Comments to referee#2 on the paper: "Organic molecular markers and signature from wood combustion particles in winter ambient aerosols: Aerosol mass spectrometer (AMS) and high time-resolved GC-MS measurements in Augsburg, Germany"

The authors thank the referee for the constructive comments and suggestions, the careful reading and the interest in this work. We discussed all comments of the referee separately point by point, except suggestions for wording and sentence structure. These comments will not be repeated below again and will be inserted directly into the text of the manuscript. The referee gave the following general comments to the paper. These comments are discussed and rewritten by the specific comments. Therefore we discuss them in the latter section in detail.

Specific comments
p 4834
lines 15 – 18 : the sentence is ackward

The sentence will be changed to:

"The offline methods, for instance the analysis of filter samples with gas chromatography (GC), provide quantitative and qualitative results of WC markers such as levoglucosan, potassium and phenolic compounds…"

line 26 : "…. source apportionment for WC…."

Here we will add the suggestion from referee#1 "source apportionment methodologies".

p 4835
line 6 : function = potential ??

We will use "potential".

lines 24 – 25 : strange sentence

We will improve the sentence to:
"…an AMS for local source apportionment set up in the mobile atmospheric pollution laboratory "MOSQUITA" ("Measurements Of Spatial QUantitative Imissions of Trace gases and Aerosols")."

p 4837
Line 6 : what are the uncertainities associated with the value of 0.5 ?

The uncertainty of this value is about 20% according to Bahreini et al. 2009. Additionally, we will improve the part according to the suggestions of referee#3 into:

"…according to Bahreini et al. (2009) this CE could vary by around 20%."

p 4840
lines 10 – 11 : the measurements of the sizes are that precise, that you can give it with 2 digits?

The referee is correct; we will change it to integer numbers.

p 4841
lines 13 – 14 : why is it surprising ? These secondary products could come from heterogeneous reactions in the liquid phase of fog, for example.

We will delete this speculative sentence.

p 4842
line 7 : is givern = is obtained ?

“Obtain” is the correct wording. We will insert it in the text.

lines 10 - 12 : so what ? is it significant or not ? what is the number of points for these correlations ?

The obtained PMF factors are in a good correlation with the literature data. Only the air contributing mass to charge ratios show some differences. We used 246 data points for the correlation. We will add a more detailed description in the paper by entering:

“The comparison of the Augsburg and Grenoble factors for OOA, HOA and WCOA over 246 data points is in good agreement with the correlation coefficient of R^2 = 0.47, 0.84 and 0.66, respectively.”

line 25 : 20 % of contribution of WC to OC on a daily average for the whole period.. How come that there is no fluctuation with daily mean temparatures that are really variable ?

Text will be changed. Reasons for missing fluctuation with daily mean temperatures would be very speculative; therefore we won’t discuss this in detail. The temperature shows diurnal variation as well as the variation in daily averages. However, in our observation the temperature is not correlated with the daily averaged WCOA concentrations.

The new paragraph will be:
“The daily averaged contribution of WCOA, with about 20% (range 10 - 30%) to total OM mass, is quite constant during the whole campaign and shows no inverse correlation with the daily averaged temperatures. Nevertheless, diurnal variation of peak values can be observed, especially in the evening and at night, when regional domestic heating starts.”

p 4843
line 5 : pb in the sentence

We will improve the sentence into:
“PMF solution with negative FPEAK values provide less correlations of calculated factor with variation with times of the source-related tracer species, while the PMF solution of positive FPEAK values showed similar correlations with tracer species as the FPEAK = 0.”

lines 18-28 : all of this section is hardly understandable, because of too long and intricated (complex)

