

Title of the paper: Evaluation of the carbon content of aerosols from the burning of biomass in the Brazilian Amazon using thermal, optical and thermal-optical analysis methods
Soto-García, L et al.

Answer to Referee #1
General comments:

The authors sincerely acknowledge the very good suggestions from this referee that certainly made for a better and clearer manuscript.

Referee #1: “The EC/BC methods inter-comparison aspect of the paper requires more attention to the role of sampling artifacts on the interpretation”.

Authors: In this regard we added in section 3.1.4 some corrections related to the BC values obtained from the aethalometer and added a discussion about the positive and negative artifact.

Referee #1: “Additional attention should be paid to the TOT and TOR results (e.g., how large were pyrolysis corrections in each case, how do these values compare to the other methods, were there day/night differences?)”

Authors: The pyrolysis (charring) correction in TOT and TOR can be addressed, but for the TOA data this is not possible because of the use of a single wavelength to distinguish OC from EC/BC and because of the absence of measurements of pure EC/BC and pure char, which would be important for determining the charring EC/BC in the sample, as stated by Hadley et al. [2008].

The actual amount of char generated during TOT and TOR should be the same if samples are analyzed under the same atmosphere (i.e., either He, O₂, or He/O₂) and with the same temperature program. If the instrument/temperature program is the same, we can expect that different TOR and TOT results are due to the optical correction alone. The TOT usually reports higher char (i.e., pyrolytic organic carbon, POC) amounts leading to lower EC_a. TOT is more sensitive to char within the filter media than TOR, which only detects char on the filter surface. Within-filter char is often minor in quantity, but absorbs light much more strongly than surface char and native EC (Chow et al., 2004; Chen et al., 2004; Subramanian et al., 2006). This leads to "over-correction" of EC. However, POC could be substantial for smoldering-dominated samples due to production of brown carbon during smoldering combustion (Chen et al., 2010; Chakrabarty et al., 2010).

The IMPROVE-TOR and NIOSH-TOT results provide bounds for EC_a measurements and the ranges are larger for some samples than others, largely depending on their charring potential. The NIOSH-TOT attributes more of the POC to OC than IMPROVE-TOR, which attributes the POC more to EC.

According to the results presented by Szidat et al. [2010], it seems that the extent of charring is smaller in an O₂ atmosphere (as was used in our TOA) than in a He atmosphere (as is used for the TOT and TOR instruments).

With respect to day/night char differences there are no data available because daytime samples were only measured by TOA (Table 1). However, we expect higher charring for night time samples since the water-soluble material is responsible for the charring, as shown in Figure 3a, and this material is present in higher concentrations in nighttime vs. daytime samples.

Referee #1: “The size-segregated results would also benefit for a more in depth analysis. These are, to my knowledge, the first, or at least among the first, size-dependent measurements of the wavelength dependence of absorption, yet the results in Table 4 are barely discussed in the text.

Organic carbon and elemental carbon data are presented as a function of size, but it would be interesting to include a discussion of changes in the EC/TC ratio as a function of size. Can this be linked to changes in the spectral absorption dependence? What broader implications would these results have on optical properties and/or CCN activity of the emissions?”

Authors: The original purpose of Table 4 was to demonstrate that water extraction of biomass-burning particle samples reduces significantly the OC content, but does not remove all OC. This can be observed from the decrease in Ångström exponents in Table 4. Nevertheless, following referee’s #1 suggestion we related the EC/TC data from Table 1 to the Ångström exponents in Table 4, and added in section 3.2 the following text:

“Water treatment removed much, but not all, of the sample OC that evolves below 400 °C (Figure 3a). Similarly, the extraction with water greatly diminished the spectral dependence of the samples, but did not reduce it to ~1.0, as shown in Table 4. This table contains the absorption Ångström exponent results for the three samples that were measured by TOA (nominal D_p between 0.1-2.4 μm (stages 3-9)). The average was between 1.8 and 3.9 for the non-extracted samples, and between 0.7 and 1.6 for the extracted samples. When the ratios of EC_a/TC and EC_w/TC at different sizes (0.5- 1.6 μm) were compared with the Ångström exponents (α and α_x) in Table 4, the stages with higher EC_w fraction (D_p of 0.2 to 0.6 μm) showed higher Ångström exponents ($EC_w/TC = 0.09 \cdot \alpha_x - 0.04$ and $r^2 = 0.94$, excluding one outlier). This was only observed for samples that were extracted with water and suggests that this behavior is probably due to the brown carbon left after the extraction process.”

