online-ACSM results.

Page 23, Lines 1-14. I'm confused about what message the authors are trying to convey with this discussion. Are the authors trying to attribute nitrocatechol formation to a chemical process, or is the focus to show that offline measurements can't capture the chemical evolution of these tracers due to their high reactivity and the low time resolution of offline analysis?

The discussion at P23, L1-14 aims at demonstrating that rapidly formed secondary aerosol compounds (such as nitrocatechols) are likely apportioned by PMF to primary factors rather than to secondary or OOA factors. Such fast SOA formation is not captured by offline-AMS, but it is also probably not captured by online-AMS, unless in the proximity of the source or directly within the plume. In order to better convey the message we added the following text at the end of the discussion (P23, L14).

Overall these findings suggest that rapid SOA formation is not well captured by PMF and rapidly formed SOA compounds (such as nitrocatechols) can be systematically attributed by PMF to factors commonly considered as "primary" (BBOA in this case).

Page 24, Lines 7 – 17: The authors mention that the levoglucosan:nss-K ratio was 3.35 in winter at line 8, but then describe a minimum ratio in Jan/Feb of 6.3. I'm assuming this is a mistake, since I observe a minimum of ~3-4 from Fig. 11.

We thank anonymous reviewer #2 for reporting this mistake, we corrected the values as follows:
PL24 L7-8: showed lower average values in summer (0.23) than in winter (3.14).
P24 L 12-13: shows higher values during March and late autumn (up to 7.11) and lower in January, February (minimum = 2.79; Fig. 11)

Figure 6: The x-axis is very difficult to read. The authors could remove the year from the dates, or average the collection interval to present a single value rather than a range.

In order to better display the x-axis we displayed sticks for individual filters from each composite, instead of one stick per composite.

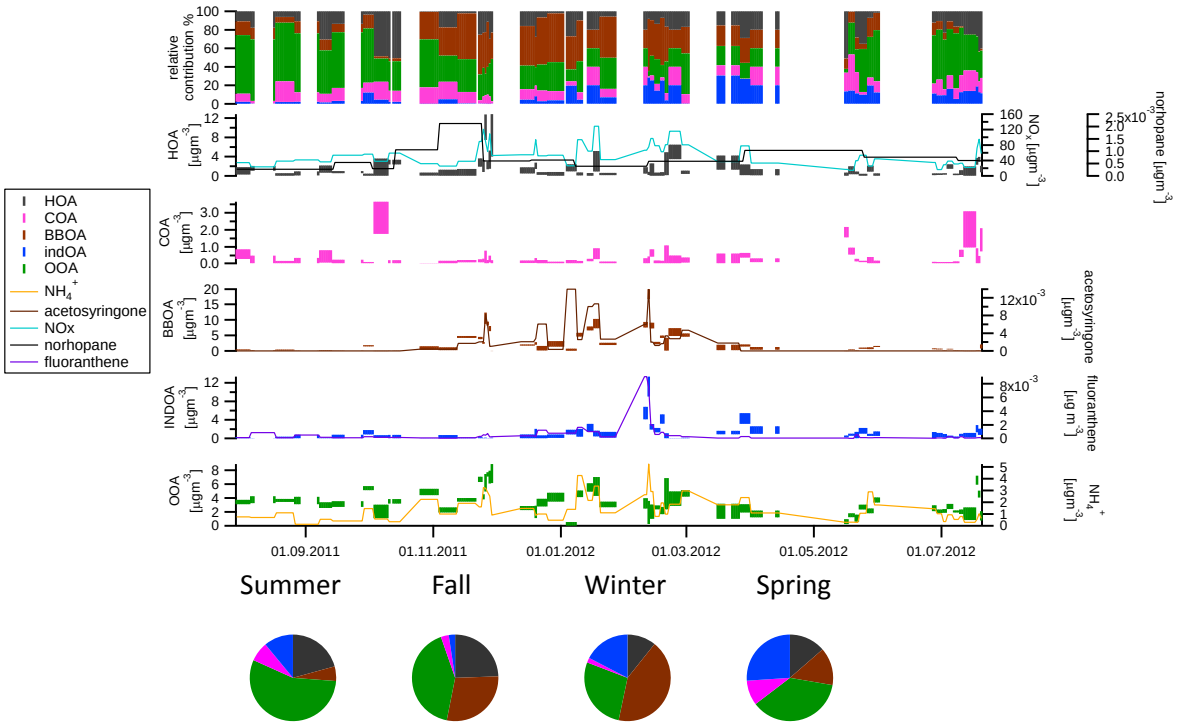


Figure 10: I find this figure to be misleading. The authors note that the reader should only consider the monthly changes and not the day-to-day behavior since these measurements were not performed simultaneously; however, as a reader, my first intuitive response is to believe these measurements were conducted at the same time. Only after reading and interpreting the caption do I understand what the authors are conveying. In my opinion, the temporal profiles should be placed on separate axes or presented differently.