We will improve this whole section into:
“The WCOA factor correlates well with the WC marker ion of m/z 60 (R^2 = 0.77, Figure 3). The correlation of OOA with OOA marker ion m/z 44 is even higher (R^2 = 0.95). The main differences between the temporal variations of OOA and m/z 44 data are observed during the times when the HOA concentration is notably high. The HOA is highly correlated with the primary marker ion m/z 57 (R^2 = 0.97). Chirico et al. (2010) showed that aged diesel emissions contain high amounts of oxygenated fragment from m/z 57 which is produced through oxidative processes. However, the high correlation of m/z 57 and HOA found in our study is not surprising, because both main fragments which contribute to m/z 57, the oxygenated fragment ($C_3H_5O^+$) and the non-oxygenated fragment ($C_4H_9^+$), show a high correlation with HOA (R^2 = 0.85 and 0.88, respectively). Additionally, the latter fragment contributes the most to the m/z 57 signal, which is approximately 47%. It can also be seen that only the oxygenated fragment ($C_3H_5O^+$) provides good correlations (R^2 = 0.80 and 0.72) with WCOA and OOA, respectively.”

sentences, because the meaning of “course” (lines 20 and 23) is not defined, and because the ideas that are to be demonstrated are not clear. These lines should be rewritten completely.

We will improve this sentence together with the abstract as discussed above. Additionally, the referee is correct. There was a translation error. We will improve the meaning of “course” in the whole manuscript. On the one hand it means variation with times and on the other hand it means “gradient” or “slope”.

p 4844
lines 7-8 : this sentence is too general ; BC is not always and everywhere attricbuted to traffic.

That is true; BC is not always only related to traffic. Therefore, we wrote BC is “mainly attributed to traffic and other combustion emissions like wood combustion”.

Lines 9 and 10 : you should comment on this result : how come that the AMs results (for PM1) are better correlated with PM2,5 filters than PM1 filters ?

We discussed this point in detail. We considered that there could be statistical reasons for this difference, among other things, due to the lower number of data points from the $PM_{2.5}$ filters (17) compared to the 87 data points of the PM_1 filters. Therefore we made a new statistical calculation to find statistical reason for this difference, during which we found a new regression correlation of $R^2 = 0.86$. This correlation is now in the similar magnitude like the PM_1 filter samples ($R^2 = 0.84$). We will change this part in the manuscript according to this value.

Lines 15-22 : this method for the calculation of an equivalent levoglucosan concentration needs more explations for at least 2 points. i) What is considered as the "organic background" is not clear. ii) it seems that an implicit hypothesis is that there is no other species contributing to the m/z 60 ? What are the consequences (in term of uncertainties of the recalculated concentrations) of these 2 hypotheses ?

Point i)
We will include the explanation of the organic background in the paper. The organic background was measured in periods and areas with absence of WC impacts and it was found that this part has an impact on m/z 60 of 0.3% of the total organic mass.

The explanation will be:
"The organic background has been found to be approximately 0.3% of the total organic aerosol signal in several field campaigns, in periods and areas with absence of WC impacts…"

Point ii) The referee is correct, it is more of a estimate, however several studies have found that the m/z 60 is strongly correlated to WC emission. But exactly this estimation and calculation was discussed as an important part in the following section 3.4.

p 4845
Line 21 : as opposed to what is described in the text, figure 6 indicates only a very limited increase during mid-day (10h00 to 12h00), that should on top of it be within the uncertainties of the determinations. Lines 22-25 : this hypothesis could be checked to some extent with the measurement of the global radiation.

The mistake in line 21 will be corrected and we will delete the hypothesis and change it by:

"The OOA is the biggest fraction of the organic matter at any time and shows no distinctive maximum like the variations of HOA and WC."

p 4846
line 12 : is this coherent ? where / when was the study by Lanz et al ?

Lanz et al. (2008) found in Zurich at an urban background site in January 2006 a lower content of levoglucosan to WCOA organic mass compared to our study. We made our measurements in the city; therefore, the location could have an influence on the ratio. However, as shown in Table 1 of the manuscript, the levoglucosan to OC ratio could vary with different burning conditions or fuel types. With varying levoglucosan to OC ratio the WCOA or OM ratio will also vary. We will enter in the manuscript: "…Lanz et al. (2008) found a ratio of 8% at an urban background site in Zurich during January 2006."