With respect to the implication of our results for the CCN activity, it mainly depends in the size distribution of the inorganic components. EC is not CCN-active, and brown carbon may not have a large effect on CCN activity. Investigation of the effects of the size distribution of brown carbon, BC, and OC on the optical properties cannot be addressed here, since it requires more information.

Referee #1: “The organization of the paper could also use improvement. It isn’t clear why the topics described in sections 4 and 5 are worthy of their own sections while a large number of the other results are combined into section 3.

Authors: Following the referee’s suggestion, sections 4 and 5 were eliminated and now section 3 is the one where we present and discuss the results. Section 3 was also rearranged so that the discussion reads and flows better.

Referee #1: “If the two topics can be better organized and expanded the significance of the findings would be clear, or if the focus of the paper was shifted to either topic, the manuscript would suitable for publication in ACP.”

Authors: We hope that with the modifications in previous sections 3, 4 and 5 (now only Section 3) and with the added discussion both topics are clearer. We also hope that it is clearer now that this manuscript seeks to evaluate different methods for determining the carbonaceous material in biomass burning samples, so that we can eventually present and discuss the size distributions of the species that composed this fraction (i.e., EC/BC and OC).

Specific comments from Referee #1:

Referee #1: 12861 (16): D_p is not defined.

Authors: Now D_p is defined in the abstract as well as in the experimental section.

Referee #1: Introduction

The introduction provides a detailed review of previous biomass burning aerosol composition measurements in the Amazon, including size-segregated results that can be linked to aerosol hygroscopicity and CCN activity. A significant amount of the manuscript justifies previous organic composition (e.g., WSOC) measurements, but there is little motivation provided for size-segregated OC/EC measurements. The introduction itself states that existing measurements were sufficient to predict aerosol hygroscopic properties and CCN ability over the Amazon (12864, lines 5-6), so what additional benefits do the observations presented in this study bring? This could be addressed by a discussion that gives some of the benefits size-segregated OC/EC measurements specifically provide (e.g., better constrain EC lifetime, improve treatment of biomass burning optical properties).

Authors: Following the referee's suggestion we improved the Introduction by adding more information regarding the value of size-segregated OC/EC measurements. We added the following "There are very few studies that present size-resolved information about the carbonaceous fractions during biomass burning at tropical locations (e.g., Echalar et al., 1998; Falkovich et al., 2005; Decesari et al., 2006). Size-resolved EC/BC and OC information is important since it provides a better understanding of the lifetimes and optical properties of these species. In the Amazon Basin, prior to LBA-SMOCC, the only study is the one by Echalar et al. [1998], which reports size-resolved BC concentrations, determining BC using a light reflectance technique. To our knowledge, ours is the first study that presents both EC and OC size distributions for the dry season in the Amazon Basin. This type of study is essential for improving our understanding of the climate impact of, for example, BC or EC, species whose climatic effects strongly depend on their physical and chemical properties, as well as on their residence time and distribution in the atmosphere [Jacobson, 2001; Novakov et al., 2005]."

Experimental

Referee #1: 12865 (20): vegetation should not be hyphenated.

Authors: The mistake was corrected.

Referee #1: 12865 (19-21): Can some measure of distance to fire activity be given here? Is the site surrounded by the fire activity or at the margin?

Authors: In this regard, the following information was added in the manuscript: "This site has experienced intense deforestation by vegetation fires over the last 30 years [Andreae et al., 2002; Kirkman et al., 2002; Trebs et al., 2005]. Maps of the fire locations in Fuzzi et al. [2007] clearly show that the sampling site was under the influence of emissions from fires extending to 2000 km upwind of the site during the sampling period. Also there was local burning nearby, which was particularly an influence at night-time because of the trapping of smoke in the nocturnal boundary layer."

Referee #1: 12865 (24): Should be reported as the particle aerodynamic diameter here and elsewhere in the manuscript unless a correction for density has been applied.

Authors: We added and defined the acronym D_p ("particle aerodynamic diameter") both in the Abstract as well as in the Experimental sections, since no correction for particle density was made.

Referee #1: 12866 (20): The potential for negative artifacts (e.g., underestimation of carbonaceous particle mass due to volatilization from filters) should also be mentioned here. There should also be some mention of how these artifacts could affect interpretation of the size-resolved data (e.g., redistribution of semi-volatile organic species across different filter/impactor stages) here or in section 5.1.

