

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 #2 for his or her comments and appreciate the time and energy that must have been spent on this detailed and constructive review. Below we quote each specific criticism before responding to it. Referee comments are shown in blue while direct quotations from the manuscript are *italicized*.

The abstract really only mentions SP-AMS for a tool and assumes that the reader knows what and AMS is (more specifically the difference between “SP-AMS” and “AMS”) when it is mentioned late in the abstract. This needs to be clarified. Abstract: The authors both state that CO₁₋₂₊ ions are oxy-

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generated surface groups (L16) and hypothesize that they are (L18/19). The hypothesis should come before the categorical statement. Overall, I would find it much clearer if the authors simply used the terms “laser-on” and “laser-off” rather than “SP-AMS” and “AMS”.

Thank you. This has been clarified in the revised version. The AMS is defined immediately following the first mention of the SP-AMS, the hypothesis/categorical statement contradiction has been corrected.

We are not completely enamoured with the “SP-AMS” vs “AMS” distinction drawn in the paper but we chose to do this because “laser on” vs. “laser off” does not clarify whether the AMS vaporizer was continually-on or not. Many recent SP-AMS studies have been laser-vaporizer only. We have revised the abstract to clarify the distinction between dual-vaporizer SP-AMS and AMS, and have emphasized that the SP-AMS was in dual-vaporizer mode.

P9580: I disagree with the authors’ introduction of the term “light absorbing refractory PM” (LR-PM), or at least it’s use. LR-PM should really be the difference between the SP-AMS (laser on) measurements and the AMS (laser off) measurements, not of just species from the SP-AMS (laser on). Further, refractory materials co-emitted with rBC but that are non-absorbing may be vaporized and detected; these would not be “LR” but only “R”.

We mostly agree with everything said here, and think that part of the perceived disagreement here is due to our definition continuing in a second sentence after the first statement. The text has been revised:

In SP-AMS mode, 1064nm -Light-absorbing Refractory PM (LR-PM) is vaporized. heated to vaporization by the continuous-wave laser. Due to this heating, any internally-mixed material which is refractory below the LR-PM vaporization temperature may

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also be vaporized. In this study, the LR-PM was rBC, which vaporizes at $\sim 4000\text{K}$ (Schwarz et al., 2006; Moteki and Kondo, 2010), so that non-refractory PM (NR-PM, here mostly OM; Corbin et al., 2015a), ash, or BC surface functionalities (Corbin et al., 2015c) are vaporized when internally-mixed with rBC.

The initial statement is intended to emphasize that the SP-AMS *requires* LR-PM to detect non-LR-PM, and the second sentence is intended to say more-or-less what the Referee is saying (as we interpret it).

Regarding the detection and separation of the CO⁺ from N₂⁺, it is difficult for this reviewer to assess the authors' true ability to do this accurately given the in submission reference not available for inspection. Indeed CO⁺ is normally difficult (near impossible) to fully separate from N₂⁺, and it is especially so when the instrument is operated in "V" mode as opposed to the higher-resolution "W" mode. They note that their results were validated against literature AMS CO⁺:CO₂⁺ ratios, but it is not clear how such ratios would have been determined since the authors also state that the CO⁺ signal is usually estimated from the CO₂⁺ signal. The lack of detail here or ability to read more about the procedure used leaves me skeptical and concerned.

The cited paper is in press at AS&T and has been uploaded to ACP for the Referee's convenience. However, we have added more detail from that paper to the current manuscript:

CO⁺ signals were directly quantified in PIKA as described in detail in Corbin et al. (2015a). That is, the height of an empirically-defined pseudo-Gaussian peak was fitted simultaneously to each of CO⁺ and N₂⁺. The fitted pseudo-Gaussians were constrained in position by the m/z calibration and in width by a peak-width calibration. While these signals normally suffer from poor resolution from N₂⁺, the current mass

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spectrometer able to resolve the two peaks when CO⁺ signals were very high (Corbin et al., 2015a). As shown in Figs. 1 and 2 and as scatterplots in Corbin et al. (2015a), the CO⁺ fits resulted in reproducible CO⁺ : CO₂⁺ ratios for each experiment. In the aged experiment, this ratio was 1.22 ± 0.01 in the AMS; in the filtered-and-aged experiment (see Corbin et al., 2015a), this ratio was 0.86 ± 0.02 in the AMS. These values are consistent with literature-based expectations (Corbin et al., 2015a). The possibility that other unidentified ions remained poorly-resolved from N₂⁺ is very unlikely, as also described in that publication.

