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Interactive comment on "Biogenic and biomass burning organic aerosol in a boreal forest at Hyytiälä, Finland, during HUMPPA-COPEC 2010" *by* A. L. Corrigan et al.

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Answer on Referee #2 - The authors thank the referee for improving the manuscript by his/her helpful comments. The authors feel the manuscript has been streamlined by moving the STXM-NEXAFS section to the SI. The manuscript will be revised based on the referee's comments as follows:

Comment 1: P. 16155, Line 1-10: Compare also "Minguillón, M. C., et al.: Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain, Atmos. Chem. Phys., 11, 12067-

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12084, doi:10.5194/acp-11-12067-2011, 2011”.

Reply: We appreciate the suggested reference, which has been added to our introduction and Table 1.

“Other apportionment techniques have applied a combination of factor, radiocarbon, and tracer analysis to quantify the biogenic fraction [Minguillon et al., 2011], but also indicated substantial uncertainties in these methods given the greater biogenic fraction identified during wintertime (30%) than summertime (23%) at the Mediterranean city of Barcelona [Minguillon et al., 2011].”

Comment 2: P. 16158, Line 14: The AMS time resolution can also be higher and depends on the mass spectrometer. If 5 min was the time resolution of the data presented here then this should be stated explicitly.

Reply: The general statement that all AMS instruments have a ∼5 min time resolution was removed.

Comment 3: P. 16158, Line 15 – 18: Please give also information on the resolution of the C-ToFAMS

Reply: The time resolution of the C-ToF AMS was 5 min. This has been updated in the text.

“The variant of the device used in this study was a C-ToF AMS with 5 minute time resolution that . . .”

Comment 4: P. 16158, Line 24: Define DMPS. Was the comparison of AMS and DMPS done including black carbon data?

Reply: The text in section 2.3 has been updated. A more detailed explanation of the CE determination has been included, in addition to a definition of DMPS. Black carbon volume was removed from the DMPS volume distributions prior to determining the CE, this has now been included in the text.

“The collection efficiency (CE) of 0.43 was determined from a comparison with a Differential Mobility Particle Sizer (DMPS, [Aalto et al., 2001]) derived mass concentrations in size range 3-600 nm. The DMPS number distributions were converted to volume distributions, and integrated over the size range in question. Black carbon (BC) volume derived from an aethalometer was then subtracted and the remaining volume multiplied by time-dependent particle density, estimated with a weighted average of chemical species densities from the AMS. The neutral-aerosol (base) CE was determined from the average ratio of AMS total mass per DMPS derived mass (minus BC) and was found to be 0.43 with a standard deviation of 0.08. This CE was applied for time periods when the aerosol acidity was neutral, as determined by the ratio of ammonium to sulfate plus nitrate.”

Comment 5: P. 16159, Line 27: Was there no off-gassing from the HEPA filter observed?

Reply: The gas-to-particle partitioning was shifted to the gas phase and the organics trapped by the HEPA filter were therefore very low in volatility. For a detailed description of the instrument, please see Vogel et al. [2013].

Comment 6: P. 16160, Line 22 -23: Please specify what is meant by “baselined” spectra.

Reply: The “baselining” refers to the spectral manipulation used to correct sloped baselines in FTIR spectra. The algorithm applied uses a 3rd-order polynomial to baseline the spectra, which is discussed in detail in Takahama et al. [2013]. The word “baselined” has been removed from the sentence, as “baselined AMS spectra” does not make sense.

Comment 7: P. 16162, Line 22: How do you explain the higher sulfate fraction during the sawmill events? And didn’t you state on P. 16157, Line 20 – 22 that organosulfate was below LOQ?

Reply: We attribute the sulfate fraction to fossil fuels, which powered the boiler used for mechanical wood processing. On average, boilers in Finnish sawmills that generate sawn wood are powered 50% by fossil fuels and 50% by biomass (i.e. bark) [Pingoud and Lehtila, 2002]. Organosulfate was detectable by FTIR during sawmill events, however the organosulfate group mass was below the limit of quantification.

