

Comments to referee#3 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 careful reading, the constructive comments and the interest in this work, especially the GC-MS part. The referee gave general critiques. These comments (critiques) are mostly discussed and rewritten by line-by-line comments. Therefore, we discuss them in the latter section in detail, except for the comments which are not repeated in the line-by-line comments.

Comments to referees general critiques:

(5) To the extent possible, the authors should make a more explicit connection between the AMS data (m/z 80) and the IDTD-GC/MS data (perhaps even using levoglucosan as a calibration factor) for a semiquantitative apportionment of WC, provided that there are negligible changes in AMS-CE with time.

Comments to point 5: This would be an interesting point, but the problem is that the ratio between AMS calculated levoglucosan from m/z 60 and levoglucosan from GC-MS can change. For example, we found for the ratio the value 2.8 in comparison to Aiken et al. (2009) value 3.2. In addition, the impact of the m/z 60 signal on the PMF solution of WCOA could vary. These all would make the error of this apportionment randomly high. Aiken et al. (2009) present a good estimation of levoglucosan with m/z 60 and the subtracted organic background (0.3% of the total organic matter), but it is not possible to get the exact quantitative amount of levoglucosan with this estimation.

Line-by-line comments:

(Page 4834, Line 17; hereafter page and line number(s) will follow in succession) The abstract should include quantitative information on the findings from the PMF and IDTD-GC/MS comparisons. For example, an average or median contribution of WC to air pollution (i.e., PM) should be provided, given that this Zhang appears to be one of the major objectives of the study (4834, 10).

We will include the correlation coefficient, provide some clearer expressions and improve the text. Unfortunately, we could not measure the PM₁ mass. Therefore, in the preceding paragraph we discuss the impact of the organic matter (OM) on the total measured mass (Sum of AMS and Aethalometer data) and the impact of WCOA on the total mass of the latter OM. Additionally, we provide the ratio of levoglucosan to WCOA.

The new paragraphs of the abstract will be:

During the measurement period nitrate and OM mass are the main contributors to the defined submicron particle mass of AMS and Aethalometer with 28% and 35%, respectively. Wood combustion organic aerosol (WCOA) contributes to OM with 23%

on average and 27% in the evening and night time. Conclusively, wood combustion has a strong influence on the organic matter and overall aerosol composition. Levoglucosan accounts for 14% of WCOA mass with a higher percentage in comparison to other studies. The ratio between the mass of levoglucosan and organic carbon amounts to 0.06.

This study is unique in that it provides a one-hour time resolution comparison between the wood combustion results of the AMS and the GC-MS analysed filter method at a PM₁ particle size range. The comparison of the concentration variation with time of the PMF WCOA factor, levoglucosan estimated by the AMS data and the levoglucosan measured by GC-MS is highly correlated ($R^2 = 0.84$), and a detailed discussion on the contributors to the wood combustion marker ion at mass-to-charge ratio 60 will be given. 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.”

(4834, 26) It is unclear what “offset of the latter” means.

We will improve the sentence as follows:

”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”. The “offset of latter” in this case means the overestimation of the levoglucosan calculated from the AMS data in comparison to the levoglucosan measured by the GC-MS.

(4836, 11) Presumably “hotspots” refer to areas or sites of increased PM emissions. I suggest replacing with a less ill-defined term. (The term “hotspot” is generally considered colloquial speech and should be avoided, if possible.)

We will replace the expression with “possible areas of mature traffic activities”.

(4836, 18) The authors should check the transfer function for aerosol in the AMS lens system for aerosol in the range 500-2500 nm. Any reasonable interpretation of the term “considerable transmission” would not include the AMS transmission of particles above PM1. Admittedly, the ambient particle mass is falling off above 500 nm, but this is not captured in the terminology used.

We only cited the literature for the characterisation of the lens; for a detailed discussion in the literature please refer to (Jayne et al., 2000; Zhang et al., 2002).

(4837, 5-7) The use of the AMS-CE of 0.5 is perhaps the most important factor in the analysis, especially for comparison purposes, and the choice needs to be supported in the main text and not simply in the SI. I would consider the information more essential than supplementary. My recommendation would be to take the salient findings in the SI and move them up to the main text.