Related to the CO⁺ signal, the authors do not discuss possible gas-phase interferences from CO₂ itself that are not fully accounted for in the background (chopper on/off) subtraction. CO₂ is a byproduct of combustion and has been found to interfere with AMS ion signals when sampling combustion emissions (Collier and Zhang, 2013). Although the reference I give is for vehicle sampling, there is no reason to think that similar potential issues could arise when sampling wood combustion directly.

Thank you for noting this oversight in the manuscript, which is quite important given that the entire analysis rests on these two signals. We have added the following subsection:

Gas-phase interferences at CO₂⁺ were corrected for using filtered-aerosol measurements taken periodically throughout each experiment. This method has been detailed by Collier and Zhang (2013). The CO₂⁺ correction was smaller than that needed for atmospheric measurements, due to the factor-of-200 dilution by synthetic air, and the correction factor was dynamically scaled by continuous gas-phase carbon-dioxide measurements. The resulting correction factor was 7–15% (interquartile range, both experiments). Gas-phase interferences at CO⁺ were not corrected for. For the periods when CO⁺ signals were high enough to be quantified (see above), the CO₂⁺ correction factor was 0.6–2% (interquartile range, both experiments). These periods corresponded to MCEs > 0.97, so the CO⁺ correction factor would have been < 3.1%

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of the $CO + 2$ correction factor, which is negligible relative to the uncertainty in the $CO +$ due to the fit described above.

The authors note that a “collection efficiency” based on comparison of the SP-AMS measurements with some external measurement here does not make sense because of the variable shape and size of the particles here. This is not correct. A constant collection efficiency would not make sense, but a point-by-point comparison between measurements would (theoretically at least) allow for calculation of the time/burn-condition specific CE. I don't think this really matters to the current study, but the authors should revise their statement as it is not correct.

This seems to be a misunderstanding, as the Referee's statement “A constant [...]” is exactly what we had meant by our statement. We clarified by changing to “a single collection efficiency”, which is what was used in the cited study. Thank you for pointing this out.

Section 2.4.1: It is not clear why peak overlap uncertainty would not be important for this study. It is also not clear what the authors specifically mean when they say “high signals” are >1 kHz. Is this at a given m/z ? Total signal? How often is this the case? Can this number be related to some concentration, which would be more meaningful to the non-AMS expert?

It seems that this section could have been more clear, so we have revised it.

The fractional imprecision term discussed in 2.4.1 actually refers to *isolated* rather than overlapping peaks, peak-integration imprecision is not negligible for isolated peaks.

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We clarified that the ‘high signals’ referred to the total counts for a single peak, and changed the units to counts per second. This is often the case, for the present data set. It would often be the case when a few hundred micrograms of PM per cubic meter are measured, but since mass loadings are calculated by summing all relevant ion signals this qualitative statement cannot be meaningfully quantified. Another reason we had avoided a quantitative statement is that the crossover into the high-signal regime depends on the imprecision of the peak-width and m/z calibrations. Further discussion is given in Corbin et al. (2015) which is now cited more clearly.

Table 1 implies that the absolute signal rate of the overlapping ions is what is used to estimate the uncertainty in the target ion for $CO+$ and CHO_2+ , but the text gives something different, indicating that some uncertainty value was used. This should be clarified.

In Table 1, the Uncertainty column contains σ rather than the signal I . We are not sure why the Referee interpreted the Table as implying that the absolute signal was used to estimate uncertainties.

Regarding C_3H_3 (P9586), it is not clear how “background” spectra would help to separate C_3H_3+ and $K+$. Isn't “background” equivalent to “chopper in the way” and thus representative of gas-phase? I find this to be confusing.

