Atmospheric
Chemistry
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Discussions

Interactive comment on "Atmospheric Evolution of Molecular Weight Separated Brown Carbon from Biomass Burning" *by* Jenny P. S. Wong et al.

Anonymous Referee #2

Received and published: 8 November 2018

The authors present results from lab and field observations of absorption by brown carbon, generated from pyrolysis (lab) or from ambient fires (field). The lab experiments are well-done, although limited in scope given the focus on one source type (wood pyrolysis) that the authors have previously studied using similar methods (Wong et al., 2017, ES&T). Nonetheless, I believe the lab results are sufficiently novel and publishable after the authors address the reviewer comments. Regarding the field observations, I am much more skeptical of the results as they are currently presented and suggest they are removed unless further justification can be provided to provide a preponderance of evidence that they are correct for the reasons put forward.

In the intro (P2/L30 or so), the authors might consider also mentioning results from one of their earlier studies, Zhang et al. (2017, Nat. Geosci.).

P3/L15: It is not clear to me that the Zhou study observed "negligible concentrations of levoglucosan" in aged BBOA. They saw a small f60 in their AMS mass spectrum for the BBOA-3 factor. F60 is not the same as levoglucosan. It is also not completely clear, to me at least, that the Zhou BBOA-3 factor doesn't include secondary formation, given the extremely large O:C. The same comment applies to the Bougiatioti et al. study. Their BBOA factor is transformed over time to an "OOA" factor, but it is also not clear whether this completely excludes the influence of secondary formation: factors cannot tell one directly about the processes that led to their occurrence. The use of f60 is problematic simply because it can vary as a result of dilution by secondary material in addition to heterogeneous oxidation.

In describing their "biomass burning" in the abstract and introduction (P3, L18) I suggest that the authors identify this as "biomass burning particles produced from pyrolysis." It is, in my view, critical that the source of the BB particles be clearly identified for lab studies so that the reader, in the abstract, can begin to think about how this study compares to others. This is also important because the authors produce their BB particles under oxygen free conditions. It is not clear to me the extent to which this leads to the production of particles that are broadly representative of particles produced from open combustion, which includes oxygen. I suggest that the authors also comment on how representative they believe the particles produced from pyrolysis under oxygen-free conditions to be.

P4/L10: The authors note that most absorption comes from WSOC (77%). However, given that they find differnces in behavior between different WSOC fractions, the potential for the non-WSOC to behave differently than the WSOC seems large. Can the authors comment on this?

Figure S1: I think this would be better if the y-axis were a log scale, allowing the reader to compare at lower wavelengths better.

P8/L4: It would be helpful to the reader if the authors were to cmoment here on the

extent of the losses. While some loss is evident, it is also clear that over the first 20 h period the extent of loss is quite small (5%?). Also, the vials used for the experiments were sealed with Teflon-lined caps. Given this, where do the authors suspect the losses occurred? Did highly volatile vapors leave escape through the caps?

P8/L13: The authors state: "Given that a loss in WSOC was observed during this photoenhancement period, the increased MAC values may be driven by a loss in non-absorbing WSOC and/or the formation of more absorbing WS BrC." I find this argument to be relatively weak because the extent of increase (factors of 2) is substantially larger than the loss in WSOC mass ($\sim$5%).

P8/L14: The authors indicate that the MAC increase with H2O2 was simllar to that from UVB only. I agree that they are "similar" but it does seem that the changes in the H2O2 experiment was systematically larger. This is also connected with their observation of a steeper slope for H2O2 once things start to decline.

Abstract/L23: I suggest being more specific than "a few" hours. I would take this to mean around 3 h. Someone else might have a different number in mind. I suggest the authors just say over $\sim$10 h (or whatever the right values are to insert). A numerical scale is given for the decay, so should be given for the rise as well. Also, the "rapid photobleaching" of the low-MW stuff doesn't seem to really capture the overall behavior, which has multiple components, including a slower component. I suggest that this is revised to more fully capture the behavior shown in Fig. 4

Data fitting: The authors extracted photoenhancement and photobleaching rate coefficients by fitting over different time periods. If the model proposed were robust, the authors should be able to describe the entire curve by fitting to both simultaneously. By fitting to separate regions, there is a strong assumption that there is no overlap in terms of the processes. Yet, they must overlap to obtain the flat-top region. I suggest it would be better if the authors were to perform a comprehensive fit across the entire data set to extract their parameters, showing the results of the fitting on the associated graphs.