We will conclude and include the main results of the SI part from the AMS-CE in the paper. Please take a look at the conclusion:

“A collection efficiency (CE) of 0.5 was used for this instrument and applied to all AMS data. In a detailed discussion provided in the Sect. SI-1 of the Supplement it is shown that an acidity balance and nitrate dependence is given. However, a novel calculation of an alternated CE (Middlebrook et al., 2012) shows that the nitrate dependence does not affect the obtained results with a constant CE of 0.5. According to Bahreini et al. (2009) this CE could vary by around 20%.”

(4837, 26 ff.) I do not believe there is a need for the general discussion of PMF as represented in Eq. 1 and Eq. 2 and the associated text.

We will delete the part from the manuscript and will include it in the Supplemental Information at the beginning of Sect. SI-2.

(4838, 20) Additional essential information noted above should be provided especially the limit of detection for the on-column sampling masses of the major analytes being detected – levoglucosan,

We agree with the referee and include the LOQs of the major analytes at comment (4839, 20).

For levoglucosan, mannosan, galactosan, and dodecanoic acid we reached LOQs of 0.06, 0.05, 0.02, and 0.06 ng, respectively.

(4839, 2) Give time frame over which samples were collected to be consistent with (4838, 22).

We will insert the sampling time and data points in the text:

”Additionally, 17 daily PM_{2.5} samples were collected during the period of 1 to 24 February and analysed using the same method.”

(4839, 11) From a mass balance, was there any evidence for PM mass between PM₁ and PM_{2.5}. Note level of consistency in Section 3.

We didn't measure the total PM₁ mass; therefore we cannot correlate the PM₁ and PM_{2.5} masses. However, we will add in the manuscript that no significant difference between the analytes mass of PM₁ (hourly filters) and PM_{2.5} (daily filters) was found. This is reflected by the comparison of daily averaged PM₁ and daily PM_{2.5} samples of levoglucosan in the following table:

Table 1: Measured concentrations of levoglucosan on a daily average from both filter samples.

	16.02.2010	17.02.2010	18.02.2010
PM ₁	326.3	464.4	701.4
PM _{2.5}	292.9	460.0	641.4

(4839, 20) Give the value for the LOQ; stating that the LOQ is low is insufficient. This is especially crucial since the sampling volume for each 27 sq mm strip is only 47 liters. Also some comments should be made about efforts to avoid contamination during the filter handling process (i.e., cutting the strips, spiking with MSTFA and the reference compounds, inserting in the heater, etc.). This does not appear to have been addressed in Orasche et al., although I could have missed it.

We will insert the LOQ values from comment (4838, 20). All measured analyte concentrations are above the LOQ. Even the lowest value of galactosan (1.0 ng m^{-3} , respectively 0.05 ng of 47 l sampled air) found on the February 18 between 4 pm and 5 pm was beyond the LOQ (0.02 ng). For each of our measurement and analysis steps we followed GLP guidelines. Beside these handling steps, field blanks and laboratory blanks were analysed. All blank values were < LOQ of the respective analytes, the values of dodecanoic acid were subtracted from the blank values.

(4839, 23) The parenthetical comment is much too cryptic for the average reader and appears to be misplaced. Were the GC liners manually inserted into the injection port or was it conducted using the autosampler?

The referee is correct. We will improve this in the following sentence and clarify the question regarding the transportation of GC liners.

“For analysis an autosampler decapped the liners, added MSTFA directly onto the filter punches and put the GC liners directly into the injector (autosampler, Combi PAL, CTC Analytics AG, Zwingen, CH; LINEX-TD system, ATAS-GL, Veldhoven, NL). The injector increased its temperature to 300°C from room temperature and kept the temperature for 16 minutes (injection port: Optic III , ATAS-GL, Veldhoven, NL).”

(4839, 23) Include in the text the catalyst that was used. Was the catalyst also enriched in the vapor phase? Does enrichment in the gas phase simply replenish the derivative on the filter or does the derivatisation occur at least partially a gas-phase reaction. If so, it is not clear how the catalyst would work in this case.

This is also a special part of the GC-MS method; we do not use a catalyst (Orasche et al., 2011).