Following the suggestions of anonymous reviewer #2 we display the two traces on different time axes (bottom and top). In order to better identify the tracers, we used different markers and different colors.

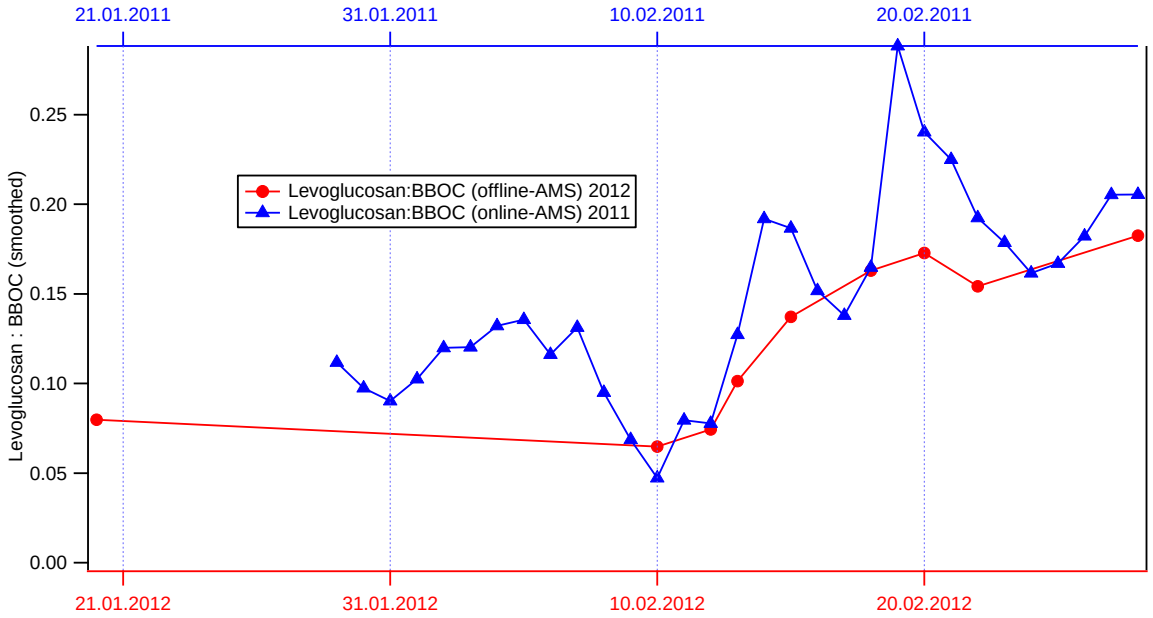


Figure 11: I find Figure 11 to be very difficult to read. The marker sizes are quite small, similar in shape (circles), and displayed on top of similarly colored, easter-egg-like backgrounds (lignin combustion period, cellulose-combustion period). Personally, I think the figure is too busy and I struggled to immediately grasp its message. To simplify the figure, the authors could remove the measurements from 2011 and plot them separately in the supplemental information since these appear to be auxiliary evidence.

Following the suggestion of anonymous reviewer #2, and #3 we corrected Fig. 11 as follows:

- Background colors were changed
- Markers were changed
- Other modifications suggested by other reviewers were introduced

