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Comment

***Interactive comment on* “Black-carbon-surface oxidation and organic composition of beech-wood soot aerosols” by J. C. Corbin et al.**

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We thank Anonymous Referee #1 for his or her comments and appreciate the constructive criticisms. Below we quote each specific criticism before responding to it. Referee comments are shown in [blue](#) while direct quotations from the manuscript are *italicized*.

[it seems that the “fresh” and “aged” particles were assess during different experiments \[...\] isn't it possible that the higher relative CO+ and CO2+ signals in the aged experiment were due to slightly different combustion conditions \(i.e., different fresh rBC composition\)”?](#)

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[...]

Additional evidence that the composition of the fresh emissions was well constrained as a reference point for the aging experiments is needed. For example, is the variability of the C₃+CO₊ ratio during the fresh smoke experiments significantly less than the 46% change observed between the fresh and aged experiments (Pg. 9597, line 22)?

The referee is correct, fresh and aged experiments were performed on different particles. This was done in order to allow the temporal evolution of the aerosol composition to be probed. This is now clarified in the text.

The last point here is actually answered by our PMF analysis. Since over 97% of the relevant variance in the data was explained by the PMF model (P9592,L7), the variability of the mass spectrum of each identified component, including the fresh and aged BC factors, was much smaller than the 46% stated on P9597,L22. This fact was underemphasized in the manuscript and is now clarified.

Additional discussion of the stability and reproducibility of the combustion conditions is now included in the Experimental section, where a companion paper has also been cited.

Is it possible that minimally coated fresh rBC particles (particularly during the flaming stage) exhibited poor collection efficiency on the tungsten vaporizer in the AMS due to particle bounce thereby underestimating the non-refractory organic species internally mixed with rBC particles? Given that the C₂H₄O₂⁺ signal (from non-refractory anhydrosugars) persists into the flaming phase in the SP-AMS measurements (Figure 1), but is negligible in the AMS measurements (Figures 1, 3d), suggests that NR-PM components were missed by the AMS during the flaming phase. Further, the SP-AMS

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$C_2H_4O_2^+$ signal appears to be higher than the AMS signal by a factor similar to the difference between the two instruments for CO^+ and CO_2^+ ions (Figure 1), indicating that the SP-AMS is much more sensitive overall. So, unless it can be demonstrated that the AMS did not merely “miss” non-refractory sources of CO^+ and CO_2^+ associated with rBC, it’s not clear that CO^+ and CO_2^+ can be unequivocally assigned to refractory BC surface groups.

It is absolutely possible that the SP-AMS is more sensitive to coating signals than the AMS, as has been recently discussed by Willis et al. (2014). Conversely, the SP-AMS may vaporize a smaller fraction of rBC particles when they are poorly-focused into the laser beam (P9583,L22–28). These were actually the original reasons why we did not report mass concentrations for the SP-AMS, even though they have been reported by other studies. Finally, the reviewer is of course correct that the bounce-related collection efficiency on the AMS vaporizer could be lowered by minimal coatings on fresh soot particles. We refer to these issues as “complications” below.

With these complications in mind, we are not comfortable interpreting Fig. 1 as quantitatively as the reviewer has. It is of course true that the persistence of $C_2H_4O_2^+$ into the flaming phase of Fig. 1 indicates that the AMS was not seeing some OM. But this could have been due to a combination of the reduced AMS collection efficiency combined with the enhanced SP-AMS sensitivity.

The second-last comment above, that the SP-AMS to AMS signal ratio for $C_2H_4O_2^+$ and for CO^+ or CO_2^+ appears to be similar, appears to be referring to the start of each burn only. At this time, the signal ratio may again be explained by the above complications. However, during the flaming phase of each burn, it is clear that the SP-AMS to AMS signal ratio for CO^+ and CO_2^+ is much, much higher than for $C_2H_4O_2^+$. This suggests an alternative source of these signals in the SP-AMS.

Finally, we would like to again emphasize the PMF results. These showed that the

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OM mass spectra measured by SP-AMS and by AMS were very similar, with very high correlation coefficients. The SP-AMS OM factors were present even in the absence of BC (Fig. 5, first two hours), which demonstrates that they did not originate from the BC itself.

