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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Black carbon over Mexico: the effect of atmospheric transport on mixing state, mass absorption cross-section, and BC/CO ratios" *by* R. Subramanian et al.

Anonymous Referee #1

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The authors present results on "black carbon" concentration measurements made during MILAGRO on the C-130 using a single particle soot photometer (SP2). They consider their observations in the context of concurrent measurements of CO and of light absorption by particles. Additionally, they consider how the nature of coatings on particles depends on air mass age. Although I find the measurements to be interesting, I find the presentation of the material and the discussion and conclusions to be weak in terms of clarity, organization, rigorous consideration of uncertainties in the measurements, and most importantly consideration of the qualitative vs. quantitative nature of their results. My specific concerns are discussed below.

There is a lot of discussion mixed in with the results, which by itself is not a problem, but quite often I find the discussion that does exist in the results section to be unclear and unfocused. One notable example is encountered with the discussion of the CO background contribution to the observed signal and why it may have been different in the Dickerson et al. study from INDOEX. Here, the authors seem to be arguing that Dickerson overestimated their background contributions (and thus also the BC/CO ratio), but then later seem to argue that there are legitimate reasons why the CO background in Mexico City might be quite different than that near the Indian sub-continent. Perhaps I am reading this incorrectly, but the language is ambiguous enough that it is difficult to tell. In any case, my point is that the authors should attempt to better separate results from discussion. Also, the discussion section could probably benefit from the use of sub-headings just as in the results section.

I found the rigor of the uncertainty analysis to be inconsistent. For example, although the authors provide uncertainty bounds on their SP2 BC measurements (+/- 22%), they make comparisons to other measurements without consideration of uncertainties. For example, with the BC/CO measurements, they state that their measurements are "similar" to some other measurements (2.5 ng/microgram vs. 1 ng/microgram), however I believe this is outside of the uncertainty of the measurements. What do the authors mean by "similar"? This is again a specific example, but this sort of issue (i.e. a lack of precision in the language used) is encountered throughout the manuscript. Also, it is not clear when the uncertainties reported by the authors are derived from propagation of errors or are the actual precision of the measurements (i.e. observed atmospheric variability).

Of perhaps more serious concern to me with respect to uncertainties or limits of the system is the discussion of particle ageing (Figures 8 and 9). Firstly, the authors show size distributions as a function of scattering/incandescence lag-time that go from ca. 65 nm to 400 nm. However, it is stated clearly (and Figure 2 indicates) that the data are not to be trusted below ca. 145 nm or above 330 nm. Thus, the data shown in

these figures should be truncated accordingly or the authors must very carefully justify the inclusion of data outside of this range. However, much of the "interesting" data in Figures 8 and 9 is right around 145 nm and the conclusions are to some extent based on shifts within this region. The ageing of particles should be re-considered in the appropriate experimental framework (i.e. within the limits of the system).

I also find the particle ageing discussion to be unnecessarily qualitative. The authors claim that there is "an apparent increase in the modal BC MED (BC mass/particle) of the thinly-coated BC mode" for aged vs. fresh particles. The authors can presumably determine log-normal fits during these periods from the data. They should do this and explicitly report the number based mean and median diameters along with uncertainty bounds. In other words, there is no reason that this increase needs to be "apparent" when it can be quantified.

Of further concern with the particle ageing studies is that the largest change in the thickly vs. thinly coated fraction does not appear to derive from particle ageing, but from a change in altitude sampled on a given day (Figure 8, bottom left and bottom middle panels. . .as an aside, it would help if these were labeled a, b, c, etc.). If such large changes in the thick vs. thin coatings can be observed just from changing altitude, how can the authors be confident that they are indeed encountering the same air mass one or two days later? It is argued that they knew where to sample from chemical forecasting, but have they attempted to track the sampled air masses back in time to provide confidence that they are sampling the same air masses? This observation is only very briefly noted at the very end of the manuscript but should be dealt with more prominently if the authors are going to provide confidence in their conclusions. Related to this, the authors also state at the end that "distinct" patterns in the coating thickness and mass distributions with age are observed. I find that, based on the current presentation of the results, the "distinct" nature of these changes is difficult to see. As it stands, I find the discussion relating to these ageing experiments and the conclusions drawn to not be very compelling – there are too many complicating factors

(mixing, continued emissions, etc.) that have not been adequately dealt with and it ends up appearing, to me at least, that the authors are reaching for broad conclusions that are not necessarily justified by the data as presented.