Thank you for pointing this out, there was a hole in the flow of the logic. See bold text:

*The final ion in Table 1, C_3H_3 was overestimated in the presence of high SP-AMS $K+$ signals. This overestimation was made apparent by examining background mass spectra (**chopper blocking the particle beam**), in which $K+$ signals were negligible **but C_3H_3 signals remained**. These background spectra were used to estimate a C_3H_3 overestimation,*

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We also added a note explaining background, as highlighted.

P9589/L4: The authors note that “OM” levels were highest during the initially flaming stage as shown in Fig. 1 and 2. But neither figure directly shows “OM,” only marker ions, some (most) of which are actually associated with rBC and “surface” groups. Thus, it is not clear to the reader where to look in the figures to see the increase in “OM” specifically. Is this implied by the AMS (as opposed to SP-AMS) measurements? This should be clarified.

Changed to cite Figs. 3 and 4.

Fig. 3: Is unclear what the difference is between thick and thin bars.

Added *The estimated signals have been plotted with thinner bars.* to the caption, which follows “the signals HxO+ have been estimated from CO2+”.

Fig. 3/4: I suggest that combining these figures would be helpful so that they are more easily visually compared by the reader. Or perhaps including a difference spectrum.

We will ensure that these figures are combined by printing them directly adjacent one another, on the same page, in ACP. (The same for Figs. 1 and 2.) If this is not possible in ACP they will be combined as a single figure.

P9592: it is not clear from Section 2.2 why there are half as many SP-AMS data as AMS. Perhaps I am missing this, but I don't think the laser duty cycle is reported.

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To the first point, we added:

*In SP-AMS mode, the instrument was operated in two separate mass-spectral configurations, one of which extended to 1000 m/z to monitor for the fullerene-ion signals that have been previously observed (citations). No fullerenic signals were observed, so these data are not presented. **Because of the omission of this additional mode, relatively-more AMS data are presented below.***

To the second, we added:

The laser was observed (via a camera) to stabilize after roughly 5 seconds when switching on (going from AMS to SP-AMS mode) and almost instantly when switching off (vice versa). Since each chopper cycle began with a Closed measurement (no rBC), no additional wait time was specified when switching the laser on or off.

P9592: The authors state “The association of the CO+x signals with C+x in the Fresh–BC factor suggests that the two species originated from the same physical source.” This could be made clearer if the authors were to include the CO+x time-series on the PMF figure (Fig. 5). Additionally, this doesn't fully make clear that there are CO+ and CO2+ signals in the two other PMF factors, i.e. these ions are not exclusively associated with Cx+. This could be clarified, as I think that the point the authors are aiming to make is that there is CO+x signal in the Fresh-BC PMF factor, not that they are only found with this factor.

We appreciate the first suggestion, but we instead added “See also Fig. 1” where all the information is shown (the PMF figure is already quite complex).

We changed the text to *the observation of both COx+ and Cx+ in the Fresh–BC factor [...]* to clarify, thank you.

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P9594/L11: The authors should again be careful to clarify when they are talking about ions associated with specific PMF factors vs. ions in general. The statement “No analogous AMS factor was observed, indicating that the CO+x source remained refractory.” Could be misinterpreted to imply that there is no CO+x contribution to the AMS measurement at all, which is not true. The authors mean (I think) that the BC-associated CO+x or the COx+ in the Aged-BC factor remained refractory, not all CO+x. This could be clearer both here, and in general.

Thank you, changed to:

The absence of an analogous AMS factor suggested that the source of this BC-associated CO_x⁺ remained refractory.

We reviewed the text of the manuscript to check that this is clear in general.

P9594: I find the discussion associated with the OOM-Flame factor to be somewhat confusing in the context of the POM-Flame factor. The authors noted that POM-Flame does not correlate well with the C₂H₄O₂⁺ ion (or at least not as well as C₄H₇⁺), and that the POM-Start factor does. But then here they indicate that the OOM-Flame factor correlates with C₂H₄O₂⁺. They do not discuss the reasoning for this difference. They also do not discuss whether the OOM-Start factor correlates with C₂H₄O₂⁺, although show them together in Figure 5. Overall, I find that there is a bit of a disconnect between how the results are presented and discussed here for the OOM vs. POM factors.