Also, the OM factors showed similar trends for AMS and SP-AMS factors, although the AMS signals were consistently lower. Such similarity between mass spectra and temporal trends, in spite of a consistent difference in sensitivity, is consistent with the cause being the complications named above.

The lack of discussion regarding AMS collection efficiency toward rBC particles is a significant weakness of the manuscript. Additionally, an improvement in the AMS collection efficiency following aging could explain the smaller difference in OOM signals than POM signals (pg 9601, lines 25-27). OOM coatings were discussed as potentially influencing SP-AMS collection efficiency (pg 9602, lines 3-5); it should be considered for AMS, as well.

We agree. We had discussed AMS collection efficiency extensively in the related paper Corbin et al., AS&T, 2015, in press. We have now added a section (new section 2.3.4) dedicated to the discussion of AMS and SP-AMS collection efficiencies. We have also moved some of the discussion in the RIE subsection (old section 2.3.4, new 2.3.5) to this section, which should address the comment of that section being confusing to the reader.

Are CO measurements available in addition to CO₂ to estimate the modified combustion efficiency (MCE) during each phase of burning? That may better elucidate the relative contributions of flaming and smoldering combustion during the various burning stages. It would also help to cite the

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MCE during the time periods that the mass spectra in Figures 3&4 were collected so that readers may better gauge how similar the burning conditions were during the fresh and aged experiments.

Thank you for this suggestion, the MCE has been added to Figs. 1 and 2 and 3 and 4.

0.1 Specific comments

Pg. 9583, line 15: Why does the presence of refractory CO^+ species influence the relative ionization efficiency (RIE) of C_x^+ if the neutral species are vaporized prior to ionization? I found the discussion of RIEs occasionally confusing, as the authors discuss factors other than ionization (e.g., collection efficiency- pg. 9583, line 16) as impacting RIE even though RIE is defined as only the efficiency of ionization (pg. 9583, lines 11-12). Perhaps “effective RIE” or “detection efficiency” would be better terms if this is meant to account for all factors influencing instrument sensitivity?

(i) Calibration is normally performed by preparing an aerosol of “rBC particles”, which is typically defined as a particle known to be composed of mostly refractory BC, without significant organic content. The single-particle mass of these rBC particles is then taken as the reference for calibration of C_x^+ signals. If rCO_x -producing species contribute significantly to the total particle mass, they would lead to an overestimation of the reference mass and an underestimation of the C_x^+ ionization efficiency.

(ii) Due to the new subsection on collection efficiency, the discussion should now be clearer.

Pg. 9583, lines 22-23: How much smaller were the particles relative to the transmission range of the aerodynamic lens? Please include independent size distributions (e.g., SMPS) in the Supplement.

We changed the citation to (as discussed in Corbin et al., 2015a) rather than adding this information, because the answer is complex and depends on the stage of the burn and the experiment. The cited paper contains size distributions for all times for each burn. However, on P9583,L22 the comment is made in passing and to discuss size distributions here would confuse the discussion. Since the actual interpretation made in this manuscript is independent of size, we think the reference to the other paper – now made clearer – is the best option here.

Pg. 9589, lines 20-23: “K⁺ and CO_x (= CO₊ + CO₂) remained extremely high during [the flaming] phase (Figs. 1 and 2). These signals dropped to negligible levels in the AMS (dashed lines in Fig. 1), confirming that they were generated from LR-PM particles. The CO_x signals were not only present in the LR-PM but also in the NRPM.” This seems contradictory. If the CO_x levels were negligible in the AMS during the flaming phase, then how can these species also be attributed to NR-PM? Is the last sentence now including the starting phase?

