

Interactive comment on “Sources of carbonaceous aerosol in the Amazon Basin” by S. Gilardoni et al.

S. Gilardoni et al.

sgilardoni@gmail.com

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Anonymous Referee #1

This paper deals with measurements of fine and coarse aerosol chemical composition at a background station in the central Amazon basin, providing an overall good mass closure on the identified chemical species during the wet and dry seasons in 2008. A comparison between the concentrations of ‘soot’ determined by thermal-optical methods and by light attenuation techniques was carried out and a first measure of the mass absorption coefficient was provided. Beside that, the main observations on the fine and coarse aerosol chemical composition and principal sources reflect the results already published in the review by Martin et al. (Rev. Geophys., 2010) and in the paper by Poeschl et al. (Science, 2010). The Authors are encouraged to emphasise the real

C14523

progress in understanding the chemical nature of Amazonian aerosol with respect to the above studies.

The authors thank the referee for pointing out the need to emphasize the relevance of this paper content. For this reason the following sentences are added to the text.

Page 29947 line 19:

“This paper illustrates the first long term measurements performed in an Amazon forest undisturbed site since 2001 (Martins et al. 2010), characterizing the chemical composition of fine and coarse aerosol mass during both dry and wet season. This new set of data is extremely useful to show how the Amazon fire reduction of the last decade affected the regional background aerosol composition and to point out the need of up-to-date biomass burning inventories.”

Page 29948 line 3

“PMF analysis of thermograms was applied for the first time to the characterization of carbonaceous aerosol sources in ambient air. Although this approach can be used only to differentiate carbon classes that showed clearly different thermal behaviors, it allowed us to give an estimate of biomass burning and SOA contributions to fine carbon mass and of PBAP to coarse carbon mass.”

Page 29948 line 9:

“Traditional techniques quantify primary biogenic aerosol particles by measuring their number concentration and assuming a known density (Poschl et al 2010). Otherwise carbon content of PBAP is quantified by means of tracer method (Bauer et al. 2002) assuming a known and constant tracer emission factor. The PMF analysis of thermograms is a valuable tool to quantify directly the OC associate to PBAP without assumptions about the particles properties.

Clearly, one original result is the source apportionment of OC based on thermogram analysis. I have some worries about the validity of this approach:

C14524

- The identification of thermograms is based on the comparison with standards. One problem is that the thermo-optical analysis proceeds step-wise, therefore a substantial degree of covariance between samples and between samples and standards is given by the fact that they will all show peaks in the same positions in the thermogram (OC1, OC2, etc.). If the information in each thermogram can be essentially reduced to the intensity of the seven peaks, corresponding to the steps in the analysis, thus the correlation between factors and standards for $n = 7$ is not significant at a significance level of 95% even for $r^2 > 0.90$, that means the resolution of your technique is not good enough.

The authors agree with the referee about the limitations of PMF analysis of thermograms data based on step analysis. For this reason the PMF analysis is performed on the smoothed thermograms without reducing the information to the carbon evolved at each heating step. So the carbon content is not simply described by volatility classes. This guarantees to keep the information about the evolution curve of each class. The way each class evolves depends on the thermal properties of the species that compose that class. For clarification, the following sentence is added at page 29931 line 8:

"The information that can be obtained by thermal-optical analysis is often summarized by volatility classes, i.e the amount of carbon that evolves during each heating step. The PMF analysis of thermograms allowed us to use the information about the thermal evolution curve at each heating step to obtain further insights about the properties and composition of each class. In fact, the way each class thermally evolves depends on the thermal properties of the species that compose each class (Peralta et al. 2007, Grosjean et al. 1994)

In addition, the use of standards is important because it shows that the dominating carbon sources at the study site clearly have different thermal behaviors. The following sentence is added at page 29948 line 3:

C14525

"PMF analysis of thermograms was applied for the first time to the characterization of carbonaceous aerosol sources in ambient air. Although this approach can be used only to differentiate carbon classes that showed clearly different thermal behaviors, it allowed us to give an estimate of biomass burning and SOA contributions to fine carbon mass and of PBAP to coarse carbon mass"

- Even when correlation is significant, the Authors must acknowledge that their reference standards cannot be considered fully representative for the conditions and sources of the central Amazonian basin, and that therefore the similarity between the thermograms of the samples and those of best-fitting standards can be incidental, due to the low specificity of the analytical technique employed. Ancillary information, like the correlation of F2 occurrence with EBC concentrations and with fire counts, are essential for a more robust attribution of ambient thermogram types to reference materials. In this reviewer's opinion, a more prudent conclusion from section 4.2 is that F2f can actually trace biomass burning products but that both F1f and F3f are compatible with the volatility features observed for standard SOA. For coarse particles, certainly the standard of pollen is the best fitting. But what about calcium carbonate?

