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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical transformations in organic aerosol from biomass burning" *by* A. Hoffer et al.

Anonymous Referee #1

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After a very nice introduction, the authors describe particulate carbon results from a sampling campaign in Brazil both during and after periods of local biomass combustion. In addition to examining total carbon concentrations, they have also determined amounts of (operationally defined) "high molecular weight" carbon, as well as levels of water soluble organic carbon and specific organic molecules. From their results they suggest that photochemical aging of the biomass burning aerosols generate more refractory particulate carbon such as humic-like substances.

Overall, the manuscript is worthy of publication, although there are two major issues, and a suite of minor ones, that deserve more attention during revision.

Major Comments

Page 8034, lines 18-21. The authors assume that CO2 generated at temperatures above 280 C came from high molecular weight (HMW) organics, but no justification is provided and the size of “HMW” is not described. Given the importance of the 280 C HMW “cutoff” in this paper, there should be more experimental exploration of how different MW organics behave in the EGA and an explanation of the approximate size of “HMW” organics. It seems feasible that the EGA behavior depends not just on MW but also on chemical composition (e.g., degree of oxygenation) and perhaps on differences in the chemical matrices of the particles. In addition, does elemental carbon (e.g., soot) appear as a HMW organic (especially in aged samples)? These issues should be examined and discussed. Similarly, the possibility of LMW organics appearing as HMW compounds because of charring (page 8035, line 2) should be examined. While I don’t expect that the authors will provide an exhaustive exploration of these issues for the present paper, using only one species (levoglucosan) to choose 280 C as the transition to “HMW” compounds is an unjustified assumption and the technique overall is poorly characterized. Note that although the term “refractory”, as used more in the second half of the paper, is a better (less specific) term than HMW, it still begs for experimental verification.

Page 8040 - 8041. This is an interesting discussion of PM reactivity and the resulting change in concentrations of marker compounds. One missing point, however, is the potential (photo)chemical production of the phenolic acids from precursors. For example, the oxidation of vanillin (a common component in wood combustion PM) should be a source of vanillic acid, and this is probably more rapid during the day than at night. This complicates the day/night differences in the ratios of phenolic acid/levoglucosan, since (photo)chemistry could be both a source as well as a sink of the phenolic acids. Perhaps this is a reason for the less clear diel pattern of vanillic acid?

While I agree that the data suggests photochemical processing of less refractory material leads to more refractory compounds, there is no good evidence in the current

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manuscript that the products are necessarily “HULIS” (as described in the introduction). In addition, at the same time that there is formation of more refractory material, it’s likely that there is formation of low molecular weight compounds (e.g., formaldehyde) that evaporate from the particles.

Minor Comments

Page 8032, top paragraph. The “day” and “night” times for sampling should be more explicitly defined. They appear to be 12-hour windows, but what were the times and were they consistent for each sample? Given the time of year, it seems the “night” window in fact contained some daylight hours.

Pages 8032-33. What are the errors or uncertainties for the WSOC measurements? Since the values are determined by difference, the uncertainties could be large.

Page 8033. The internal standard (IS) was added to the filtered solution made from extracting the sample filter, but it seems that a more representative technique would have been to add the IS to the sample filter prior to extraction. Have the authors tried this? Does it make a difference? It seems that chemisorption of the oxygenated compounds to the filter could be significant.

Page 8033, end: It would be useful to add another sentence or two about how the hydrolysis methylation works (e.g., the types of bonds that are hydrolyzed and the efficiency of hydrolysis).

Page 8035, lines 19-20. From my reading of Fig. 2, the day-night difference in HMW/TC is certainly not statistically significant for the transition period (given the large overlap in error bars) and probably not significant for the biomass burning period (although this depends on what the error bars actually represent; see comment for Fig. 2 below). What p-value is considered significant?

Page 8037, section 4.3. No speciation data is presented for the semi-clean period. This is probably because the PM mass, and amounts of tracers, were very low during

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this period, but regardless of the reason it should be addressed.

Table 1. It would be useful to include the TC mass concentrations for each sample (even though the average values for each period are in Fig. 2).

Figure 2. The meaning of the error bars needs to be better described since the term "variability (confidence interval)" is too vague. Do they represent ś 1σ? 90% confidence intervals?

Figure 4. The figure would be better (i.e., it would offer truer comparisons) if the two y-axes both had the same zero point.

Statistics. The statistics in the paper need some attention. For example, the interpretation of p-values appears to be inverted (e.g., pages 8037, line 3 and 8038, line 27). In these instances the p-value, roughly speaking, should be the probability of obtaining the two sets of sample data if the two populations are the same. For example, in the case of two sample means, $p<0.05$ indicates that there is less than a 5% chance of obtaining these sample means if the population means are the same (i.e., it's unlikely that there is not an actual difference). $P>95\%$ (p. 8037) would mean that the population means are almost certainly the same, not that they are different.

Although it has been stated in previous papers, it is worth repeating in this manuscript that the very high WSOC content of these particles has important implications for their ability to act as CCN and influence cloudiness, climate, etc.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 8027, 2005.