(4841, 13) See Schnell et al. (2009) "Rapid photochemical production of ozone at high concentrations at a rural site during winter," Nature Geosci. 2:120-122 to determine if any of their arguments are applicable.

The work of Schnell et al. (2009) presents an interesting approach. However, we had low global radiation and cloudy weather exactly in this period, which made it impossible to use the explanation offered by Schnell et al. (2009). Therefore we decided to delete our speculative sentence.

(4842, 19 ff.) Is OOA interpreted as formation of SOA under wintertime conditions. If so, to what extent can gas-phase WC components be a source. In addition to relevant citations in this manuscript, see articles by S.B. Hawthorne (Env Sci Technol: 1988-1992) for detailed organic analysis from WC for ideas on SOA precursors.

The OOA is associated with SOA, for example: the high correlation of OOA with secondary inorganic aerosol marker sulphate. SOA is a fraction of the OOA, but in addition OOA includes aged and thereby oxidized POA. As is indicated by the four factor PMF solution, some parts of the OOA could come from WC. For example, Heringa et. (2011) showed that WC gas phase compounds (Hawthorne et al., 1989) could increase the SOA production. So far it has not been possible to estimate the impact of WC gas phase on OOA/SOA product. The discussion on this topic will be added to the manuscript.

4842, 21) The authors should be more explicit on what "high" PM period, especially when considering high resolution data.

We will clarify the expression using "period of high PM concentrations".

(4842, 28 ff.) This paragraph completely lacks context. Please provide some.

We will move the paragraph to a different section of the manuscript.

(4844, 11 ff.) Any thought given to nebulizing an aqueous solution of levoglucosan to provide some information on the AMS-CE for this compound?

We did not make an AMS-CE determination for levoglucosan. We measured the relative signal of m/z 60 from levoglucosan of this AMS. If you only use a levoglucosan aqueous solution and vary the concentration, this could probably lead to different particle sizes and therefore could affect the CE or the transmission of the lens. However, if more ambient aerosol (with ammonium nitrate and some organics or BC) will be generated and then the levoglucosan concentration will be varied the CE is not affect that much. It has been found that changes of the organic fraction did not show a clear effect on the AMS-CE (Middlebrook et al., 2012).

(4844, 12) The first sentence of this section is self-evident. I suggest deleting.

Sentence will be deleted.

(4846, 12) Compare 0.06 obtained for the levoglucosan fraction in WC with the value of 0.079 reported by Fine et al. 2004. In fact, this would be one of the more useful findings of the study.

FINE, P.M., CASS, G.R., and SIMONEIT, B.R.T. (2004). Chemical characterization of the fine particle emissions from the fireplace combustion of wood types grown in the midwestern and western United States. *Environ. Eng. Sci.* **21**(3), 387.

FINE, P.M., CASS, G.R., and SIMONEIT, B.R.T. Chemical Characterization of Fine Particle Emissions from the Wood Stove Combustion of Prevalent United States Tree Species, ENVIRONMENTAL ENGINEERING SCIENCE Volume 21, Number 6, 2004

Unfortunately, we could not find the value of 0.079 in the studies of Fine et al. 2004. However, we will include the ranges of the different levoglucosan to OC ratios from Fine EES publication in Table 1 in the manuscript. It is important to note that Fine et al. made emission studies and provided the OC of particle from wood combustion emission. In contrast, our ambient study only has the OC value of the whole organics matter and not only from the WC organic matter. This point is identical for the other exemplary ambient studies mentioned in our manuscript.

(4847, 13) The difference between the factor of 3.2 (from Aiken et al., 2010) and 2.8 in the present work is simple speculation. First, systematic errors in the measurements, let alone the random errors, are more than sufficient to explain the 18% difference.

Second, perhaps the authors should consider that the difference between the two values is in the denominator (levoglucosan values) and not necessarily in the numerator (AMS values). I would rethink this paragraph and give a somewhat more balanced discussion of the differences in the ratio.