Comment 8: P. 16163, Line 24 – 26: The AMS CE was established earlier to be 0.43 for all AMS species, a not particularly high value. The authors suggest here that one of the reasons for the strong agreement between FTIR OM and AMS OM is a high AMS OM CE. This seems contradictive.

Reply: The reviewer is correct. The statement has been corrected. We attribute the strong agreement between FTIR and AMS OM on completeness of the OM quantification of both methods and accuracy of the AMS collection efficiency.

Comment 9: P. 16164, Line 16 -18: This statement is not necessarily true. Even in cities other OA types than HOA can be more important (compare e. g. "Jimenez, J. L., et al. Evolution of organic aerosols in the atmosphere. Science 2009, 326, (5959), 1525-1529").

Reply: In regards to FTIR source apportionment, Fossil Fuel Combustion (which may include both POA and SOA) is typically the major contributor to OM in urban regions [Liu et al., 2012; Russell et al., 2009]. The text has been updated to include cooking and residential wood burning as other possible sources of urban OM.

"Typically the major contribution to organic mass in populated areas is from fossil fuel combustion (which includes both POA and SOA), primarily from motor vehicles [Liu et al., 2012], with smaller contributions from cooking and residential wood burning [Mohr et al., 2012]."

Comment 10: P. 16164, Section 321: It would be helpful for the reader if the clusters were given names. On P. 16166, Line 6, I cannot see how this very strict conclusion

– that there was no sawmill activity identified in FTIR clusters – can be drawn. Cluster 1-T is clearly connected to sawmill activities, and Cluster 1-T and 1-IR are mentioned to be overlapping. And couldn't the high carboxylic acid fraction of 1-IR hint at sawmill activities? Are the mentioned high NOx values grouped into Cluster 1-T related to traffic to/from/at the sawmill?

Reply: Since the article contains two sets of named PMF solutions, we wanted to minimize confusion by not adding additional names. It was not our intention to conclude sawmill activity is not identifiable by FTIR, instead we are suggesting that the sawmill events are not distinguishable (by IR spectra) from biogenic organic aerosol and are clustered together with the enhanced biogenics during week 1 of the campaign. We suggest that Cluster 1-IR is both biogenic organic aerosol and biogenic aerosol from the sawmill events. We believe the high NOx is from vehicular traffic associated with the sawmill activity. Liao et al. [2011] also report high NOx during anthropogenic monoterpene events (i.e. sawmill events) at Hyytiälä.

Comment 11: P. 161167, Line 10 -22: It would be helpful if the percentage of FFC2_FTIR was stated as well.

Reply: We have added the percentage (27%) of FFC2FTIR in this section.

Comment 12: P. 16170, Section 3.2.3: It would be helpful if the percentages of the AMS PMF factors of AMS OM were stated.

Reply: The percentages of the AMS factors have now been included in this section.

Comment 13: P. 16172, Line 16 – 18. I cannot really see a high mass fragment 57 in OOA-2. Do the authors mean 67? But more importantly, m/z 55 and m/z 57 are commonly tracer mass fragments for HOA (and, more recently, COA, and thus primary) and not OOA (see e. g. "Zhang, Q., et al. Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry. Environ. Sci. Technol. 2005, 39, (13), 4938-4952"). Also from looking at OOA-2, and its corre-

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lation with AMS nitrate, it seems to me this PMF factor might rather be interpreted as HOA related, or OOA/SOA related to fossil fuel emissions.