Authors: The following text was added in the Experimental section: “A complete assessment of corrections for positive artifacts (overestimation of carbonaceous particle concentration due to adsorption of organic gases to the quartz filters) and negative artifacts (underestimation of carbonaceous particles due to volatilization of semi-volatile organic carbon from the particles collected on the filters) was not possible in this study because our sampling systems did not provide for this. However, an estimation of the positive artifact for the DLPI was performed by comparing TC concentrations measured with other filter samplers (Sec 3.1.3). The positive artifact during SMOCC 2002 was determined with the HVDS. The OC was measured on the back filter placed in a tandem position. This back filter OC could come from both positive and negative artifacts [Mader et al., 2003]. However, it is generally assumed that the positive artifacts prevail [Turpin et al., 2000; Mader et al., 2003]; therefore, OC(front) – OC(back) is considered a measure for “artifact-free” particulate OC. On the other hand, we could assume that the positive artifacts are negligible and that the back filter OC is actually due to negative artifacts (OC that was volatilized from the front filter). If this were the case, OC(front) + OC(back) would be a measure for “artifact-free” particulate OC. One problem with the latter approach is that the OC that is lost (by volatilization) from the front filter may not be fully captured by the back filter. There are certainly better approaches to assess the extent of negative artifacts, as proposed by Eatough et al. [2003], but they were not used in SMOCC 2002.”

In section 3.1.3 we included “redistribution of semi-volatile organic species across different filter/impactor stages” as a factor that could affect interpretation of the size-resolved data.

Referee #1: 12866 (24): UPR not defined

Authors: Now it was defined as “University of Puerto Rico (UPR)”

Referee #1: 12866 (28): Please provide a reference for the aethalometer (e.g., Hansen et al., Sci. Tot. Environ., 1982).

Authors: Reference was added.

Referee #1: 12868 (2): Were any attempts made to correct the aethalometer observations for measurement artifacts (e.g., Weingartner et al., 2003; Arnot et al., 2005)?

Authors: We added corrections for the artifacts in the aethalometer by using the equations given by Schmid et al. [2006]. All results presented in Table 1 and Figure 5 were corrected. In the Experimental section we added: “In addition, the aethalometer results were subjected to artifact corrections for filter loading and multiple scattering given by Weingartner et al. [2003] and Schmid et al. [2006]. Briefly, from the equivalent black carbon mass concentration reported by the aethalometer and the specific absorption cross section of $14,625/\lambda$ [$\text{m}^2 \text{g}^{-1}$] ($16.6 \text{ m}^2 \text{g}^{-1}$ for 880 nm) the attenuation coefficient σ_{ATN} was calculated using the equation $\sigma_{\text{ATN}} = \text{BC}_e * 16.6$. The absorption coefficients σ_{abs} were obtained by applying corrections given in Weingartner et al. [2003]: $\sigma_{\text{abs}} = \sigma_{\text{ATN}} / (C \cdot R(\text{ATN}))$ [Mm^{-1}], where R(ATN) accounts for the reduction of the optical path length in the filter with increasing filter load and C corrects for the multiple scattering effects of the filter fibers. The filter loading correction equation used was: $R = (1/f - 1) / (\ln \text{ATN} - \ln 10) / (\ln 50 - \ln 10) + 1$ [Weingartner et al., 2003], where $f = 1.2$ during the SMOCC 2002 campaign [Schmid et al., 2006]. The equation for the wavelength-dependent multiple scattering $C_\lambda / C_{\lambda 0} = \lambda^{-0.1178 \ln(\lambda/\text{nm}) + 1.982} / \lambda_0^{-0.1178 \ln(532) + 1.982}$ was used, where C at 880 nm is equal to 6.54 [Schmid et al., 2006]. After applying the corrections, corrected BC_e was calculated using the absorption cross section α_{abs} of soot carbon at 880 nm ($4127/\lambda$ [$\text{m}^2 \text{g}^{-1}$] = 4.69 at 880 nm) as follows: $\text{BC}_{e \text{ corr}} = \sigma_{\text{abs}} * 1000 / \alpha_{\text{abs}}$. Concentrations were not corrected for the sampling spot size and changes in flow rate of the instrument [Müller et al., 2001]. These corrections are likely to be small in comparison to the other uncertainties.”

Also, in the section used to compare EC_a and BC_e (Sec 3.1.4) we added: “Results from the aethalometer after correcting for the filter loading and multiple scattering for BC_e at 880 nm were ~ 40%

lower than the values reported from the aethalometer without corrections (average of $1.9 \pm 1.0 \mu\text{g m}^{-3}$ with corrections, compared to $3.3 \pm 1.7 \mu\text{g m}^{-3}$ without).”