Maybe there was a misunderstanding concerning the factor of 3.2 (from Aiken et al., 2009). We did not search for an explanation for the difference between our factor 2.8 and the factor of 3.2 from Aiken et al. (2009). We said that Aiken et al. also found a high factor. Later we discussed the general factor of 2.8 and the offset. We will clarify the sentence as follows: "Aiken et al. (2009) also found a higher factor of 3.2, respectively an overestimation (offset) of the AMS levoglucosan equivalent concentration. This offset found in our study can be explained due..."

(4848, 10) The background signal should be given as 0.003 x 11.4.

Unfortunately, we do not understand this factor. Where does the 11.4 come from? In the literature the organic background of m/z 60 is given as 0.3% of the total organic mass. As the total organic mass varies in time the background signal can not be given as a fixed value.

(4849, 14) Provide more of the quantitative data in the Conclusions.

Conclusions will be rewritten.

The related section in the conclusions will be:

“The main submicron aerosol fractions obtained by the AMS are organic matter with 35% and nitrate with 28% in Augsburg during winter. This is typical for winter in Central Europe (Lanz et al., 2010). 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 influence of WC is particularly important for the aerosol composition with 28% in the evening and the night hours, while the primary HOA emission factor is of higher concern during the morning rush hours. Here HOA contribution increases to 38%. The levoglucosan to OC ratio on average amounts to 0.06 in this study and is comparable to other ambient WC observations.”

The comparison of GC-MS levoglucosan measurements from the high time resolved PM₁ 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.”

Copy edit corrections:

(4833, 19) The usage of the word “courses” is unclear. Is it meant to be a synonym for “route”?

The referee is correct. There was a translation error. We will improve the meaning of “course” in the manuscript. On the one hand, it means variation with times and on the other hand it means “gradient” or “slope”.

(4833,23; 4843,20; 4843,23; 4848,15; 4849,17) Similar comment for “course”.

It will be improved, as discussed above.

(4835,10; 4843, 14; 4844,21; 4847,7; 4847,13; 4849,19) Replace Aiken et al., 2009 with Aiken et al., 2010 to be consistent with the reference.

We will replace the address of the reference. There was a problem with the transfer from the sent word manuscript into the ACPD manuscript. The reference is Aiken et al., 2009 and not Aiken et al., 2010.

(4835, 24) Capitalize the name of the study; I assume “imission” is intentionally misspelled for the sake of the acronym. There is no evidence that “imission” is a variant spelling of the intended word, emission.

Please note that MOSQUITA is the name of the mobile laboratory van that the PSI has built up. In the acronym the “I” stands for the expression “immission”, which admittedly is rarely used English.

We will change this sentence according to referee#2 and your suggestions:

“...an AMS for local source apportionment set up in a mobile atmospheric pollution laboratory “MOSQUITA” (“Measurements Of Spatial QUantitative Imissions of Trace gases and Aerosols”).”

Literature:

Aiken, A. C., Salcedo, D., Cubison, M. J., Huffman, J. A., DeCarlo, P. F., Ulbrich, I. M., Docherty, K. S., Sueper, D., Kimmel, J. R., Worsnop, D. R., Trimborn, A., Northway, M., Stone, E. A., Schauer, J. J., Volkamer, R. M., Fortner, E., de Foy, B., Wang, J., Laskin, A., Shutthanandan, V., Zheng, J., Zhang, R., Gaffney, J., Marley, N. A., Paredes-Miranda, G., Arnott, W. P., Molina, L. T., Sosa, G., and Jimenez, J.L.: Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) - Part 1: Fine particle composition and organic source apportionment, *Atmos. Chem. Phys.*, 9, 6633-6653, 2009.

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Orasche, J., Schnelle-Kreis, J., Abbaszade, G. and Zimmermann, R.: Technical Note: In-situ derivatization thermal desorption GC-TOFMS for direct analysis of particle-bound non-polar and polar organic species. *Atmos. Chem. Phys.*, *Atmos. Chem. Phys.*, 11, 8977–8993, doi:10.5194/acp-11-8977-2011, 2011.

Zhang, X., Smith, K. A., Worsnop, D. R., Jimenez, J. L., Jayne, J. T. and Kolb, C. E.: A Numerical Characterization of Particle Beam Collimation by an Aerodynamic Lens-Nozzle System. Part I: An Individual Lens or Nozzle, *Aerosol Sci. Tech.*, 36, 617-631, 2002.