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Comment

Interactive comment on “Brown carbon and water-soluble organic aerosols over the southeastern United States” by A. Hecobian et al.

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We thank the reviewer for their insightful comments (C). Following each comment is our response (R).

(C) Page 7602, I suggest the authors modify the title a little bit. As stated in the last sentence of Introduction, this paper mainly focuses on discussing light absorption of water-soluble organic aerosols (WSOC). Brown carbon was then inferred from the results in the context. Regarding the current title, it seems that brown carbon and WSOC are two separate categories investigated in this paper.

(R) The title has been modified, it now is: Water-Soluble Organic Aerosols and the Light-Absorption Characteristics of Aqueous Extracts Measured Over the Southeast-

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ern United States

(C) Page 7604, line 23, this sentence is confusing to me. Are the compounds with conjugated systems most absorbing among all types of chemical compounds? Or are they most absorbing near-UV region among the whole UV-vis spectrum?

(R) To reduce confusion we have removed the reference to conjugated bonds.

(C) Page 7604, line 24, incomplete combustion is not just smoldering, and it also includes flaming which produces black carbon.

(R) Line 24 has been changed from: Incomplete (smoldering) combustion to: Incomplete and smoldering combustion.

(C) Page 7606, line 6, 0.6N HCl provides a highly acidic environment. I noticed that the authors also used Milli-Q water to clean the system, which would possibly remove the acids. Did the authors measure the pH value of the system after the cleaning procedure? Will this affect the absorption measurement?

(R) We did not measure the pH after cleaning, but thoroughly flushed it with MilliQ water (at least 3 times the wave-guide volume) following the manufacturers' instructions. There is no evidence that cleaning influenced the measurement based on no evidence for a systematic change following the cleaning procedure.

(C) Page 7607, line 1, the filters had been stored at below freezing temperature for approximately one year prior to analysis. To a personal experience, one year is a long period that the properties (such as absorption or mass) of the materials on the filters change to some extent even the filters are stored below freezing temperature. Did the authors investigate the effect of their results caused by the long-term storage?

(R) We did not systematically investigate any possible effects due to sample storage and recognize that it may be an issue. However, as discussed in this paper, the filter and online results are consistent in identifying sources (mobile sources and SOA formation). Furthermore, a comparison of our measurements of inorganic aerosol com-

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ponents (K^+ , NH_4^+ and SO_4^{2-}) from the stored filters to measurements done by the regulatory agency (i.e., filters that were not stored for such a long period) were in reasonable agreement ($r^2 > 0.80$ and slopes between 1.15 and 0.88, see the companion paper: Zhang, X., Hecobian, A., Zheng, M., Frank, N., and Weber, R. J.: Biomass burning impact on $PM_{2.5}$ over the southeastern U.S.: Integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis, *Atm. Chem. Phys. Disc.*, 10, 7037-7077, 2010). Overall, we believe that the consistent conclusions provided between the filter data (prone to artifacts) and the online data (not as prone to artifacts) indicate that our results are robust.

(C) Page 7610, Eq (1), I think the subscript for C in the term after the third “=” should be i instead of l.

(R) The subscript has been changed

(C) Page 7610, line 17, I suggest the authors just pick one definition of epsilon either molar absorption efficiency or mass absorption efficiency, and stick to it.

(R) The reference to molar absorption efficiency has been deleted.

(C) Page 7610, line 21, it is reasonable to correct absorbance by removing the absorbance from pure water blanks. Could the authors state how much absorbance is from pure water blanks? How much percentage does the absorbance of pure water contribute to the total absorbance of a sample?

(R) Absorption of a liquid sample is made relative to some reference, generally the solvent, which in this case is water. The reviewer requests the absorption of pure water, but with reference to what? The procedure for making an absorption measurement is to define the zero as that of the solvent (e.g., water blank) and the max as the dark spectra. The measurement of solvent containing solute falls between these values. Saturation of our optics was generally not an issue except for filter samples collected in strong fire plumes, and indicated by AL greater than 1. In these few cases the filter

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extract was diluted a known amount and the absorption spectra re-measured.

(C) Page 7611, Eq. 2, I tried to reproduce the derivation of this equation and it seemed that the authors derived this equation by assuming the same mass absorption efficiency for OC in both bulk liquid phase and particulate phase, but they are actually different. I suggest the authors only use the absorption coefficient obtained directly from UV- vis spectrophotometer measurement to avoid the confusion. This will also help the discussion in Sect. 3.2.1 since Abs/WSOC will be the actual absorption per mass of WSOC, indicating how absorbing WSOC is.

(R) In essence the reviewer is asking to report the measured absorption data as it was recorded in the liquid samples (that is as A_λ or $Absl$, both are defined in Eq. 1). However, as clearly stated in the paper, this does not account for how the sample aerosol was collected and so the reported absorption depends on how much aerosol was collected and the extent of dilution for subsequent analysis. This makes any comparison between different methods and studies difficult (and impossible if sample flow rates, collection times, and dilution volumes are not given). We used two very different methods in this paper, a filter-based and an online system. We tried to make the data from both methods comparable and not a function of the collection method. To get around this problem we multiply $Absl$ (i.e., what the reviewer is asking us to report) by a constant, V_l/V_a (see Equation 2), the volume of the liquid sample divided by the volume of air the sample was collected from. (Note that we also normalize to absorption at 700nm and convert the spectrophotometer data of log-base 10 to log-base e by multiplying by $\ln(10)$). This makes no assumptions about the mass absorption efficiency of particle phase OC versus liquid phase WSOC as suggested by the reviewer. For the filter data we are simply multiplying $Absl$ by a constant of $30\text{mL}/24,048\text{L}$ (or $30\text{mL water} / (16.7 \text{ L air/min} * 24\text{hr} * 60\text{min/hr})$), and a constant of $(1.3\text{mL/min})/(15\text{L/min})$ for the online data. These two factors are constant for each method reported here and so one could easily calculate back to $Absl$ if that is of interest.