Reply: The reviewer is correct; we meant to say m/z 67. The mass fragments m/z 43, 55, 57, and 67 are common tracers for OOA-2 (also referred to as SV-OOA) factors [Lanz et al., 2007; Sun et al., 2011; Ulbrich et al., 2009]; however, there is high variability of the relative intensities of m/z 43, 55, and 57 within OOA-2/SV-OOA factors [Ng et al., 2011]. Due to the presence of m/z 43, 55, and 67, in addition to correlation with nitrate, we attribute this factor as OOA-2. Please see comment 14 for our interpretation of OOA-2.

Comment 14: P. 16173, Section 3.2.4: Whereas the identification of biomass burning and biogenic emissions OM is supported by both AMS and FTIR spectroscopy finding similar results, I am less convinced about the interpretation of AMS PMF factor OOA-2. Apart from the reasons stated in my previous comment – FTIR identifies 40% of OM as of fossil fuel origin (FFC1_FTIR and FFC2_FTIR). The AMS factors, however, are all interpreted as OOA, even though HOA is usually a PMF factor that is most likely to be identified in AMS PMF analyses. How can this discrepancy be explained? Is it possible that OOA-2 might also be related to coal burning emissions? Statements on P. 16174, Line14 – 23 concerning SOx emitting regions would support that theory.

Reply: In the four-factor PMF solution, a more traditional HOA factor emerged (m/z 43 > m/z 44). However, this factor represented less than 7% of the reconstructed OM and contained little temporal variation, suggesting the solution was over-interpreting the available data. Additionally, the mass that generated this fourth factor primarily came from OOA-2. The four-factor solution also had no temporal variation in the additional factor and unrealistic mass spectra in other factors. It is likely the case that there is background level HOA at the remote site and it is being included in the OOA-2 factor, as suggested by the PSCF analysis that revealed high probability near SOx emitting regions. Studies in remote regions have also noted a lack of HOA in PMF solutions, consistent with not sampling within an urban area, the absence of local sources, and

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low m/z 57 in Hyytiälä [Hildebrandt et al., 2010].

In regards to FTIR identifying 40% of OM as FFC1 and FFC2, it is likely the case that the source of the combined FFC factors is very similar to the source of OOA-2.

Comment 15: P. 16178, Line 3: Are there really no FTIR spectra of emissions from burning vegetation growing in the boreal forest?

Reply: Unfortunately we are not aware of any FTIR spectra from boreal forest burning emissions. Due to the high content of cellulose in vegetative material and strong similarity amongst olive tree burning spectra with biomass burning factors from previous campaigns, we feel the olive tree burning spectra is a good representation of organic functional groups in biomass burning emissions.

Technical corrections:

1) P. 16151, affiliations: “Lausanne” is spelt with 1 s and 2 n

Reply: The typo has been corrected.

2) P. 16203, Fig. 2: Has a box on the x-axes of top panels C) and D)

Reply: The text box has been removed from the figure.

3) P. 16205, Fig. 4: AMS PMF spectra have a wrong y-axis label

Reply: The typo has been corrected.

References:

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Hildebrandt, L., et al. (2010), Aged organic aerosol in the eastern mediterranean: The finokalia aerosol measurement experiment-2008, Atmospheric Chemistry and Physics, 10(9), 4167-4186.

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Liao, L., et al. (2011), Monoterpene pollution episodes in a forest environment: Indication of anthropogenic origin and association with aerosol particles, Boreal Environment Research, 16(4), 288-303.

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Russell, L. M., et al. (2009), Oxygenated fraction and mass of organic aerosol from direct emission and atmospheric processing measured on the r/v ronald brown during texaqs/gomaccs 2006, Journal of Geophysical Research-Atmospheres, 114.

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Ulbrich, I. M., et al. (2009), Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data, Atmospheric Chemistry and Physics, 9(9), 2891-2918.

Vogel, A. L., et al. (2013), Online atmospheric pressure chemical ionization ion trap mass spectrometry (apci-it-ms) for measuring organic acids in concentrated bulk aerosol – a laboratory and field study, Atmospheric Measurement Techniques 6, 431-443.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 16151, 2013.