

We thank the reviewer #1 for instructive comments to help us improve the manuscript. Below are our responses (in normal fonts) to reviewer comments (in bold and italic) including descriptions how we have modified the manuscript.

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

We changed the sentence to "a larger portion of the absorption came from"

- 2. 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.**

We changed the sentence to "Higher wood temperature is the main factor creating organic aerosol with higher absorption; changing wood temperature from a devolatilizing state of 210 C to a near-flaming state of 360 C causes about a factor of four increase in mass-normalized absorption at visible wavelengths."

- 3. 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.**

When we consider the whole solar spectrum, where visible light contributes most of the solar energy, BC is still the strongest absorber.

We changed the sentence to "BC is known to be the most absorbing aerosol in the visible wavelengths in the atmosphere, the optical properties....."

- 4. 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.**

We agree with the reviewer, and added the following sentence (a point which we have made previously). "Furthermore, even if such an array of measurements was feasible, the detail could not be applied in an emission model."

- 5. 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.**

We removed the discussion of disadvantages of filter-based measurement (from “many previous measurements of light absorption ...” to “...with increasing filter loading...”. The reason why we measure absorption of liquid extracts is that we want refractive index as input for the Mie model. We kept the writing of “We employed UV-vis spectrophotometry to measure the light absorption of liquid extracts of aerosol samples...”

6. 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?

We observed that some BC was also extracted by methanol and acetone in the samples taken from combustion when oxygen was present, which may affect the subsequent absorption analysis. We prohibited the formation of BC to avoid this interference.

We added the following paragraph in P. 20475 Line 8 to address the reviewer's first question: “Wood combustion comprises at least two distinct processes that affect the properties of the resulting aerosol: release of volatile material from the solid, and its condensation or combustion in the atmosphere. Our combustor simulates the release of volatile matter at realistic wood temperatures; there is no oxygen either inside the wood or in the diffusion flame. In a real burn, after this material leaves the solid wood, it may either condense to form “organic carbon” or burn in a diffusion flame to produce black carbon. Our goal in this experiment is to understand the nature of the devolatilizing material generated by wood pyrolysis. This material is, emitted directly.”

7. 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 flow rates. Have they run their experiments at different dilution ratios?

We agree that the particle loading does affect the partitioning of OC in the gaseous and particulate phase. The analysis of semi-volatile OC in Sect. 2.5.2 and Sect. 4.2 was aiming to solve the problem proposed here and to provide OC properties in the ambient atmosphere.

The particle mass loading on the filter is typically 2.5mg per filter. The particle mass loading during the sampling (mass concentration) is typically 10 μ g/L, which is different from what we mentioned for the concentration of fresh OC on the filter in Sect. 2.5.2.

We added the following paragraph in the paper (P. 20476, Line 17): “A change of dilution ratio from 4:1 to 40:1 did not change the measured absorption per mass (i.e., the difference was within experimental uncertainty). Other effects of gas-particle partitioning are discussed in Sect. 2.5.2.”

8. 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?*

We added the following statement in P. 20475 Line 11: “Preliminary experiments had indicated that wood size affected emission rates and particle properties. Heat transfer into the wood is most rapid into the shortest dimension, but mass transfer of the volatile material out of the wood occurs along the wood grain—the longer dimension—until cracks form in the wood. Thus, volatile material can be held at a high temperature for a long time. This situation is similar to observations of wood used for cooking (Roden et al., 2006), where white smoke escaped mainly from the end of the fuel.”

9. 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.*

The detection limit is provided by the manual of the instrument and is confirmed by the dilution experiment to test the validity of Beer-Lambert Law. It is a good idea to use dashed line when $A < 0.05$. The figures are revised accordingly (Fig. 4, Fig. 5(b), Fig. 6, Fig. 7(a), Fig. 7(b)).

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

We deleted this paragraph.

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

We changed the sentence to “The main values reported in this paper are absorption cross-section divided by organic carbon density α/ρ (in the unit of cm^2/g), where α is ...”.

In Line 21, we deleted “which has unit of cm^2/g ”

12. 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.*

Line 15, after “easy to translate to radiative-transfer models”, we added “The absorption cross-section per mass for particulate matter must be determined using Mie theory combined with a refractive index.”

13. P. 20482, Line 20: Are these units correct? Should they be $\mu\text{g}/\text{m}^2$? If they are correct, how is the concentration on the filter determined? More specifically, how is the volume determined?

Yes, the unit is correct. To determine the volume, the thickness of the sample on the filter was assumed 1mm. Based on an averaged OC loading around $200\mu\text{g}/\text{cm}^2$ on the quartz filter, with a thickness of 1mm and OM/OC ratio of 1.3, we roughly estimate the concentration of fresh organic carbon on the filter as $2.6 \times 10^6 \mu\text{g}/\text{m}^3$.

14. 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 $10 \mu\text{g}/\text{m}^3$ 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 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 ($\sim 10^6 \mu\text{g}/\text{m}^3$) 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.

Under ambient conditions, the total OC concentration is around $10\mu\text{g}/\text{cm}^3$.