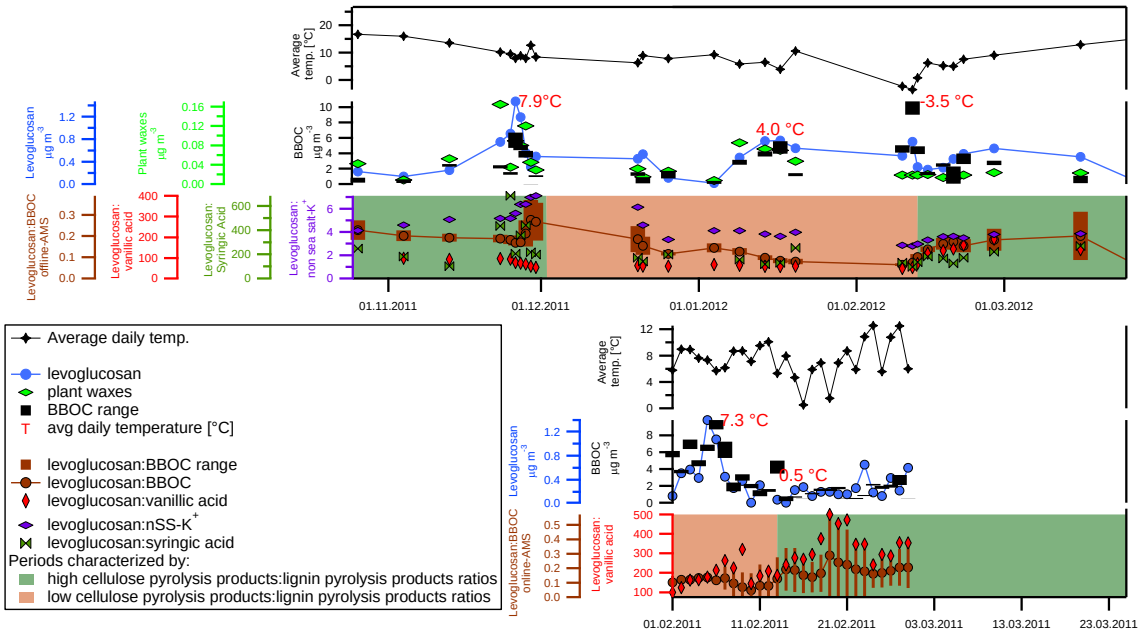
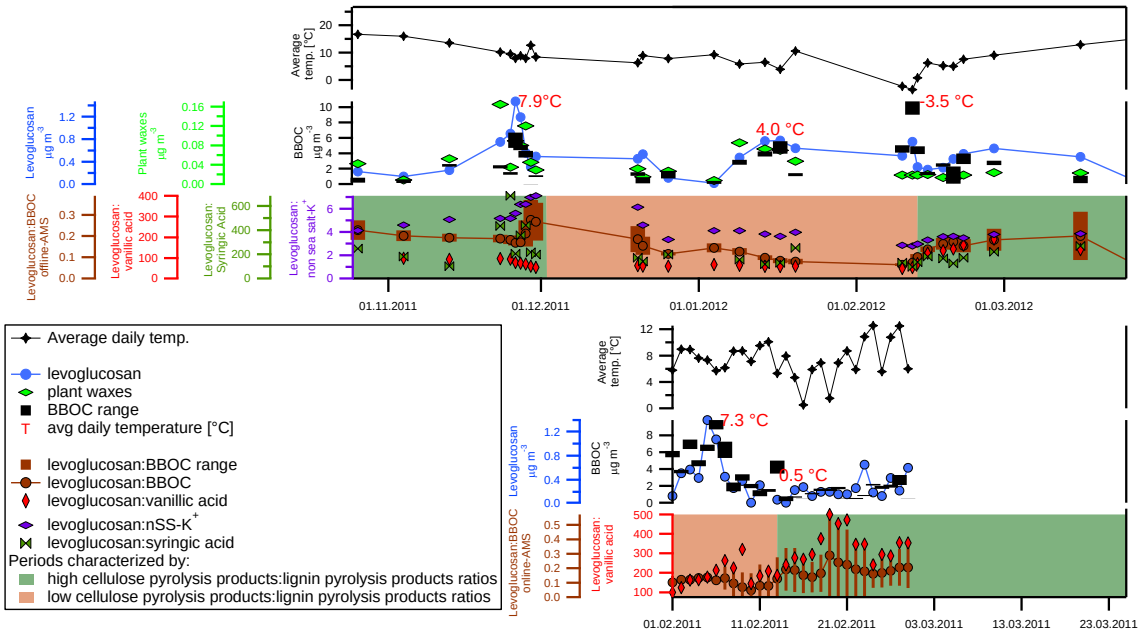


Figure 11: I'm confused how the authors derive the levoglucosan:vanillic acid ratio from the 2011 measurements. Are the authors using AMS tracers, or were filters collected? I'm assuming these represent AMS tracers since the scale is drastically different than that for 2012.

We thank anonymous reviewer #2 for finding this issue, Fig. 11 was corrected as follows (see below). As also indicated in the manuscript (P7-8 L29-4) and in Table S1, filters were also collected during February 2011. This batch of filter samples was defined as "Batch B2", while the set of filters collected during the yearly cycle monitoring campaign was defined as "Batch 1". A subset of the same analyses conducted for the Batch 1 was carried out also on Batch 2 (see Table S1). Both levoglucosan and vanillic acid were measured by chemical derivatization GC-MS (El Haddad et al., 2009; Favez et al., 2010)



Minor Comments

Page 5, lines 6 -7: How frequently were the filters extracted from the sampler and stored? Weekly? Daily? I'm curious how long each sample was "aged" in the sampler prior to freezer storage.

Filters were collected from the sampler every Monday, Wednesday and Friday and immediately freezer stored.

Page 11, Line 2: I do not see a reference to Elser et al. 2015 in the bibliography.

We thank anonymous reviewer #2 for finding this error. The reference in the main text was corrected to Elser et al., 2016.

Page 14, Line 3: Do the authors refer to the Pearson's R for COA, or its factor recovery?

R_{COA} referred to the COA factor recovery, this was clarified in the main text as also suggested by anonymous reviewer #1.

Page14, lines 5-7: I believe the authors mixed up KOA and WSKOA?

Corrected as suggested.

Page 18, Lines 6-7, Page 23, Line 24, Fig. 11: At times, I'm confused as to whether the authors are referring to levoglucosan and vanillic acid measured by GC-MS or AMS. Can the authors please specify?

According to anonymous reviewer #2 we clarified in the text that levoglucosan and vanillic acid measurements are from GC-MS.

Editorial Comments

Page 20, Line 3: Add "of" between "one" and "the"

Corrected as suggested