Referee #1: How were wavelength differences between the MAAP and aethalometer accounted for (e.g., $1/\lambda$ or some measured value)?

Authors: We did not use a MAAP in the SMOCC project. Maybe the referee is referring to the LTM measurements, but both the LTM and the aethalometer used the same wavelength, 880 nm. Also, as we measured the wavelength dependence of absorption with the 7-wavelength aethalometer, this dependence was used to correct the absorption measurements at other wavelengths for the other instruments.

Referee #1: The wavelength(s) of both instruments should be provided, particularly the wavelength used to convert the optical absorption to BC_e that corresponds to the absorption cross section (should be the specific absorption cross section) of $10 \text{ m}^2 \text{ g}^{-1}$.

Authors: It was not correct to state a specific absorption cross section of $10 \text{ m}^2 \text{ g}^{-1}$, the sentence should have said “a specific absorption cross section of $16.6 \text{ m}^2 \text{ g}^{-1}$ ”. Now it is clearer that the BC was determined at 880 nm.

Referee #1: 12870 (25): The aethalometer and LTM measurements use different constant to convert the measured attenuation to BC_e (10 vs $19 \text{ m}^2 \text{ g}^{-1}$). Is there a physical justification for this? If not the same factor should be used for the conversion.

Authors: The aethalometer uses a conversion factor of $16.6 \text{ m}^2 \text{ g}^{-1}$ (already corrected in the text) and for the LTM previous authors have typically used $19 \text{ m}^2 \text{ g}^{-1}$, e.g., Gundel et al. [1984]. The use of $\sigma = 19 \text{ m}^2 \text{ g}^{-1}$ is consistent with the calibration factor of the early versions of the commercial aethalometer that employed the same optical transmission method for measuring BC concentrations [Bodhaine, 1995] and the value stated by Liousse et al. [1993] for black carbon in smoke particles. In both cases, this constant is an empirical value, which depends on instrument and filter geometry, but also strongly on the type of aerosol collected, as stated by Liousse et al. [1993]. Given that a calibration of neither the aethalometer nor the LTM has been specifically performed for the SMOCC aerosols, there is no objective justification for choosing either constant over the other, and for reasons of consistency, we use the value of $16.6 \text{ m}^2 \text{ g}^{-1}$ for both instruments, as suggested by the reviewer.

We added in the LTM Experimental section: “In order to be able to compare BC_e concentration obtained from the LTM and the aethalometer, a specific absorption cross section of $16.6 \text{ m}^2 \text{ g}^{-1}$ was used for both instruments.”

Referee #1: 12871 (20): Please state which filters were these measured on and the diameter range of the measurement. The uncertainty value provided should be defined (e.g., standard deviation, standard error, inter-quartile range, etc.).

Authors: The sizes for the fine and coarse fractions were added here. The information about the type of filters/substrates used is in Section 2.2. The uncertainty values of the concentrations (i.e., standard deviation, STDEV) were defined.

Referee #1: 12872 (5): A minor point, but it is probably more accurate to say that the TC observations in the current study were within the range of values observed in the previous campaign rather than being “consistent” with them. How do the averages and medians compare?

Authors: The text was modified following the referee's suggestion.

Referee #1: 12872 (8-11): Do the individual samples agree well? What was the strength of correlation between the sampling methods?

Authors: The main purpose of this manuscript was to report the size resolved concentrations of BC/EC and OC, in particular for the dry period in the Amazon Basin, and not to perform a detailed comparison of the individual samples for the mass concentration. A detailed study of individual samples would make the manuscript much larger and with too many details. The average mass concentrations were taken from Decesari et al. 2006.

Regarding the strength of correlation of TC concentration between the sampling methods, we found a correlation of $r^2 \sim 0.80$ for all the systems used here.

Referee #1: 12872 (25): Also provide standard deviation or other measure of variability about the mean.

Authors: The standard deviations were included in the revised version: "Concentrations of EC_a averaged $18 (\pm 9) \mu\text{g m}^{-3}$ in the fine particle mode ($D_p < 2.5 \mu\text{m}$)."

Referee #1: 12873 (12): Changes in embedded soot morphology may also play a role in altering the optical properties of material in the filter.

Authors: We have added the following text: "Changes in embedded soot morphology may also have played a role in altering the optical properties of material in the filter after the extraction with water."

