**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Light absorption by organic carbon from wood combustion" *by* Y. Chen and T. C. Bond

Anonymous Referee #1

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This is an interesting paper that takes a new look at absorption by OC produced from pyrolysis of various wood types at various temperatures. The authors have determined that the OC that is extractable into methanol is more strongly absorbing than that extractable into either water or hexane, per gram of extracted material. This suggests that there are some very strongly absorbing compounds produced during pyrolysis that are neither polar enough to dissolve into water nor non-polar enough to go into hexane. Angstrom exponents of absorption for the extractable material are very large (> 5). The authors attempt to place their experimental results into the context of the influence of absorption by OC on climate. They conclude that, overall, absorption by OC may be unimportant as it only changes radiative forcing by a few percent. In light of their actual reported numbers, I believe this final conclusion may need to be revisited (discussed more below) and it shouldn't be forgotten that absorption by particles in the UV can

have a strong influence on tropospheric photochemistry. Overall, I find that this paper should be publishable after consideration of the below specific comments.

P. 20472, Line 12: Please be more specific in what is meant by "a larger portion". Larger portion of what? Absorption?

P. 20472, Line 17: This factor of four increase should be put in the context of the actual temperatures used. It lacks precise meaning when reported alone. In other words, if the factor of 4 increase were for a change in wood temperature of 5 degrees this would be huge, but if it's from a change of 500 degrees then it's smaller.

P. 20473, Line 13: More specifically, BC is the strongest absorber per mass in the visible wavelengths. Recent work (c.f. Barnard et al.) suggest that in the UV OC might be just as important as BC.

P. 20474, Line 29: This is an unnecessary statement and overlooks the point that it might not actually be useful to measure the properties of OC from every wood type since no realistic model would incorporate this level of detail. The following statement (starting on p. 20475) is more to the point.

Line 20475, Line 12: This is true, but it seems to neglect the fact that newer, non filter based methods for measurements of aerosol absorption have recently become quite prevalent (e.g. Arnott et al., Lack et al.) This statement appears to discredit real-time measurements to an unfair extent.

Section 2.1: The authors need to address the question of to what extent does their experimental methodology actually mimic a "real" burn where, e.g., oxygen will be present. Since the authors are extracting the organic components anyway, is there any benefit to prohibiting black carbon formation?

Section 2.1: The authors should discuss to what extent a dilution factor of 4-to-1 mimics what would be typical of a real biomass burn. Have the authors considered to what extent particle loading might play a role here? If the loading is particularly high, then

compounds that would not normally (normally being the atmosphere) end up in the particle phase to any significant extent will be in the particle phase (c.f. Robinson et al, Science). Can the authors estimate particle mass loadings? They should be able to from their OC filter measurements and the known flowrates. Have they run their experiments at different dilution ratios?

P. 20476, Line 20: The authors might consider addressing here (or in the introduction) why they hypothesize that wood "size" will matter? What is the underlying physical principle involved here?

P. 20478, Line 16: How was the detection limit determined? If this is truly a detection limit, then the measured absorbances below this value should not be included in any further analysis and (perhaps) not included in the figures. Or perhaps the authors could indicate the below detection limit range in the figures by using dashed lines when A < 0.05 and solid lines above in addition to the circle markers. This would make clearer that this data is not used in any analysis, but only presented for completeness.

P. 20479, top: It is unnecessary to mention the real time measurements as they are not discussed at all in this paper.

P. 20479, Line 7: Units for the alpha/rho values should be given here.

P. 20479, Line 22: Can the authors comment more specifically on how the absorption per mass and mass-normalized absorption cross section do differ? It is not overly clear.

P. 20482, Line 20: Are these units correct? Should they be ug/m^2? If they are correct, how is the concentration on the filter determined? More specifically, how is the volume determined?

P. 20482, Paragraph at Line 19: It is not entirely clear what is being done here. Is this suggesting that the actual loading after dilution was 10 ug/m^3 or is this referring to some theoretical "ambient" conditions? I find this section to be extremely confusing. It was stated in the methods that the purpose of the dilution (besides dilution) was to

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cool the samples to room temperature. Therefore the temperature on the filter should not have been 443 K, but actually closer to 298 K. And at such apparently very large loadings (~10^6 ug/m^3) it is hard to imagine that the distributions at 443 K compare well to low concentration distributions at 298 K in terms of the expected composition. This seems just too good to be true. The authors should provide a figure which shows the calculated particle phase composition for the two conditions. As it stands, I have a difficult time believing this result.

P. 20484, Line 24: Why were these functions chosen? Why not extrapolate using either the Angstrom exponent model or the above advocated band-gap and Urbach model? The use of an exponential and linear function seems quite arbitrary and unjustified.

