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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Ground based aerosol characterization during the South American Biomass Burning Analysis (SAMBBA) field experiment” *by* J. Brito et al.

Anonymous Referee #2

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Review of “Ground based aerosol characterization during the South American Biomass Burning Analysis (SAMBBA) field experiment” by Brita et al.

The authors report on measurements made during the dry-to-wet transition period (Sept.) in the Brazilian Amazon in 2012. A suite of instrumentation was deployed to characterize particle composition in real time (equivalent BC + non-refractory submicron mass), as well as size distributions and CO. They find that organic aerosol (OA) dominates. They find that the OA can be decomposed into fresh biomass burning-derived OA (BBOA) and aged BBOA, along with an oxygenated OA component. The observations themselves are certainly unique, as detailed characterization of particles

in this area has been extremely limited until recently. I have some concerns that the authors are over-interpreting their OA composition data in terms of atomic ratios. I suggest that the authors focus on what was actually measured (e.g. f43, f44 from the ACSM) rather than the derived properties (H:C and O:C), and carefully consider how strongly their conclusions can actually be made regarding variations in particle composition, and also how good a metric O:C (or f44) is for atmospheric processing in this region.

Specific comments follow below:

P12284, L12: The ACSM is not only a “compact” version of the AMS, but is a low resolution version that is incapable of directly determining atomic ratios of the organic particles being sampled. This is a key limitation, given that a fair amount of the analysis presented in this study relies on “atomic ratios,” that are actually estimates of atomic ratios based on previously established relationships between single peaks in the organic mass spectrum and the actual atomic ratios. With these relationships, especially the conversion between the observed fraction of signal at m/z = 43 and the derived H/C atomic atomic ratios, comes substantial uncertainty. This will be returned to in a separate comment.

Aethelometer: It is entirely unclear how the multiple scattering effects correction was performed given that Aethelometer correction algorithms require knowledge of the particle scattering. It is not stated that scattering was measured. Was scattering calculated from the size distributions? More information is required. Without further information, I have concerns over aethelometer accuracy.

ACSM calibration: Calibration was performed using size-selected ammonium nitrate particles. Undoubtedly, there were some fraction of multiply charged particles present following size selection. The much larger size of the multiply charged particles means that they have much greater mass per particle than the singly charged particles. In the AMS, this can be accounted for in part because the size distribution can be measured as there is a chopper wheel within the AMS. No such component exists in the ACSM. It is thus unclear how multiply charged particles are accounted for in the calibration. This must be addressed.

ACSM+BC vs. SMPS+OPC comparison: It is not clear that differences in definition of diameter are taken into account when making this comparison. The ACSM measures by aerodynamic diameter. But the SMPS measures by mobility diameter and the OPC by an optically-defined diameter. These are not all identical, and thus the upper-limit for integration of the SMPS+OPC distributions is not clear in relation to the 650 nm upper limit for the AMS. Perhaps this is why the SMPS+OPC distribution is integrated to 750 nm, but this is not stated. This must be addressed. The authors argue for good closure between the ACSM+BC vs. SMPS+OPC, but this has a few assumptions built in, such as the ACSM CE and the particle density. The CE is assumed to be 0.5. Such a value has been shown to be appropriate for ammonium nitrate, but it is not clear to me that this same value is appropriate for a system that is strongly dominated by biomass burning organic particles. Although Middlebrook et al. argue for no strong deviation from a CE = 0.5 for organics, it is clear in their ARCPAC data, which has the largest BBOA contribution from any of the studies considered, there is a noticeable upturn in the CE at the highest organic mass fractions (see their Fig. 4). Here, the BBOA mass fractions were very large, and thus it is possible that the ACSM CE in this study is too small (leading to an overestimate of the Organic concentration).

Atomic ratios: The authors convert their observed fraction of signal at m/z = 43 to H/C ratios using the relationship in Ng et al. (2011). One only need look at the relationship in Ng et al. (2011) (their Fig. 2) to realize that it is of limited utility, as it is exceptionally flat over a large range of f43 and within this flat region substantial differences are observed between different studies. In other words, the uncertainties are substantial because f43 is not a particularly sensitive metric of H:C, except when f43 is small. Now, it is possible that for a given instrument/region, there is a stronger relationship between H:C and f43 than is indicated when the various campaigns are combined (c.f. Fig. 2 in

Ng et al.). But since the authors adopt the multi-campaign fit from Ng et al., there is an inherent weak relationship between f43 and H:C.