Referee #1: 12874 (3): In addition to LTM measurements a more direct comparison to the $EC_{w572\text{nm}}$ values would be to use the ATN measured through the filter after the OC has been evolved.

Authors: Indeed this is exactly the definition used to determine $EC_{a572\text{nm}}$ and $EC_{w572\text{nm}}$. However, this section is used to present the different ways and concentrations used to determine the light absorbing carbon, like the BC_c from the LTM at 880 nm ($BC = ATN/\sigma$, Sec 2.3.3).

Referee #1: 12874 (11): The potential role of negative artifacts should be added to this discussion.

Authors: We have added the following text: "In addition, it is important to state that the carbonaceous material observed in the DLPI might come also from a redistribution of semi-volatile organic species across different filter/impactor stages (negative artifact), and not only from the adsorption of gases (positive artifact)."

Referee #1: 12874 (21): If the positive artifact for the HVDS system was only 5% why are the impactor artifacts 3-6 times larger? Can this be attributed to differences in face velocity or other phenomena?

Authors: We still do not have a good explanation for this behavior, but factors that might have influenced this are the following: accuracy of the volume measurement in the DLPI, losses of volatile/semivolatile organic compounds from the upper stages to the lower ones due to the low pressures that impactors use and, a small contribution due to differences in the face velocities. We modified the sentence in question in the following way: "Also, the differences (3 to 6 times higher) found between the HVDS and the DLPI might have been due to accuracy of the volume measurement in the DLPI, the higher losses of organic compounds from the upper stages (coarse particles) to the lower ones (fine particles) in the DLPI due to

the low pressure (much lower than the HVDS) it uses and, a small contribution from the high face velocity also in impactors.” Nevertheless, this topic needs more study!

Referee #1: 12876 (12): This is an opportunity to include the IC results in the analysis...a strong correlation between EC and potassium would also support this conclusion.

Authors: We added the following sentence: “Also, the strong correlation ($r^2 \sim 0.99$) of BC_e with potassium, a tracer of biomass burning [Andreae et al., 1983], makes it clear that biomass burning is the dominant aerosol source.”

Referee #1: 12876 (24): 5-10% BC by mass.

Authors: This was corrected.

Referee #1: 12876 (29): Avoid use of the term soot as its definition is somewhat arbitrary, as pointed out in the introduction.

Authors: This was corrected.

Referee #1: 12877 (1): If available, measurements of excess carbon monoxide and carbon dioxide mixing ratios would support the claims made regarding the role of fire behavior. A comparison to similar measurements for well-characterized fires (e.g., aircraft or laboratory studies) would be helpful. The addition of secondary organic aerosol would lead to lower EC/TC ratios and mask the nature of the fires responsible for the EC emissions and should be mentioned.

Authors: The referee’s suggestions were followed and the text was modified as follows: “Also, the addition of secondary organic aerosol could have led to lower EC_a/TC ratios and mask the nature of the fires responsible for the EC emissions. However, aircraft and ground-based measurements of CO-to-CO₂ emission ratios during SMOCC-2002 and other campaigns have shown that smoldering combustion, which releases aerosols with low EC_a/TC ratios, makes a large contribution to the emissions from deforestation fires, especially when sampled at ground level [Guyon et al., 2005; Yokelson et al., 2008].”

Referee #1: 12877: Is this the same method as presented by Hadley et al. (Environ. Sci. Technol., 2008)? If so reference should be given. It is not clear if BC concentrations were measured using the method of Hadley et al. (2009) or the earlier single-wavelength approaches.

Authors: We used the earlier single-wavelength approaches, and not the Hadley et al. [2008] method. This is explained before (Sec 2.3.1) in the text that says: “To refine the estimate of EC_a , and consequently OC, the intensity of light (at 572 nm) transmitted ... was measured with a spectrometer.”

Referee #1: Section 4 could be combined with the other results. Sections of it are also repetitive and should be removed.

Authors: Section 4 was eliminated and combined with section 3.

Referee #1: 12878 (19): Please state which time period and/or samples these values represent.

Authors: They are from the dry season and this was added in the text: “Our results show that from the total estimated mass collected during the dry season 89% was POM, 2% was the estimated BC_e , and 9% was the inorganic fraction. The residual mass was not significant.”

Referee #1: 12878 (21): The OC to POM conversion factor could be compared with the value obtained from a mass closure that compares the measured gravimetric PM_{2.5} mass to mass reconstructed from measured species.