P9595: I find the statement “A tinder factor was also observed for the first two time points of the fresh-emissions experiment, but these two mass spectra were simply downweighted threefold (Supplement) since this factor

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represented a contaminant.” To be confusing. I don’t see why the authors would consider this a contaminant in one experiment (fresh) but not in the other (aged). This is ultimately inconsequential to the main conclusions of this paper, but I find it nonetheless a point of confusion.

We rephrased to clarify:

Note that tinder was also used at the beginning of the fresh-emissions experiment, and an analogous PMF factor did initially result for that experiment. However, only the first two measurements of the fresh-emissions experiment were strongly impacted by this contaminant. To simplify the PMF model needed to describe the data, the first two measurements of that experiment were downweighted threefold (see Supplement) for the fresh emissions.

Section 5.1: The authors begin by discussing the CO⁺ and CO₂⁺ ions in the context of Figs. 3 and 4, which are the total spectra. However, I would think that this particular discussion should be more restricted to the discussion of the PMF spectra for the BC factors as these actually indicate the refractory CO⁺ and CO₂⁺ materials. If I look at Figs. 5 and 6 instead of Figs. 3 and 4, it is evident that the CO₂⁺ normalized peak intensity increases (i.e. the C₃⁺/CO₂⁺ ratio decreases) upon oxidative ageing. But it is also clear that the C₃⁺/CO⁺ ratio barely changes. Thus, the statement that “These rCO_x⁺ signals become more intense after oxidative ageing” may be too general as really only one of the ions seems to become substantially more intense.

We changed the reference from “Figs 3 and 4” to “Figs 3c–d and 4c–d”. We wished here to highlight that our conclusions in Section 5.1 can be made without the complex statistical analysis involved in the PMF analysis. Although PMF is a sound technique when applied soundly, which we believe we have done, we want to point out here that the complexities of PMF are not required for this specific discussion.

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P9596/L4: The authors state “Finally, the majority of the refractory oxygenated species must be on the soot surface and not incorporated into the soot core because the rCO+x signals changed after oxidation.” It is not clear to me that this necessarily indicates that the majority of the signal comes from the surface, only that there were a sufficient abundance of surface species that could be oxygenated such that a change was observed in the mass spectrum.

We concur and have simply removed the statement because the following description of the soot formation process is the real point we wished to make here.

P9598/L12: I find that the statement “Given that most BC is emitted when little organics are emitted, and that BC was overall the major species emitted by this fire (Corbin et al., 2015a), the BC surface may represent the dominant reactive sink for atmospheric oxidants,” stretches the conclusions too far. The last part of the sentence is much too broad and general. If all biomass fires were exactly like the ones studied here then this would be true. But this is not the case globally. Further, oxidants can react with many gas-phase species, which are then a “sink”. This would need to be put in a fuller context to be justified. In fact, the authors essentially make this point at the bottom of this page (L26) when they note that their results are specific to this study. The generality of this statement should be changed.

Yes, this was indeed much too general and an error on our part. We were imagining local chemistry within a plume of similar composition to this one, and changed “reactive sink for atmospheric oxidants” to “oxidant sink during the initial aging of a similar combustion plume”:

*Given that most BC is emitted when little organics are emitted, and that BC was overall the major species emitted by this fire, the BC surface may represent **a significant***
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oxidant sink during the initial aging of a similar combustion plume. *The actual significance of the BC in this case would depend on the degree of mixing between starting and flaming phases after emission, and on the fate of co-emitted nitrogen and sulfur oxides.*

P9601/L20: The authors state “This thermal-stability argument does not explain the relatively poor correlation of the OM time series in Fig. 5b–c.” I think that the authors more specifically mean “absolute signal levels do not agree.” The correlation doesn’t actually seem that bad (i.e. a scatter plot might give a relatively straight line).