This would help demonstrate the robustness of the model being used. Additionally, if the authors were to fit the observations using a more complete model they would not have to take a difference between the kUVB and kH2O2 to determine the OH-specific value. It would come naturally from fitting to the separate experiments. (Also, there appears to be a typo in Eqn. 2).

P10/L5: Given the many commas in this sentence, I find it somewhat difficult to follow.

P10/L29: It is not clear how this indicates that changes occurred "only up to 500 nm". More convincing would be an actual plot of the MAC at 500 nm, showing that there is no photoenhancement. But the use of the AAE difference seems to me a more indirect way of getting at this when a direct method is available.

Figures: On many, it would be helpful to the reader if tickmarks on the right sides were added.

P10/L27: The "slight decrease" in the high-MW AAE is not abundantly clear to me, especially for the OH experiment. There's a quick drop but then an increase and at 10 h the AAE seems even higher than at the start. Also, are the error bars alluded to in the caption of Fig. 5 smaller than the data points? The somewhat random behavior of the low-MW data suggests that error bars are lacking.

P11/L8: it is not clear to me how the authors are concluding that OH is the dominant loss mechanism. Fig. 4 shows that the low-MW stuff decays both from the UVB experient and the OH experiment to similar extents.

Field observations: I do not find the results presented especially compelling. There are two individual points for the WSOC MAC showing the increase. The data points around these two do not show evidence of any continuous evolution over time. Instead, there is a step function. And this step function is not seen with the MeOH MAC values. (Also, the increase in the MeOH absorption the authors mention at 10 h is not apparent to me. It seems to be flat within the data variability.) What can I take the uncertainty

as on these measurements? What should I make of the WSOC being substantially higher than the OC at the 33 h point in terms of uncertainty? What steps have the authors taken to convince themselves that this is not some artifact? Also, samples were collected for 22-24 h. Given this, what does it even mean to have an aging time of only 5 or 10 h? And were these daytime hours, given that there was sampling during day and night? If half the transport occurred at night, should the aging times be divided in two? Did the backtrajectories indicate that the air reaching the sampling site had been at the surface where the fire was in all cases? HYSPLIT gives altitude as well as location. Also, were these two samples for the same fires as at shorter or longer times? What if the nature of the fire and combustion conditions differed? Saleh et al. (2014, Nat. Geosci.) showed that the MAC (or the equivalent imaginary component) for the BrC varies with the combustion conditions. How can the authors rule out changes in conditions? I need to be further convinced about this analysis overall. Currently, I do not think it is sufficiently supported to be included in the manuscript.

P12/L18: I have a hard time believing that the AAE values are inversely proportional to the BC-to-OA based on the data presented. In my view, the observations show zero relationship, and the range of BC/OA is too small to show a relationship anyway. And, the authors are not accounting for the potential for secondary formation in the atmosphere, w hich would skew the relationship. I think this discussion should be struck as Fig. S7 does not show what the authors purport. I would need to be convinced with an R^2 at minimum.

The authors might consider commenting on the typical amount of time that BrC spends in a cloud droplet, since their results are most relevant to material in cloud droplets.

Levoglucosan: To what extent is it known whether the amount of levoglucosan produced relative to all other OA (or to BrC specifically) is a constant across varying burn conditions? This seems important to me to consider to understand the different relationships. The "total" hydrous sugars, I would speculate, is more likely to be consistent between burns than is a single sugar. As is something like K+, which would be relatively

independent of burn conditions (although would be fuel dependent). Nonetheless, the authors do convincingly show that the total sugars is more robust than levoglucosan alone.

It might be useful to know which two data points in Fig. 7 correspond to the two elevated MAC points in Fig. 6. It is not apparent than both of the elevated points are included in Fig. 7, because there should be two points with absorption > 2e-6 (from Fig. 6) but there is only one. The point that must be one of these is clearly one for which the relationship with levoglucosan is completely different than for any other points. Also for K+. This could indicate that the combustion conditions were, indeed, different for these high MAC points and thus that the elevated MAC was driven by differences in burn conditions and not aging.

There is no indication of where the data are archived, which I believe is now required by ACP.