Authors: We did the comparison and no significant differences were found, therefore, we added the following text: “Comparing the measured gravimetric mass for $D_p < 2.5 \mu\text{m}$ to the mass reconstructed from measured species in our samples yields a closure within experimental uncertainties, indicating that for our sampling site the use of a conversion factor of 1.8 is appropriate for the conversion of OC to POM.”

Referee #1: Section 5 could also be moved to the results section.

Authors: The content of section 5 was introduced into section 3.

Referee #1: 12879 (9-23): Move this discussion to the experimental section. Please give an estimate of the magnitude of the size shift.

Authors: We moved the text to the Experimental section. Also, we added the following in order to give an estimate of size shift magnitude: “Figure 7 shows that the size shift is less than one stage ($\sim 0.2 \mu\text{m}$ for stages between $0.6\text{-}1.0 \mu\text{m}$), i.e., significantly less than a factor of 2.”

Referee #1: 12880 (15): Another possibility is a small contribution by gas-phase adsorbed species to the absorption signal.

Authors: The referee’s suggestion was introduced in the text and now it reads as follows: “The BC_c in the coarse mode was probably due to an internal mixture of BC_c and other coarse mode particles, to the absorption of light by large particles (e.g., primary biogenic aerosols) [Guyon et al., 2004], and possibly also to a small contribution by semi-volatile adsorbed species to the absorption signal.”

Referee #1: 12880 (20): Do the IC results confirm this? Not sure the reasoning here is valid. Mixing of BC with SOA etc. will produce the exact same result as the sizing is done on an internal mixture.

Authors: The use of SOA here was a mistake and we apologize for that. Here we are talking about the possible mixing of BC with POM (and not SOA); and coarse POM contains a lot of primary biogenic aerosol (which is not SOA). Also, we never measured organic compounds with the IC. The size-resolved data for organic tracers of biogenic sources given by Fuzzi et al. (2007) in their Figure 7 were not obtained by IC, but by GC/MS. However, we added the following sentence: “The size distribution of BC_c was different from OC in the supermicron size, in part because the OC coarse mode may have been derived from plant debris, plant pollen and fungal spores, as suggested also by Fuzzi et al. [2007] for the size-resolved organic tracers of biogenic sources; or due to an internal mixture of BC_c with primary and secondary organic aerosols.”

Referee #1: 12880 (26-28): I believe the Reid et al. (2005) paper discusses total aerosol volume/ mass distributions as opposed to OC and EC mass.

Authors: We wrote earlier that most of the aerosol mass (84 %) consists of POM. Therefore, it is possible to compare the OC mass size distribution with the aerosol mass (or volume) size distribution.

Referee #1: 12881 (1): The comparisons to the droplet mode should include the caveat that the measured particle diameters reported here are aerodynamic diameters. It is also difficult to

compare the results to previous studies without a discussion of the uncertainties in diameter due to the stage uncertainty.

Authors: In many previous publications [Maenhaut et al., 2004; Fuzzi et al., 2007] when authors talk about the “droplet mode” they usually refer to cascade impactor data and thus to aerodynamic diameters. Nevertheless we included a note about the diameter uncertainty so that this is also considered: “However, this can also be due to the uncertainties in diameter when using quartz fiber filters as substrates in an impactor.”

Referee #1: 12881 (3-16): Figure 10 support the conclusions presented here and they should be removed. While POM is higher at night for stages between 0.39-2.4 μm , it is lower at night for all stages below 0.39 μm , nor is BC_e “almost the same” for day and night stages. Nighttime BC_e is at factor of 2 higher than daytime BC_e for stages 0.62 μm and larger. Though it is difficult to integrate the data by eye it appears that total BC is also higher at night by at least a similar relative magnitude as observed for POM. No uncertainties are given, either, so the significance of the relationship cannot be determined. Do the bulk samples support this conclusion? What about the average of all day and night size-segregated samples?

Authors: Figure 10 was changed to Figure 9. Figure 9a shows clearly that the size distribution of POM peaks at a larger size during the night than during the day. This is supported by the bulk data presented before (Table 1), which show higher OC concentrations during the night, with average concentrations of $\sim (37 \pm 21)_{\text{day}}$ and $(49 \pm 19)_{\text{night}}$ for $D_p < 2.5 \mu\text{m}$ for day ($n=2$) and night ($n=3$) samples, respectively. Also, the diurnal carbonaceous aerosol results presented in previous work from SMOCC, like WSOC species [Decesari et al., 2006] and TC [Fuzzi et al., 2007], clearly showed that concentrations for samples at night time were higher than those at daytime. This shift in size distribution can be explained by the much higher RH during the night than during the day and the fact that the POM was moderately hygroscopic (POM was around 60-70% soluble in water, from the PM_{2.5}, during the dry and transition periods; Decesari et al., ACP, 2006). Thus, the POM can grow to larger sizes at high RH, as encountered during the night.