Line 25 : " …. in the french city of Grenoble, and higher than the results obtained in Beijing (reference ?), where …."

We will include the reference (Zhang et al., 2008).

p 4847
line 5 : how can you say that m/z 60 is mainly coming from levoglucosan ? the isomers of levoglucosan are not leading to m/z 60, for example ?

A main part of m/z 60 comes from levoglucosan; therefore, it is a marker mass for wood combustion as mentioned in several studies (Aiken et al., 2009; Alfarra et al., 2007). However, it is true that also other anhydrosugars and for example carboxylic acids are contributing to m/z 60. These contributions to m/z 60 and problems connected to this estimate is one main point, which is discussed in the following pages of the paper.

line 7 : where / when were these other campaigns ?

These mentioned campaigns were referenced in the following literature (Aiken et al., 2009; Mohr et al., 2009; Lee et al., 2010). Lee and Mohr had made emission campaigns for wood burning and other sources and Aiken et al. made ambient measurements in Mexico City in 2006.

line 15 : well, this is the opposite of line 5 on the same page !!

See comments to line 5.

lines 22-23 : could you explain what is this expression, and why it could be more suitable ?

The expression AMS levoglucosan equivalent concentration set the focus only on levoglucosan, but the other anhydrosugars like mannosan and galactosan additionally increase the m/z 60. Therefore it is more suitable to cover all anhydrosugars, which derive from WC, in just one expression, namely the AMS

anhydrosugar equivalent concentration; because it is not possible to say whether the fragment $C_2H_4O_2^+$ (m/z 60) derives only from levoglucosan or also for example from mannosan and galactosan.

p4848 :
line 4 : where did you showed that ?

Contributors to m/z 60 could be long-chain carboxylic acids, e.g. fatty acids. This we explained a few sentences ahead. With GC/MS we measured carboxylic acids like dodecanoic acid and octadecanoic acid. These acids are also known in the literature as contributors to aerosols. The contribution to m/z 60 and fragment $C_2H_4O_2^+$ derive from the McLafferty rearrangement of these long-chain carboxylic acids.

lines 5-7 : this sentence is not precise enough : what is this important role, and why is it important in the context of the study ?

This sentence is important as an introduction of the following results and as a reference of the discussion above, like to the comments to line 4.

lines 9-11 : why should the cooking source be in the substrated background, and not a source factor by itself ?

It is not only the cooking or in this case the long-chain carboxylic acids by itself. It is a question what is contributing to m/z 60, for example, the long-chain carboxylic acids "should be" covered by the organic background, according to the definition of this estimation.
To subtract the source factor and the contribution from each factor to m/z 60 signal by itself is not possible. Additionally, for cooking, we could not find a cooking factor in our PMF analysis. But the most important point here is that one has to know the exact contribution of each PMF factor to m/z 60.

line 11 : there should be a synthesis of your arguments at the end of this section, in order to clearly understand what is your point and what is the conclusion of this discussion.

We agree with the referee and we will provide a short conclusion of this discussion at the end of the paragraph:
"…this detailed view at signal of m/z 60 can only show that the subtracted organic background is in a reasonable range for the SOA. Additionally, this discussion shows that beside levoglucosan as a main contributor other compounds are contributing to the signal of m/z 60 too. These compounds could come from WC (e.g. mannosan, galactosan or cellulose) or could be long-chain carboxylic acids (e.g. from food cooking, WC or SOA), which couldn't be completely covered by the subtracted background."

line 15 : what means “course” in this context ? (and all over the text)

As explained in the comments before, there was a translation problem; we will improve at each point the meaning of “course”. It means on the one hand variation with times and on the other hand gradient or slope.

lines 12 – 20 : since you have not been clear on what is the “organic background” (re, comment for page 4844), it is difficult to understand what you intent to do in all of this section