We removed the part from line 19 till the end of this section, and added the following paragraphs instead. We also added figures (which will be Fig. 3 in this paper) showing the calculated OC partitioning at three conditions ($2.6 \times 10^6 \mu\text{g}/\text{m}^3$, 298K, $10\mu\text{g}/\text{m}^3$, 298K, $10^6 \mu\text{g}/\text{m}^3$, 443K) to support our discussion.

Based on an averaged OC loading around $200\mu\text{g}/\text{cm}^2$ on the quartz filter, with a thickness of 1mm and OM/OC ratio of 1.3, we roughly estimate the concentration of fresh organic carbon on the filter as $2.6 \times 10^6 \mu\text{g}/\text{m}^3$. The theoretical partitioning of OC to the gas phase and particle phase under these conditions is shown in Figure 3 (a).

If the material were diluted to achieve ambient conditions, with a total OC concentration around $10\mu\text{g}/\text{m}^3$, the partitioning of SVOCs in the two phases would be that in Figure 3 (b).

As compounds are warmed, the equilibrium shifts. The saturation concentration for each log-spaced bin at an elevated temperature T_2 can be related to that at 300K (sampling conditions) based on the Clausius-Clapeyron Equation.

$$C_i^*(T_2) = C_i^*(300K) \cdot \exp\left[\frac{\Delta H_v}{R} \left(\frac{1}{300K} - \frac{1}{T_2}\right)\right] \quad (5)$$

According to Donahue et al (2006), we assume an ΔH_v for the compounds with saturation concentration of $1\mu\text{g}/\text{m}^3$ as 100 kJ/mole, the factor of 10 spacing in saturation concentration corresponds to a succession of enthalpies (ΔH_{vap}) separated by 5.8 kJ/mole.

Figure 3 (c) shows the equilibrium partitioning of OC on the filter at filter concentration and 443K. In order to compare with the original ambient temperature, the x-axis is still the C^* at 300K, not at 443K. The partitioning distribution under 443K at filter concentration is comparable with that under ambient conditions and low concentrations.

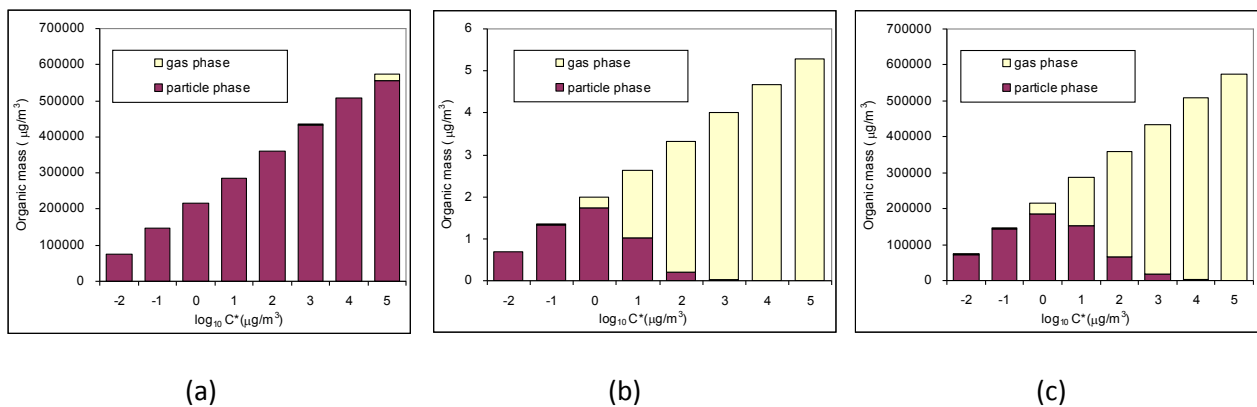


Figure 3. SVOC partitioning. (a) Partitioning of original SVOC from wood combustion after 4:1 dilution ($2.6 \cdot 10^6 \mu\text{g}/\text{m}^3$, 298K); (b) Partitioning of SVOC with the same volatility profile under ambient conditions ($10 \mu\text{g}/\text{m}^3$, 298K); (c) Partitioning of SVOC with the same volatility profile at 170C ($2.6 \cdot 10^6 \mu\text{g}/\text{m}^3$).

15. 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.

The exponential function was poorly stated. The Angstrom exponent model was used for ultraviolet wavelengths and we have changed the text to reflect that.

We would have used the Urbach model on the visible side except for three reasons: (1) Using that model would require presenting it, and convincing the reader of its validity, when it is not central to the discussion. (2) The data needed extrapolation only beyond

600 nm, where the absorption and the difference from the non-absorbing aerosol is very small, so the choice of extrapolation matters little. (3) The absorption values near 600 nm are very low, and the values produced are quantized (varying little compared to wavelength). This makes the curve-fit to the Urbach model rather questionable. To answer this question in other readers' minds, we added the statement: '(The linear extrapolation is not based on physical reasoning, but affects the forcing very little.)'

Change in P. 20484 Line 24: "...an exponential relationship" to "the Angstrom exponent relationship" And add the sentence above.

16. 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?