(C) Page 7612, line 12, could the authors explain or provide some citations on how the

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wavelength dependence can be used to infer the imaginary refractive index?

(R) For brevity and to keep the focus on aerosol chemistry and not aerosol light absorption properties this line was deleted.

(C) Page 7613, line 6-7, Angstrom exponents were determined by applying linear regression over different ranges for different samples (e.g., 330-600nm for South DeKalb site; 330-475nm for levoglucosan less than 50ng/m³ for Yorkville site). I would suggest the authors to determine Angstrom exponents over the same range for all the samples. In that way, will the conclusion of similar Angstrom exponent (6-8) still be held?

(R) The log-log plots (where a linear relationship indicates a power law dependence and the slope is the exponent) of Figure 4 show that Angstrom exponents are similar over the linear regions of each curve since the lines are parallel (same slopes). In refitting all 8 curves over the same (smallest) wavelength range of 330 to 475nm, as expected there is little change in the Angstrom exponents. We make note of this in the manuscript by adding the line: (If all curves are fit over the same wavelength range of 330 to 500nm, Ångstrom exponents remain largely unchanged with a maximum difference of 9% and span the range of 6.2 to 8.3). The results are summarized below:

South DeKalb:

03/07 Å was 6.0 now is 6.4

11/08 Å was 7.4 now is 6.8

08/16 Å was 6.8 now is 6.2

06/23 Å was 7.6 now is 7.2

Yorkville:

12/20 Å was 7.2 now is 7.0

03/01 Å was 7.8 now is 7.6

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08/16 Å was 8.3 now is 8.3

06/17 Å was 7.8 now is 7.8

(C) Page 7613, line 18, the authors should add some citations on “biomass burning is a significant source for brown carbon”.

(R) No citations are added since this is discussed in detail and a number of references are cited in the background (see Pg. 7604 lines 24-27)

(C) Page 7614, line 9, the authors stated that the classification of biomass burning and non- biomass burning-influenced periods using levoglucosan concentrations of 50ng/m³ was somewhat arbitrary, but this classification has still been used throughout the paper. I would expect to see more explanation or validation on the use of this dividing point.

(R) As stated in the manuscript 50ng/m³ of levoglucosan is an arbitrary choice, but Figures 5 and 6 demonstrate that it is reasonable. In Fig. 5 it can be seen that in most cases summer levoglucosan levels are below 50 ng/m³, a period when the companion paper (Zhang et al., ACPD 2010) shows was not significantly influenced by biomass burning, as expected. The scatter plots of Abs₃₆₅ vs WSOC also show that 50 ng/m³ is generally a good divider (e.g., good separation of red and blue points into two differing slopes).

(C) Page 7618, line 12, could the authors explain why the ratio of WSOC/CO or later in line 22 Abs₃₆₅/CO are used. Is there a fairly constant OC emission rate in a diurnal cycle? What can these two ratio account for?

(R) Normalizing WSOC and Abs to CO was done as a means to account for the diluting/concentrating effects resulting from changes in PBL height. The reviewer is correct in that CO is not the best parameter due to confounding effects of changes in CO emission throughout the day. PBL height would be better, but this data is not available. Thus, as has been done in other studies (see for example, de Gouw et al, 2009), we

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use CO. Despite these drawbacks we feel that the CO diurnal variability is not sufficient to obscure the diluting/concentrating effects. For example WSOC/CO in Fig 8 shows an expected clear increases during daytime due to enhanced SOA production.

de Gouw, J. A., Welsh-Bon, D., Warneke, C., Kuster, W. C., Alexander, L., Baker, A. K., Beyersdorf, A. J., Blake, D. R., Canagaratna, M., Huey, L. G., Junkermann, W., Onasch, T. B., Sjostedt, S. J., Sullivan, A. P., Tanner, D. J., Vargas, O., Weber, R. J., Worsnop, D. R., Yu, X. Y., and Zaveri, R.: Emission and chemistry of organic carbon in the gas and aerosol phase at a sub-urban site near Mexico City in March 2006 during the MILAGRO study, *Atm. Chem. Phys.*, 9, 3425-3442, 2009.

(C) The authors used several phrases such as “cool months”, “colder periods”, “colder months”, “winter”, “warmer seasons”, and “summer” to indicate certain time periods throughout the manuscript. It would be wise to use same terms for a certain period.

(R) References to cool, colder months and warm seasons etc. versus winter and summer were used because they are more inclusive than period defined by a specific season. The wording has been slightly modified throughout the text to be more precise. As an example; in contrast to the colder periods at the beginning and end of the year, during the warmer times during the middle of the year

(C) The authors should pay attention to some terms used to describe optical properties: Page 7610, line 26 and page 7611, line 4, “absorbance coefficient” should be “absorption coefficient”. Page 7612, line 6, “absorption cross-section” should be “mass absorption cross-section”.

(R) Both have been changed.

(C) Page 7636, Figure 5, in the caption, A365 should be Abs365.

(R) The figure caption has been changed.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 7601, 2010.