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

Anonymous Referee #1

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General Comments: Corbin et al. describe the SP-AMS characterization of refractory black carbon (rBC) derived from burning beech wood. A mini smog chamber was used to assess the rBC composition following aging. The authors found that CO+ and CO2+ groups were associated with rBC and infer (by comparison to AMS measurements) that these signals represent oxygenated BC surface groups. They also observed that CO+ and CO2+ increased following ~10 days of equivalent atmospheric aging. The paper is generally well written and will be of interest to the scientific community. However, additional consideration of potential artifacts is needed, as described below, prior to publication in Atmospheric Chemistry & Physics.

Although it is not entirely clear in the Experimental section, based on the time series in Figures 1 & 2, it seems that the "fresh" and "aged" particles were assessed during different experiments. If so, and there are no measurements of fresh and aged particles from the same smoke, then 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) rather than an increase in CO+ and CO2+ following aging? 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)?

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 C2H4O2+ signal appears to be higher than the AMS signal by a factor similar to the difference between the two instruments for CO+ and CO2+ 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 CO2+ associated with rBC, it's not clear that CO+ and CO2+ can be unequivocally assigned to refractory BC surface groups. 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.

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 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.

Specific comments:

Pg. 9583, line 15: Why does the presence of refractory CO+ species influence the relative ionization efficiency (RIE) of Cx+ 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?

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.

Pg. 9589, lines 20-23: “K+ and CO+x (= CO+ + CO+2) 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 COx+ signals were not only present in the LR-PM but also in the NR-PM.” This seems contradictory. If the COx+ 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?

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.

Section 5.6: “The particulate H2O+ signals were virtually negligible in the AMS, but extremely high in the SP-AMS: a factor of 40 higher than C3+” (Pg. 9603, lines 8-9). In which phase of burning was the H2O+ signal 40-fold higher than C3+? In Figures 3a,c and 4a,c, the H2O+ signal appears to be less than (flaming) or only slightly higher (starting) than C3+. 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?

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

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’.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 9573, 2015.