Related, the authors compare their derived H:C to H:C values from Heald et al. (2010). But Heald et al. determined H:C from consideration of high-resolution AMS data, not from the Ng et al. f43 vs H:C relationship. The difference in behavior could easily arise because equivalent things are not being compared. Again, if one looks at Fig. 2 in Ng et al. there does seem to be some indication of a more linear relationship between H:C and f43 for individual studies than there is for the overall combined datasets. I am not convinced that these are comparable. It is my opinion that the data are being overinterpreted here with respect to what can actually be concluded regarding the behavior of H:C, and the relationship between H:C and O:C. I am not convinced by the composition arguments that are put forward on p. 12292. The authors are working hard to provide chemical explanations for observations that may simply be wrong. I realize that the authors are trying to make the most out of the data that they have available, and that measurements in the Amazonian rainforest are no easy task, but I have concerns that they are pushing the interpretation of their data beyond what is justifiable.

P.12292: I do not see how limiting O:C to <0.6 “avoid[s] influence from biogenic aerosols.” This is not a binary system, where one does/does not have biogenic aerosols. It is a binary system with mixing. Variations in O:C can come about due to chemical processing of the BBOA, or can come about as BBOA mixes with biogenic OA (that presumably has a higher O:C). There is therefore no threshold below which contributions from biogenic OA can be ignored…the contributions simply become of lessening importance.

The authors have in no way convinced me that, for this environment, O:C is really a marker of atmospheric processing (i.e. ageing). They simply state that O:C is a surrogate for atmospheric processing, but provide no justification that this is appropriate for this location. Importantly, variations in O:C can easily come about from mixing between BBOA and biogenic (secondary) OA. The observed three factors: two BBOA factors and one OOA factor. Do they find, for example, that O:C varies with the ratio between OOA/(BBOA1+BBOA2)? Or some other combination? This is not discussed, but I think critical to any advancement of an argument that O:C is a good metric for ageing.

P.12293: It is not important that that size distributions were fit using Matlab or that this fitting was automated, unless the authors mean to provide the specific code.

P.12295, L19: I think that this mention of hygroscopicity should be removed, as the authors seem to be basing their argument on an entirely different study. I do not see how mention of this point strengthens the story here.

P12295/12296: I am not a PMF expert. But I must ask the question: if two PMF factors have a good temporal correlation, then are they really different factors? Isn't the whole point of PMF to separate components based on their unique temporal behavior?

Fig. 8 and P.12292: The authors state specifically how they determined deltaCO (difference between observed value and 240 ppb). It is never stated how deltaOA is calculated. Presumably this is the difference between the observed OA and some lower value. But what is the lower value used? Zero?

Fig. 2: Is the fit constrained to go through zero? Does it go through zero if unconstrained? What type of fit was done? Both axes have uncertainty, and thus a standard linear fit is not appropriate.

Fig. 5: For panels b and c, the differences between the axes are subtle, and thus the different lines are not easily distinguished. I suggest making the entire right-hand axis and axis label the red color.

Fig. 5: For panel a, the different axis for the organics is exceptionally subtle, i.e. the green is only transferred as a thin line. The green color must be applied to the entire axis. I had initially missed this, which led me to question the relationship between Fig. 5 and Fig. 6. The authors should aim to avoid creating such (potential) confusion for

their readers by being more explicit in their representation of the data.

Fig. 5: "Average diameter" is insufficient. This should state what type of diameter (e.g. number weighted, surface area weighted)

Fig. 6: This figure could probably benefit from adding a few lines that indicate values from previous studies, so as to place this in context. If this figure is not placed in a broader context, then it loses some of its relevance.

Fig. 7: The authors should make the x-axis minimum 0.

Fig. 10: It is not clear why the caption contains mention of Phase I and Phase II. . .these are not evident in the actual figure.

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