P. 20486, Line 12: It would be useful if the authors were more quantitative here. What is "much less"? From the figure, it appears that water soluble OC is ~50% as absorbing (per mass) as total OC. Is this generally true?

P. 20486, Line 16: I find this result to be a bit surprising and would encourage the authors to expand. Presumably, water extracts only the polar components and hexane the non-polar. Methanol will extract both. Clearly, methanol is extracting something that neither water nor hexane is extracting and this material must be very strongly absorbing. If it were not, the absorption (by mass) from the methanol extracts would end up very similar to an average between the water and hexane extracts. The authors address this to some extent by conducting their sequential extraction tests, but my question is why does this strongly absorbing material not come out in the hexane extracts? Did the authors test to see whether the residual after water extraction was soluble in hexane in addition to methanol? Since the extracted fraction from water and hexane add up to over 100%, these to solvents taken together presumably capture all of the OC (figure 3). Or do the authors believe that there are some components that are only soluble in methanol (not in either water or hexane).

P. 20488, Line 5: This is for some particular wavelength, correct? Or is it averaged over

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the entire measurement range?

P. 20489, Line 15: The Bergstrom et al. reference seems out of place here.

Section 3.5: It should be restated here that the upper wavelength cutoff for each sample was different and depended on the instrument detection limit and the lower wavelength limit depended on the condition that A < 1. The authors should consider explicitly how variability in the wavelength cutoffs between samples influences their results. This is done to some extent by only considering the Angstrom exponent when the upper (or lower) limit is restricted to 400 nm, but this does not address simultaneous variability in the low (high) wavelength cutoff due to the experimental constraints. This should be addressed, perhaps by fixing a range (say 380-450 nm) over which all samples can be considered in a consistent context. Additionally, it is not clear how it can be inferred that higher angstrom exponents should be associated with less strongly absorbing components from the temperature dependent data. This connection could be made more explicit. (I realize that the data show this to be the case, but the connection with the temperature results is not clear).

P. 20490, Line 14: This sentence is redundant with the previous sentence.

P. 20490, Line 22: This makes it sound as if I should expect to see ranges labeled as "Sun et al." in Figure 9, yet no such ranges are given.

P. 20491, 1st paragraph: This is an interesting suggestion and addresses one of my previous comments. Can the authors provide support from the literature that the addition of even a few polar functional groups will decrease the solubility of compounds with conjugated aromatic rings to such an extent that they will not be soluble in hexane?

Section 4.2: I'll reiterate that the way in which the SVOC contribution was deduced did not come across clearly at all in 2.5.2. For example, it certainly was not clear that the estimates came from heating filters in the OC/EC analyzer at 170 deg C. Nonetheless, this is an interesting attempt to account for the contribution of "SVOC" molecules that

might not normally have been in the particle phase under ambient conditions. Although I cannot think of a 'better' way to do this, I nonetheless have some concerns over the method used. First, the authors seem to consider the SVOC/NVOC balance from the perspective of the particle loading on the filter at the end of the sampling time. It is not entirely clear that this is the most important factor. The initial gas-particle partitioning of the suspended aerosol will (presumably) depend on the loading in the suspended state. As particles are pulled through the filter and trapped there, the local concentration goes up. This will have no influence on the partitioning of particles as they are emitted from the aerosol source and make their way to the filter. The question is, then, to what extent does the local loading on the filter govern the nature of the collected material vs. the ambient loading? Should the particles on the filter be considered in equilibrium with the surrounding gas phase at the end of the experiment?

During the SVOC desorption step, the filters are heated in an OC/EC oven where clean gas is constantly passed over the filter and the gas-phase is swept away. As such, the particles on the filter are not really brought to an equilibrium state at 170 deg C, but to some other kinetically limited condition. Had the samples been held at 170 deg C for a longer time, it could reasonably be expected that more material would have evaporated, thus making the SVOC/NVOC balance appear different than was reported.

Certainly, none of these concerns will dramatically alter the authors' conclusion that apparently the less volatile material in these samples is more absorbing than the more volatile material. However, I believe that to place this discussion firmly in the context of the language of SVOC/NVOC, as the authors do, is a bit of a stretch.

Figure 3: It would be useful if the authors restated what is specifically meant by "Extracted fraction of OC". Also, since it might be nice to see this figure in color.

Figure 5b: Why is there no "water + methanol after water" curve since there is such a curve in Figure 5a?

Figure 9: I would recommend differentiating this work from previous work by using

dashed lines for one or the other in addition to the color differences. Also, perhaps consider adding Kirchstetter results to this figure.

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