This section deals with a difficult subject. We improve the section to make it more understandable. We discussed here whether the subtracted organic background (0.3% of the organic mass) is comparable / equal with the contribution of the OOA to m/z 60. This is similar to the discussion before concerning the source contribution to m/z 60. It is more a theoretical approach to explain the offset of the AMS levoglucosan eq. concentration. The new section will be:

“A detailed view at the m/z 60 signal with the PMF factor of OOA (Figure 2a) shows that the contribution of the secondary aerosol source factor OOA to the m/z 60 signal matches with the amount of subtracted organic background (0.3% of the total OM) from the m/z 60 signal of the calculation of the AMS levoglucosan equivalent concentration. Both show a correlation of their time series of R^2 = 0.83. The OOA contribution to the m/z 60 signal represents 70% of the organic background during the whole campaign, except in low PM concentration periods. Then the OOA roughly provides value that is twice as low as the organic background.”

lines 21-25 : you have to discuss about the slope (7,01) between the two indicators, as compared to the ratio (organic matter / levoglucosan) proposed in the litterature (cf table 1)

We will include a comparison to a study of Lanz et al. (2008) and Aiken et al. (2009). The study of Lanz et al. (2008) estimated a high value in Zurich in January 2006 compared to our study. Lanz found a GC-MS levoglucosan to WCOA ratio of 0.08, respectively a WCOA to GC-MS levoglucosan ratio of 12.5; Aiken et al. (2009) found an even higher factor with 16.3. However, as mentioned at comment (p 4846/line 12) and can be seen in Table 1 in the manuscript, the ratio could vary, especially with other burning conditions, like in Mexico City due to a wildfire (Aiken et al., 2009).

Lines 25-26 : you introduce here the notion of “AMS anhydosugar equivalent”. Is it the same as “AMS levoglucosan equivalent” introduced page 4847, line 11?

AMS anhydrosugar equivalent concentration is the same as the AMS levoglucosan equivalent concentration. It was mentioned below that the AMS anhydrosugar equivalent concentration is a better expression and therefore we used the expression in the following parts of the paper. However, we will clarify that we will only use the expression AMS anhydrosugar equivalent concentration from this point on by writing in the text:

“However, the AMS anhydrosugar equivalent concentration used by Lee et al. (2011) may be a more convenient expression and will be used in the following discussions.”

Lines 25-29 : this seems to be the conclusion of the overall secvtion 3.4, and therefore should stand as a paragraph by its own. However, this conclusion should be very carefully worded.
First, I do not believe that the point in the second sentence proves much, since these two indicators are constructed on the same measurements (ie m/z 60), that has been shown in the previous sections not to be completely representative of the levoglucosan (or the anyhosugars in general). Therefore it shoulld not be presented as a conlusion of the section. The first sentence is more interesting and really synthetize this section. However, it would requires further associated comments on the words “suitable” and “qualitative”.

We improved this paragraph and made a more detailed alone-standing conclusion about the meanings of “suitable” and “qualitative”. “Qualitative” refers to the PMF factor WCOA and it means that only the estimation of WCOA could provide an estimated magnitude of the WC emission. The AMS levoglucosan equivalent concentration has the problem to provide the exact concentration due to the estimated “offset” (by comparing AMS and GC-MS levoglucosan results). However, both of these estimations, the AMS levoglucosan and the PMF WCOA reflected well the WC emission over the time with a variation with time correlation of R^2 = 0.84. They are both “suitable” to estimate the variation with time of WC emission. We will improve our wording in this paragraph and in the abstract and following conclusion.

Paragraph improvements will be:
“Both estimations, the WCOA and the AMS anhydrosugar equivalent concentration, allow to observe variation with time of WC emission, with a good gradient correlation of R^2 = 0.84. However, the WCOA is more suitable for the quantitative observation (estimated magnitude) of WC emission than the AMS anhydrosugar equivalent concentration, due to the measured offset by the comparison with the GC-MS levoglucosan.”

