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***Interactive comment on* “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” by M. Elsasser et al.**

**Anonymous Referee #3**

Received and published: 8 April 2012

Review of Elsasser et al., “Organic molecular markers and signature from wood combustion: aerosol mass spectrometer (AMS) and high time-resolved GC-MS measurements in Augsburg, Germany”

Synopsis of the paper:

The paper reports wintertime measurements of fine particulate matter (PM) in the ambient environment of Augsburg, Germany during the winter of 2010. The interpretation

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of the data focuses on the contributions from wood combustion to the ambient fine PM. The main measurement technique over the entire study is by aerosol mass spectrometry (AMS) and specific ions (e.g.,  $m/z$  80) which are thought to represent ion-markers of wood combustion (WC) sources to the aerosol. During a three day sub-period, chemical markers of fine PM were measured using a relatively new technique (developed in the investigators' laboratory) given by the moniker, in-situ derivatisation thermal desorption (IDTD)-GC/MS. The technique focuses on the fast analysis of previously identified chemical markers of wood combustion aerosol, in particular levoglucosan (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>), and other anhydrosugars generated during WC, e.g., mannosan, galactosan. A comparison of the two methods shows a high correlation between the markers during the selected analysis period. Some additional analyses were performed.

General comments on the paper:

The paper studies an important aspect of ambient PM source identification and measurements. Given the worldwide proliferation of the AMS technique, it is important to determine which AMS ions of organic origin might be used for source identification and to show their utility through independent measurements. I believe this paper achieves this goal for wood combustion organic aerosol (WCOA). By-and-large, the arguments and interpretation hold together and the measurements were competently performed. While I have provided a number of points of criticism and some suggestions for improvement, it is my opinion that publication of the article is clearly warranted.

The general critiques of the paper are as follows: (1) The descriptions of the upper-end cut-points of the aerosol for the different PM methods are very sketchy. Some effort needs to be made to better define what these are especially for the AMS and the integrated samplers for the IDTD-GC/MS techniques, since the comparison of two methods is a major objective of the paper. (2) The justification for the AMS-CE value of 0.5 should be strengthened and the salient points leading to this conclusion moved from the Supplementary Information (SI) to the main body of text. (3) Some discussion of the origin of OOA and its relationship to possible sources of secondary organic

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aerosol (SOA) should be addressed especially given that the wintertime production of SOA, especially at high northern latitudes (48.4 deg N), is likely to be quite small. (4) The description of the IDTD-GC/MS is weak. Orasche et al. (2011) is the sole reference for the method and that reference considers mostly model compounds with an extremely limited number of ambient samples for which the sampling volumes and possibly other conditions were of sufficient differences to warrant a better description. A paragraph summarizing the calibrations, interferences, limit of detection, precision, and accuracy would provide the reader with a better perspective on the technique. (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.

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 appears to be one of the major objectives of the study (4834, 10).

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

(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.)

(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 PM<sub>1</sub>. Admittedly, the ambient particle mass is falling off above 500 nm, but this is not captured in the terminology used.

(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.

(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.

(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,

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

(4839, 11) From a mass balance, was there any evidence for PM mass between PM1 and PM2.5. Note level of consistency in Section 3.

(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.

(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?

(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

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so, it is not clear how the catalyst would work in this case.

(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.

(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.

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

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

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

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

(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.

(4847, 13) The difference between the factor of 3.2 (from Aiken et al., 2010) and 2.7 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.

(4848, 10) The background signal should be given as  $0.003 \times 11.4$ .

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

Copy edit corrections:

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

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

(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.

(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.

(4843, 19) Replace “trough” with “through”.

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