The differences between smog-chamber and ambient SOA make challenging the investigation of ambient SOA. Moreover, the lack of tracers to track SOA evolution makes even more difficult the quantification of SOA without the use of further measurements, like radiocarbon. Nevertheless, the assignment of profile 1 to SOA is supported by literature study performed in similar sites, and showing how SOA composed a significant fraction of organic carbon. The following sentence is added at page 29943 line 17:

"The comparison among PMF profiles and standard thermograms shows that the volatility of factor 1 resembles that of SOA from smog-chamber experiments. The lack of unique tracers for SOA and the expected differences between ambient and smog-chamber SOA do not allow a more robust attribution. Nevertheless, the AMS measurements performed at the same site during the wet season confirmed that SOA dominated organic mass of submicron particles (Poschl et al. 2010)."

C14526

The carbonate concentration in the coarse aerosol mode was negligible compared to the amount of organic carbon, so we can exclude that carbonate can interfere with the thermal optical analysis of carbonaceous particles and PMF profiles (Page 29930 line 10).

Minor comments: - Page 29926, lines 9 – 12. Indeed, deep convection lifts polluted boundary layer air to high altitudes, but in the process aerosol particles are efficiently scavenged, therefore the transport is observable mainly for the insoluble gaseous compounds.

The sentence is modified as:

“...increasing the relevance of the Amazon area as source of gaseous aerosol precursors on a global scale”

- Page 29928, line 21: “filters were not pre-treated prior to analysis” means that they were not baked before sampling, or that after sampling they were analyzed without extraction or acid addition?

Filters were not baked prior to collection. Text is modified accordingly

- Page 29932, lines 8 – 11. The Q values are lower than the theoretical Q, meaning that the uncertainty is somewhat overestimated.

The smaller Q values compared to Q theoretical indicate that the model input might overestimate the uncertainty. The authors recognize that this can compromise the accuracy of the PMF results. For this reason the extra model uncertainty was removed and the uncertainty analysis was carried out to identify variables associated with large residuals. Variables with a probability larger than 10% to have scaled residuals larger than 5 were used as weak variables. This criterion identified as weak variable, the one describing the volatility behavior below 200 °C, thus corresponding to the most volatile fraction of organic carbon. This result is consistent with a larger uncertainty associated to those species that more easily partition between the gas and the aerosol phase.

C14527

The Q values improved, the factor profiles did not change significantly, the biomass burning carbon mass fraction did not change, while the contribution of SOA and volatile profiles changed. The SOA carbon contribution changed from 34% to 43%, while the volatile fraction contribution decreased from 23% to 13%. The correlation between the model unexplained OC during the wet season and the secondary organic carbon from PMF analysis was improved ($r^2 = 0.74$). Concerning the coarse mode aerosol fraction, the factor profile and the campaign average contribution of primary biogenic aerosol particles did not change, although a larger difference was observed between the carbon mass fraction of wet and dry season, consistent with the seasonality of primary biogenic aerosol. The results are corrected in the text, tables, and figures.

To explain the residual analysis, the following sentence is added:

“Variables with a probability larger than 10% to have scaled residuals larger than 5 were used as weak variables. This criterion identified as weak variables those describing the volatility behavior below 200 °C, thus corresponding to the most volatile fraction of organic carbon. This result is consistent with a larger uncertainty associated to those species that more easily partition between the gas and the aerosol phase.”

- Page 29932, line 14. By increasing the absolute value of Fpeak normally increases Q, therefore it is obvious that for minimizing Q Fpeak must be set to zero. Normally, Fpeak is applied to obtain solutions which are more easy to interpret or that looks “more reasonable” than the one with minimized Q.

Sentence was modified as follow:

“Fpeak equal to zero was chosen as the best solution, since no significant improvement was observed in the correlation between source profiles and ambient aerosol profiles by setting Fpeak different from zero.”

Page 29934, line 9. The factor of 1.4 for fresh organic particles applies to combustion aerosol or to freshly produced SOA, not to PBAP, for which a more representative value

C14528

should be provided.

To the best of our knowledge no direct measurements of the OM/OC is available for PBAP. The authors assumed that PBAP was dominated by aliphatic functional groups and consequently decided to use the lower bound of the OM/OC ratio reported by Russell et al 2003. This comment is added to the text at page 29934 line 13.

Page 29939, line 16. "N+3" is evidently a typo.

Corrected as NO₃⁺

Section 4.3. The main outcome of the comparison with the model is that the interannual variations in biomass burning activities leads to significant discrepancies in calculated vs. observed concentrations of aerosol OC and EC. However, what if we scale down the emissions based on observed proxies for biomass burning (e.g., fire counts) and their deviation in 2008 respect to the reference years for the emission inventory?

The analysis indicated by the referee requires calculating the average fire counts based on satellite data in South America during the period 1997-2001. Then the ratio between this count and the count of fires observed during the study year (2008) can be used to scale the emission inventory map used in the model. At this point the model should be re-run with scaled emission inventories. The authors thank the referee for the suggestion and recognize that this would be an interesting validation exercise. Nevertheless, the comparison of the source apportionment data with the model does not aim to validate the model itself. One of the goals of the comparison is to point out the need for accurate emission inventories, especially in an environment subject to rapid changes, and the error that can derive from the use of accessible but not updated emission data.

Table 2 at page 29960: 'BC' should be 'EBC', according to the text.

Corrected

Caption of Fig. 8. Please, indicate the variables referred to the left and right vertical axes.

C14529

Caption of figure 8 was modified accordingly.

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