We changed the sentence to "Normalized absorption for water-soluble OC is 76% lower than that for total OC at 400nm for sample generated at 360C, although this comparison varies with wavelengths and generation conditions."

17. 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 two 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).

In P. 20491, line 5, we mention that the high absorption may come from large, polar molecules which contain conjugated aromatic rings similar to PAHs but these rings are also directly attached to polar functional groups, which make the substances insoluble in hexane.

P. 20487, line 4, we added following at the end of the paragraph: "By performing another water-hexane sequential extraction, we found that the residual after water extraction was partially soluble in hexane (60%), while the remaining 40% could be extracted only by methanol. Moreover, the water-insoluble but hexane-soluble part accounted for only 6% of the total absorbance. Therefore, we believe that the strongly

light absorbing components are only extractable in methanol (not in either water or hexane) “

18. P. 20488, Line 5: This is for some particular wavelength, correct? Or is it averaged over the entire measurement range?

We changed the sentence to “At 210C, the ratio between the two is 1.3 for large size and 1.6 for medium size both averaged over 380nm to 450nm.”

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

We removed “Bergstrom et al., 2007”

20. 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).

We picked a fixed range (390nm-460nm) over which the data for all the samples are valid and perform the linear regression in this data range. Results are shown in Fig. 8, and samples at different temperatures are marked separately.

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

We deleted the sentence of “Based on limited data, Sun et al. (2007) postulated....”

22. 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.

It is awkward to include the reference in the figure. Therefore we have included an explanation in both the text and the figure caption.

Text: "...with previous values of alpha/rho tabulated by Sun et al. (2007). Ranges for water-soluble aerosol are marked "water-soluble minimum and water-soluble maximum", and "water-insoluble".

Caption: "Range for water-soluble aerosol, and an estimate for water-insoluble aerosol, are taken from Sun et al., (2007). "Acetone-soluble" is taken from Kirchstetter et al., (2004)."

23. 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?

Xia et al. (2004) investigated diesel exhaust particles and found that PAH compounds were extractable by hexane or hexane: methyl chloride (3:2), while quinones could NOT be extracted by hexane or hexane: methyl chloride (3:2), but only by methanol. As stated in the paper, quinoid compounds are strong candidates for light absorbing OC. Shima et al. (2006) also stated that most of the oxygenated functional groups of diesel exhaust particle including quinones are hexane-insoluble.

24. 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?

We agree that the time dependence of the filter-gas equilibrium during sampling could affect the result. (In fact, this is always true, and is rarely discussed in any sampling literature!) However, in this situation, the effect of the time dependence should be minimal. The gaseous concentration during sampling is always higher than the expected

ambient concentration, which drives material preferentially into the particle phase. Therefore, the filter always collects more semi-volatile material during sampling than would be expected for ambient sampling. In our final heating of the filter prior to analysis, this material is driven off to approximate an ambient equilibrium.

If the opposite were true—that is, the filter collected *less* semi-volatile material at any time than would be expected from ambient sampling—then we should have a low bias in collection. But this is not the case.

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.

Samples were held at 170C for 1200s. From sample thermograms (which show carbon released per second), after 800s, the averaged rate of OC evolving from the filter is less than $0.01\mu\text{g C}/\text{cm}^2/\text{sec}$. Carbon released after 800s is 5-6% of carbon released during the whole 1200s procedure, suggesting that most of the carbon that would be released had been volatilized.

A greater concern is whether we volatilized carbon that *should not* have been released. We did have this concern in conducting this experiment, but felt that it was better to attempt a correction for SVOC than to ignore the issue altogether. Our concern can be understood by looking at the new Figure 3(c). Carbon with $\log_{10}C^*$ of greater than 1 would be driven into the gas phase, and the equilibrium composition on the filter would be missing these components. We believe that the results here are actually characteristic of less-volatile organic carbon: that with $\log_{10}C^*$ of zero and below.

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.

The goal of this paper is to provide absorption characteristics for the less-volatile material, as we believe that these will ultimately be modeled separately. Therefore, it remains important to retain the language of SVOC.

25. 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.

We changed “extracted fraction of OC by different solvents” to “Fraction of total OC extracted by different solvents”. We also change the figure into colored one.

26. Figure 5b: Why is there no “water + methanol after water” curve since there is such a curve in Figure 5a?

We added the following sentence in P. 20507, the caption of Fig.5: “note that there is no “water + methanol after water” curve in figure (b) because the normalized absorption (i.e. absorption per mass of carbon) is not additive, while absorbance is.”

27. 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.

We changed the curves representing others’ work into dashed lines and added Kirchstetter’s results as dots in the Fig. 9.

References:

Xia, T., Korge, P., Weiss, J. N., Li, N., Indira Venkatesen, M., Sioutas, C., Nel, A., Quinones and aromatic chemical compounds in particulate matter induce mitochondrial dysfunction: implications for ultrafine particle toxicity, Environ. Health Perspect., 112, 1347-1358, 2004.

Shima, H., Koike, E., Shinohara, R., Kobayashi, T., Oxidative ability and toxicity of n-hexane insoluble fraction of diesel exhaust particles, Toxicol. Sci., 91, 218–226, 2006.