We have clarified the phrasing:

“ Although high K⁺ signals were only observed in the SP-AMS, relatively-high CO_x signals were observed in both AMS and SP-AMS. These signals therefore appear to have originated from both OM and rBC. ”

Pg. 9589, line 26-27: “In the AMS, [the CO₊/CO₂+] ratio was 3.92 – 0.01 for fresh emissions”. In Figure 1, values of the AMS CO₊/CO₂+ ratio are given only for the starting phase. In Figures 3d and 5b (POM-Flame), CO₊ “CO₂+, and CO₊ was apparently below the detection limit (Pg 9593, lines 17-18). The authors should be careful to apply the AMS CO₊/CO₂+ ratio based on starting-phase emissions to all fresh emissions, as it does not appear to apply to flaming emissions.

In Fig 1 (and in Corbin et al. 2015a) we report measured $\text{CO}^+/\text{CO}_2^+$ ratios, which for the AMS were only measurable for the starting phase. In Figs. 3d and 5b (and also 4d) we have plotted mass spectra for the flaming phase, which for the AMS no $\text{CO}^+/\text{CO}_2^+$ ratio was available. Measuring the $\text{CO}^+/\text{CO}_2^+$ was only possible at very high loadings, as the CO^+ detection limit was very high, which the CO_2^+ detection limit was much lower. Therefore, the fact that the $\text{CO}^+/\text{CO}_2^+$ ratio was not measurable during the flaming phase does not prove that that $\text{CO}^+/\text{CO}_2^+$ ratio was different at this time, nor does it prove that the ratio was the same.

We have tried to avoid plotting what was not measured, and so we plotted no signal for CO^+ in Figs. 3d and 5b. This could mislead some readers into thinking there was no AMS CO^+ , so we have added emphasis in the legends of each of these figures, along the lines of: “In the mass spectra of **(b)**, no CO^+ signal is shown as that species was below its detection limit.”

Section 5.6: “The particulate H_2O^+ signals were virtually negligible in the AMS, but extremely high in the SP-AMS: a factor of 40 higher than C_3^+ ” (Pg. 9603, lines 8-9). In which phase of burning was the H_2O^+ signal 40-fold higher than C_3^+ ? In Figures 3a,c and 4a,c, the H_2O^+ signal appears to be less than (flaming) or only slightly higher (starting) than C_3^+ . Were the logs dried prior to burning? Was the fuel moisture content measured? Please describe how the fuel was treated prior to burning and whether the amount of water observed is roughly consistent with such pre-treatment. Additionally, Popovitcheva et al. (2000) indicate that water adsorbed in BC pores is thermally stable to at least 450K. Is it expected that such water will remain adsorbed at the 873K used in the AMS vaporizer? Or could lack of water in the AMS mass spectra be related to poor collection efficiency of RBC particles on the AMS vaporizer discussed above?

We added “during the flaming phase”, to correct the oversight of missing the combust-
C5726

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tion phase. We inserted information on moisture content to this section: *[the logs] had a moisture content of 12–20% according to Swiss testing standards.*

We believe that this water simply does not vaporize rapidly enough to be detected by the AMS. In this context, the open/closed (sample/background) cycle of the AMS is crucial. This cycle was performed every five seconds during these measurements, so if the particle-bound water evaporated much more slowly than this in the AMS, a signal close to zero. AMS water signals are notoriously difficult to explain, and cannot normally be used to estimate sample RH or PM water content. Slow evaporation may be one reason for this (pyrolysis may be another). We do not believe the issue can be blamed on the collection efficiency of rBC particles on the AMS vaporizer – then the AMS would not be able to measure OM in flame-produced soot (e.g. Slowik et al., 2007). We had avoided including these thoughts in the manuscript as they are somewhat speculative.

[Figure 5, Panels b & c: Are the green traces based on the SP-AMS or AMS data?](#)

SP-AMS, legend updated, thank you.

Technical corrections: Pg. 9576, line 12: There is an extra 'as'. Pg. 9578, line 22: Change "Wood logs was" to "Wood logs were". Pg 9583, line 10: Did the authors intend to cite the following Jimenez et al. (2003) article instead?: "Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer", JGR, 108, DOI: 10.1029/2001JD001213. Pg. 9594, line 19: There is an extra 'p' in 'inappropriate'. Pg. 9601, line 26: Should be 'except' rather than 'exception'.

All done. Thank you for the extra effort, and for noticing that mis-citation!

C5727

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