The referee’s observation of higher concentration for all stages below 0.39 μm was also found in the other sample (only two day time samples available). This may be due to adsorption of gases (positive and negative artifacts) in the quartz filter for those particular sizes and especially during daytime (Section 3.1.3). The OC gases could be derived from the volatilization of POM on the coarser stages in the course of the actual sampling because of the higher temperatures during the day. Also, there may simply not be much very fine POM during the night because it may have grown to larger particles at the much higher RH during the night. To explain this observation we added in the text: “Observation of higher concentrations for all stages below 0.39 μm (Figure 9a) may have been due to adsorption of gases (positive and negative artifacts) on the quartz filter for those particular sizes and especially during daytime. The OC gases could have been derived from the volatilization of POM on the coarser stages in the course of the actual sampling because of the higher temperatures during the day. Also, there may simply not be much very fine POM during the night because it may have grown to larger particles at the much higher RH during the night. POM was around 60-70% soluble in water, from the PM_{2.5}, during the dry and transition periods [Decesari et al., ACP, 2006]. Thus, the POM can grow to larger sizes at high RH, as encountered during the night.”

In terms of the BC_e diurnal behavior we re-wrote the text, since we found the same behavior as OC and from the other BC_e size distribution. Averages cannot be given because we are only presenting results of 2 daytime samples. Now the text reads as follows: “However, Figure 9b shows that the fine mode mass of BC_e during day time was almost the same as during night time, suggesting that, at least for this sample period, only little soot carbon is emitted at night. Nevertheless, observations of diurnal samples from the aethalometer and EC_a concentrations from HVDS reported by Decesari et al. [2006] show the same behavior as for the OC concentrations.”

Referee #1: 12881 (16): Additional discussion is needed to assess the role of water uptake on the sizing results. What was the relative humidity during sampling? Can some estimate of hygroscopic growth be made based on previous measured smoke measurements and used to adjust the measurements to “dry” diameters?

Authors: Based on results from Rissler et al. [2006], we added at the end of section 3.4 a discussion on the possible impact that water uptake could have had on the particle sizes. “In order to assess the role of water uptake on the sizing of our DLPI samples, we use the growth factors measured by Rissler et al. [2006]. During the dry season it was found that the non-hygroscopic mode dominates, and we can assume that a particle growth factor, GF(80%), of 1.10 to 1.15 is representative of the total aerosol. For the average daytime RH of 70%, the wet diameters are thus about 4% greater than the dry diameters. At night, it becomes very difficult to provide an accurate estimate, because humidities can exceed 90%, and the growth becomes very steep in the RH region between 90 and 100%. To get an idea of the range to be expected, the growth of a particle at 90, 95, and 100% has been calculated. If a 100 nm particle is assumed, a hygroscopicity coefficient of $\kappa = 0.04$ is sufficient to obtain a GF (90%) = 1.09. This would represent a lower limit for the particle hygroscopicity. The GF at 95 and 100% for these particles would be 1.16 and 1.59. If, on the other hand, a 500 nm particle with a $\kappa = 0.2$ (which has been observed for aged smoke) is assumed, we get GF = 1.4, 1.7, and 6.9 for 90, 95, and 100%. In conclusion, the GF becomes very strongly dependent of RH, κ , and particle size as one approaches 100% RH. For the impactor, this means that the smallest particles are going to be deposited mostly on the same stage even at 100%, while the largest ($D_p < 4 \mu\text{m}$) and most hygroscopic particles can move up as much as two stages. To have more precise results would require very accurate knowledge of the hygroscopicity in the accumulation mode, and of the RH in the impactor, neither of which were measured. Nevertheless, the effect of water uptake during the day is small relative to the size resolution of the impactor, while the effect during the night is not possible to estimate accurately enough with the data we have, but could easily be large enough to explain the observed shifts.”

Referee #1: 12882 (17): This conclusion is not supported by the evidence provided in the paper.

Authors: We changed the text in the revised version accordingly to what was previously discussed: “The different diurnal behavior of the OC and BC_c size distributions is related to differences caused by variations in temperature, relative humidity, and the depth of the boundary layer.”