Improvements of the conclusion section will be:
“The comparison of GC-MS levoglucosan measurements from the high time resolved PM_1 filters with AMS data shows that either AMS WCOA or alternatively AMS levoglucosan equivalent concentration analysis have a high gradient correlation (R^2 = 0.84) and are therefore suitable for the observation of WC emission variation. Similar to Aiken et al. (2009), we identified the AMS levoglucosan equivalent concentration or better the AMS anhydrosugar equivalent concentration (Lee et al., 2010) to be higher than the GC-MS levoglucosan concentration. Therefore, we argue that not only levoglucosan contributes to the WC marker ion at m/z 60 (HR fragment ion $C_2H_4O_2^+$). Additionally, other components from WC emissions, like mannosan or galactosan or, as shown in other studies, cellulose (Lee et al., 2010), could contribute to the signal of m/z 60. Different analyses of additional GC-MS data and PMF results reveal that long-chain carboxylic acids could additionally increase the m/z 60 signal and that the subtracted organic background is comparable to the OOA fraction of the m/z 60 signal. Therefore an quantitative estimation of the AMS anhydrosugar equivalent concentration is difficult. The analysis of the diurnal variation of the PMF

factors appears to be important for the interpretation of the organic sources and their estimated magnitude, especially for WC. The PMF WCOA diurnal variation presents a similar profile as the hourly PM_1 GC-MS levoglucosan results."

It is true that the second sentence should not stand at the end of this section. We will insert the sentence in another part of the section.

Page 4849
lines 10-12 and line 14-15 : poor english
We will improve each of these parts into:
"The organic aerosol fraction is based on three main sources found by PMF analysis, with the secondary process associated OOA as the biggest contributor with 42% and WCOA with 23% as one of the main contributors."

"The levoglucosan to OC ratio on average amounts to 0.06 in this study and is comparable to other ambient WC observations."

lines 23-24 : poor english

We will improve each of this part into:
"Therefore, we argue that not only levoglucosan contributes to the WC marker ion at m/z 60 (HR fragment ion $C_2H_4O_2^+$). Additionally, other components from WC emissions, like mannosan or galactosan or, as shown in other studies, cellulose (Lee et al., 2010), could contribute to the signal of m/z 60."

line 25 -26 : I do not see where this has been done in the paper.

This part was done in the discussion of the offset of the AMS levoglucosan eq. concentration in section 3.4, in the discussion of the fatty acid.

Comments on the abstract
Lines 10-11 : "organics" : are you talking about OC or OM ?

We talked about the OM and we will change the "organics" in the whole paper.

Lines 22 - 27 : This is the main conclusions of the paper and what most of the readers will retain. Therefore it should be made very clear. What mean "suitable" and "description" ? By the end, the answers are needed for "Can the AMS provide a quantitative measurement of the WC fraction, and if yes, with what uncertainties ?". The discussion on that should appear first in the conclusion section, and be synthetized in the abstract

We will improve our wording in the text as written before at the comment (pages 4848/Lines 25-29). However, the AMS together with the PMF analysis could well provide the estimated magnitude of the WC, but can't provide the exact amount. It is an estimation of WC and it is not possible to measure the WCOA directly.

The new paragraph will be:
“At the end, both estimations, the WCOA factor and the levoglucosan concentration estimated by AMS data, allow to observe the variation with time of wood combustion emissions (gradient correlation with GC-MS levoglucosan of $R^2 = 0.84$). In the case of WCOA, it provides the estimated magnitude of wood combustion emission. Quantitative estimation of the levoglucosan concentration from the AMS data is problematic due to its overestimation in comparison to the levoglucosan measured by the GC-MS.”

Literature:

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Zhang, T., Claeys, M., Cachier, H., Dong, S., Wang, W., Maenhaut, W., Liu, X.: Identification and estimation of the biomass burning contribution to Beijing aerosol using levoglucosan as a molecular marker, Atmos. Environ., 42, 7013-7021, 2008.