True, changed “relatively poor correlation” to “higher SP-AMS signals”. This also clarified the rest of the argument, we believe (see below).

P9602: I do not understand the arguments regarding “brown carbon.” The authors have already argued that external mixing is negligible. Thus, any “brown carbon” would be internally mixed with rBC and thus the absorption by rBC would still lead to vaporization of the “brown carbon” components after oxidative ageing even if the brown carbon became less absorbing.

We had meant “internal mixing of secondary OM from the primary POM+rBC particles” and have now clarified this.

The most important observation here, which we have sought to clarify, is that there were periods (e.g. second fresh burn at 1 hour in) where the SP-AMS signals were higher even in the absence of rBC signals. Also, the SP-AMS POM–Flame does not spike simultaneously with the SP-AMS rBC signals (in the third burn). So the internal mixing of OM with rBC is insufficient to explain the observations. We realize that our evidence here is not extremely strong, but we believe it is strong enough to motivate

further study on this topic, especially since the trends we have observed are opposite to those of previous SP-AMS—AMS intercomparisons.

We revised the text in this section to better present the arguments:

The higher SP-AMS signals in relatively poor correlation of the OM time series in Fig. 5b–c might be hypothesized to reflect a difference in the SP-AMS sensitivity to OM when it is internally-mixed with BC, due to a change in either vaporization temperature or physical position of the vaporized particle (Section 2.3.4 Willis et al. 2014). However, this difference was observed even in the absence of rBC, as shown by the second fresh-emissions burn. In addition, the difference between SP-AMS and AMS was smaller for the aged-emissions experiment (Fig. 6b–c) than the fresh-emissions experiment (Fig. 5b–c). The apparent influence of aging is unlikely to be related to a change in mixing state: both aerodynamic-and mobility-size distributions were unimodal. Nor does a difference in particle size explain the difference, as aging would have increased the size of the particles and therefore focussed a larger fraction of them into the SP-AMS laser. The difference between fresh and aged samples may therefore reflect an influence of the chemical composition of the OM.

P9603: The authors state “The particulate H₂O⁺ signals were virtually negligible in the AMS, but extremely high in the SP-AMS: a factor of 40 higher than C₃+. When I look at Fig. 3 I do not see where the conclusion comes from that the H₂O⁺ signals are 40x greater than C₃+. I think that for this section (5.6) to be more understandable to the reader, more details regarding exactly how the H₂O⁺ signals were determined is needed, and the authors need to show the actual size distributions used to “separate these background signals [of water] from particulate signals.”

A figure explaining this has been added to the SI and cited in the text.

The H₂O⁺ signals in Fig. 3 and 4 were estimated from CO₂⁺, based on typical frag-
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mentation patterns in the AMS. We realize that CO₂⁺ originating from BC is unlikely to have the same fragmentation as typical atmospheric organics (for which this estimation is more accurate) but we have no other information to go on. This caveat was already written in both legends, but bears further emphasis, which we have now added.

Minor: I find the terminology “OOM” to be a bit odd given that the authors use “POM” for nonoxidized material. Oxidation doesn’t make it not be “particulate”. Thus, it would seem that a more consistent terminology would be either “POOM” or “OPOM”. The title of the paper uses “aerosols” but the authors use “particulate matter” (or POM) throughout. These should be made consistent. Figures should be referred to in order (see p 9578).

We defined organic PM as “OM” and then primary OM as “POM” and oxidized as “OOM”, without intending to imply that it wasn’t particulate. There is an unfortunate lack of unambiguous names in this situation, though we wanted to avoid referring to the particles as “aerosols”. We realize the title seems inconsistent with the text, but as we consider aerosols to be mixtures of particles and gases, and did oxidize soot-containing aerosols, we have kept it.

References

Corbin, J. C., Othman, A., Haskins, J. D., Mensah, A. A., Sierau, B., and Lohmann, U.: Peak fitting and integration uncertainties of the Aerodyne Aerosol Mass Spectrometer, *Atmos. Meas. Tech. Discuss.*, 8, 3471–3523, 2015.

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