Atmos. Chem. Phys. Discuss., 15, C3051–C3057, 2015
www.atmos-chem-phys-discuss.net/15/C3051/2015/

Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #2

Received and published: 28 May 2015

Review of "Black carbon surface oxidation and organic composition of beech wood soot aerosols" by Corbin et al.

The authors report measurements of particle composition and mass spectra of fresh and photochemically aged soot particles that were produced from carefully controlled combustion of beech wood in a stove. The measurements were made using a soot particle aerosol mass spectrometer with a laser vaporizer and conventional vaporizer, and toggle the laser on and off to allow for measurement of refractory components + non-refractory components (laser on) or only non-refractory components (laser off). They find that there are is a substantial contribution from oxygenated ions (specifically CO+ and CO2+) to the mass spectrum, in addition to Cx+ ions. The conclude that

these COx+ ions are likely refractory in nature and associated with the Cx+ ions. That there may be a substantial contribution of refractory COx+ ions for beech wood soot has implications for the interpretation of ambient measurements of refractory particulate matter using this technique. They find that oxidation leads to some increase in the relative amount of these refractory oxygen containing ions, especially the CO2+ ion. This implies that the surface of the soot is reacting and becoming increasingly oxygenated.

Overall, this is an interesting study that draws conclusions that will be broadly useful to the atmospheric community and beyond. I believe the work is scientifically sound, although I do have some concerns regarding how variations in gas-phase CO2 were accounted for in the data processing that can likely be addressed with further information. Additionally, I find that there are a number of points that could be better clarified prior to publication. My specific comments are below.

Comments:

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 oxygenated 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".

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”.

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.

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.

The authors note that a “collection efficiency” based on comparison of the SP-AMS measurements with some external measurement here does not make since because of the variable shape and size of the particles here. This is not correct. A constant collection efficiency would not make since, 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.

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?

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 CHO2+, but the text gives something different, indicating that some uncertainty value was used. This should be clarified.

Regarding C3H3 (P9586), it is not clear how “background” spectra would help to separate C3H3+ and K+. Isn’t “background” equivalent to “chopper in the way” and thus representative of gas-phase? I find this to be confusing.

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.

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

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.

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.

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 COx+ 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 COx+ signal in the Fresh-BC PMF factor, not that they are only found with this factor.

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.

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 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.

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 rCOx+ signals become more intense after oxidative ageing” may be too general as really only one of the ions seems to become substantially more intense.

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.

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.

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).

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.

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 C+3. 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.”

Minor:

I find the terminology “OOM” to be a bit odd given that the authors use “POM” for non-oxidized 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).

Collier, S. and Zhang, Q.: Gas-Phase CO2 Subtraction for Improved Measurements of the Organic Aerosol Mass Concentration and Oxidation Degree by an Aerosol Mass Spectrometer, Environmental Science & Technology, 47, 14324-14331, 2013, doi:10.1021/es404024h.

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