The authors present data in Figure 4 on BC concentration measurements for four days. However, in Figure 5 (BC/CO) and Figure 6 (absorption cross-section) they only consider two of these days (note: the dates are not given in Figure 6). Why are the flights on the other dates not considered in Figures 5 and 6? Presumably they would contribute further information. The same goes for Table 2.

In Table 1 the authors present average BC concentrations for different time periods during the individual flights. It would be useful if they were to also include columns for the average BC/CO and MAC during these periods, along with the appropriate uncertainties.

The discussion concerning the BC/CO ratios as they compare to other measurements is insufficient. First, the authors state "Figure 5a shows a substantial CO concentration apparently not associated with BC." It is not visibly clear what is meant by this. Although they reasonably argue that some of the CO in the sampled air masses is old, it is not clear how this can be discerned simply from looking at Figure 5a. Second, the authors state that a comparison with Baumgardner et al. is probably acceptable to within a factor of two. It needs to be made clearer why this is the case. Third, the discussion with respect to the Dickerson results is confusing, as noted above. Related to this, the authors state that the BC/CO derived here is "comparable to corrected MOPPITT data over the Pacific Ocean off the Mexican coast for March/April 2006." I assume they mean their estimate of background CO, not BC/CO. Also, much of the discussion given relating to the BC/CO is focused not on BC/CO, but on proper estimation of the background CO. Based on their data the authors should be able to provide a reasonable estimate of how a poor estimate of background CO would influence their results. In any case, the discussion of specific CO emissions from different regions of the world has little bearing on the BC/CO; it is the relative emissions of BC and CO that will be

of most importance.

Finally, I'll consider the presentation and discussion of the mass absorption efficiency measurements. First, to state that the MAE for the biomass burning period is "somewhat higher" than the other periods is not true within the uncertainties of the measurement. Second, I find the discussion of the influence of coatings on potential absorption "enhancements" to be much too simplistic. The authors state multiple times that the effect of ageing is to increase absorption by 50% over fresh values. As they are undoubtedly aware, this 50% value is only true for very specific combinations of core sizes and coating thicknesses. It can vary dramatically around this value. From Figure 1 I estimate the core diameter to be $\sim$190 nm and given the "typical" lag times the coating thickness to be $\sim$20 nm. For these conditions the expected enhancement (in a core-shell spherical particle Mie approximation) is only 20%, not 50%. My point here is that the authors have the data available to make their discussion much more quantitative and should attempt to move beyond broad (and potentially misleading) generalizations that ageing can simply be captured as a 50% enhancement in absorption. Third, I do not find the speculation about there potentially being a balance between mixing state, a bias in the PSAP absorption measurements and the absorption enhancement to be particularly strong and not necessarily supportable from previous observations. For example, Lack et al. makes no claim as to whether the PSAP bias depends on mixing state (only total organic relative to BC) and Cappa et al. actually used an external mixture yet still saw a significant bias in the PSAP measurements. Thus, it is equally plausible that coagulation would act to increase the absorption enhancement while having no influence on the potential PSAP bias, rather than leading to a cancellation of effects. Related to this, I believe the organic aerosol measurements by De Carlo et al. were made on the same platform as the SP2 and PSAP measurements. One could potentially use the De Carlo measurements along with the SP2 measurements to determine a time-series of the OC/BC ratio during each flight (rather than the single point consideration given in the manuscript), which Lack found to be a good predictor of the magnitude of the PSAP bias. Given the high organic loadings during MILAGRO, the