Referee #1: Tables: General comment – the number of significant figures reported is different for different methods...are these techniques really more precise than those reported with fewer significant figures?

Authors: No, for this reason we changed the significant figures in the Tables to all with one decimal place only, in accordance with precisions of these techniques.

Referee #1: Table 1: The aethalometer results should be shown next to the fine or coarse mode integrated values rather than on the same was the first stage.

Authors: They have been corrected.

Referee #1: Table 2: STDEV should be written out or abbreviated differently.

Authors: Since we have used it throughout in all the text we simply define the acronym, in order to explain to the reader what it means.

Referee #1: Table 3: Please also report the standard deviations.

Authors: They are reported as suggested.

Figures

Referee #1: Figures 1 and 9 should be combined. The x- and y-range of Figure 1 is larger than necessary. Please provide error bars for each stage if possible.

Authors: Errors are now provided. The figures were not combined because before presenting size distributions of EC and OC we needed to evaluate the best possible method to acquire these. The size distributions of mass and TC concentrations can be presented at the very beginning of the discussion of the results, but to be able to have a better determination of how much of that TC is EC and OC, and what the size distributions of these species are, we needed to evaluate the possible methods to acquire these and choose the most appropriate one. Therefore, the evaluation of the methods comes right after the discussion of the mass and TC concentrations. At the end of section 3.1.1 we have added a text that explains this: “We do not follow this discussion with the results of the EC/BC and OC size distributions, because in order to present the best possible EC/BC and OC concentrations we must first evaluate the possible methods to acquire these species and determine the most appropriate one. This evaluation is performed in the following sections, and at the very end of the discussion of the results, the size distributions of EC/BC and OC are presented.”

Referee #1: Figure 2: Change “more significant” to “relatively larger” or similar in the caption.

Authors: This change has been done.

Referee #1: Figure 4: Provide error bars by propagating the uncertainty in TC measured by each system.

Authors: The errors bars are provided.

Referee #1: Bottom labels of the figure are being chopped off.

Authors: It has been corrected.

Referee #1: Figure 6: remove shadows from the plotting symbols. Different symbols should be used in 6a to give the different EC measurement methods.

Authors: The shadows have been removed and the symbols are used to identify the different EC measurement methods.

Referee #1: Figure 7 is unnecessary and results could be easily described in the text.

Authors: We eliminated the figure and followed the referee’s suggestion. A text was added to describe the results: “Our results show that from the total estimated mass collected during the dry season, 84% was POM, 6% was the estimated BC_e, and 9% was the inorganic fraction. The residual mass was not significant.”

We also improved Table 1, specifically the column related to BC_e/TC results. This was because the constant for calculating BC_e concentrations (from LTM) was changed (now using $\sigma = 16.6 \text{ m}^2 \text{ g}^{-1}$), and because the ratio of BC_e/TC was calculated from the average concentration of TC and BC_e for $D_p < 2.5 \text{ }\mu\text{m}$ and $D_p > 2.5 \text{ }\mu\text{m}$. We added the details of our results in the second paragraph of Section 3.3, it reads as follows: “Our OC concentrations averaged $43 \pm 18 \text{ }\mu\text{g m}^{-3}$ (Table 1), accounting for ~100% of the carbonaceous aerosol in our samples. This result is not corrected for the positive artifact observed when using the DLPI (Figure 4a). For the carbonaceous fraction, the OC was estimated from the difference between TC and BC_e [TC (Table 2: $33.6 \pm 31.7 \text{ }\mu\text{g m}^{-3}$) - BC_e (Table 1: $3.6 \pm 0.9 \text{ }\mu\text{g m}^{-3}$)] and converted to particle organic matter (POM) by using 1.8 as the conversion factor. This is a conservative OC conversion factor since aerosol heavily influenced by wood smoke can have conversion factors as high as

2.6 [Turpin and Lim, 2001]. The inorganic fraction ($5.7 \pm 4.6 \mu\text{g m}^{-3}$) was similar to the ones reported by Falkovich et al. [2005] and Fuzzi et al. [2007]. It is important to state that the samples used here to obtain the average inorganic fraction ($n=4$) and total aerosol mass [$n=6$; ($63.9 \pm 56.6 \mu\text{g m}^{-3}$)] were from aluminum sub-strates only.”

Referee #1: Figure 9: Better to show OC rather than POM because POM requires the assumption of a constant OC to POM ratio for all sizes.

Authors: We changed POM to OC for both figures 8 and 9. Note the figure numbers have changed, after Figure 7.