uncertainty in the absorption measurements is potentially much larger than the 20% stated (as mentioned, the measurements may be biased high by 40-70%). If a larger uncertainty is taken into consideration (or more specifically, a positive bias), then the agreement between the results presented here and the fresh emissions estimates from Bond and Bergstrom are not so bad (although there are certainly reasons to think that a real difference might exist, as discussed by the authors). Finally, I would argue that the comparison of the MAE measured here to that derived by Baumgardner et al. is not a fair comparison. The Baumgardner MAE values were determined in two ways: (1) based on PSAP measurements and (2) based on Mie theory and the measured particle size distribution. Baumgardner et al. found that the PSAP measurements gave a MAE approximately a factor of two greater than the Mie theory results, yet here the results are only compared to the Mie theory results and not to the more directly comparable PSAP results. (Admittedly, Baumgardner et al. do not explicitly give a MAE from their PSAP measurements. However, since they compare the measured PSAP absorption to absorption predicted based on their Mie Theory derived MAE and observed BC mass, and the PSAP absorption was higher by a factor of 2.3, the MAE from the PSAP would be correspondingly higher by a factor of 2.3. Furthermore, it is not surprising that Baumgardner et al. determined a MAE from theory that is much smaller than estimates from measurements. Bond and Bergstrom (2006) show very clearly that, for whatever reason, Mie theory is seemingly incapable of predicting MAE's as large as are observed; c.f. Bond and Bergstrom (2006) Figure 9). As such, I would strongly encourage the authors to remove any comparison to Baumgardner et al, unless they change the discussion to include the more directly comparable PSAP-based MAE.

To summarize, I find the measurements to be potentially very interesting. However, the overall negative tone of this review derives in large part from what I found to be a lack of organization and clarity in the writing.

Specific Comments:

Figures 4,5,6,7: Any points that are truly "zero" should be removed from the graphs.

They are distracting. Also, it is mentioned that data during ascents/descents is not to be trusted in an absolute sense and so this data should be removed from all of these plots.

Figures 8 and 9: The axes labels are not acceptable.

Figure 6: The MAC was never defined as “kLAC” in the text yet it is used to label the axes.

Page 9083, L21: It is not clear why the particles must be refractory. How is this a necessary part of the definition? P. 9084, L. 9: The authors seem to be overstating the benefits of the SP2 here. Can the data retrieved from the SP2 be used confidently on a particle-by-particle basis? Or are the collected single-particle data typically averaged over some time? P. 9087, L. 4: I find this difficult to understand. What do the authors specifically mean by "adds back 18% of the BC mass"?

P. 9088, L. 3: I would recommend including a table that shows the log normal fit parameters and scaling factors as determined for each flight.

P. 9088, L. 15: More detail is needed here, such as the RI’s assumed for the BC and non-BC material and a clearer discussion of the mixing rules employed.

P. 9090, L. 5: What is the time-resolution on the reported data?

P. 9090, L. 11: It is not clear why only the flight on March 18 is discussed here. I thought there were four flights being considered?

P. 9091, L.18: It is not clear what is meant by the lowest frequency peak. I would recommend showing something more explicit.

P. 9091, L.21: I might argue that this is a judgment call. One could reasonably look at the figures, as presented, and conclude that there is actually a lot of variability in the BC/CO ratio. Since the focus here seems to be on the average BC/CO values observed in different air masses being approximately the same, perhaps the data could be binned

to show averages for specific regions (with uncertainties).

P. 9099, L.15: It is not clear whether this is meant to be a general statement or specific to these measurements. If it is specific, the authors should consider whether or not it rained. If it did not rain during the measurement period, then wet removal processes would have had no influence on the observations.

Nit-picky comments:

Data are plural.

p. 9097, Line 3: This is a hypothesis, not a theory.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 9081, 2009.