**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on **"Characterization of the organic composition of aerosols fromRondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds"** *by* **S. Decesari et al.**

S. Decesari et al.

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Reply to Referee 1.

Answers are given specifically for each of the comments and questions risen by the Referee:

1. During the SMOCC campaign, only CO_2 and CO concentrations were measured, not VOCs. Although we hypothesize that most of the polar fraction of the aerosol forms through a progressive gas-to-particle conversion process starting in the fires and con-

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tinuing during the aging of the plume, we have actually no direct evidence for that from this experiment. The experiment was conducted at a single (fixed) station, impacted by the hazes formed by widespread fires in the region, while the smoke directly emitted by single fires was never sampled at the ground site. From the aircraft, no aerosol chemistry data are available. Clearly, the sampling strategy was unsuitable to study the transformation of biomass burning aerosol and oxygenated VOCs in the plumes. For this reason, the hypothesis of formation of the polar organic aerosol components was only presented as a background in the Introduction section and not further discussed in the paper. The picture of the organic chemical composition we are presenting is essentially "static". Some insights in the ongoing photochemical processes in the aging smoke are presented in the paper by Hoffer et al. (Atmos. Chem. Phys. Discuss., 5, 8027-8054, 2005; ACP, in press).

2. As indicated by the Referee, the possible degradation of the organic material during prolonged sampling could not be avoided during this experiment, since the impactors and filters used for organic analysis were undenuded. On the other hand, although during the wet period the sampling time was extended to two to four times that adopted in the dry period, the concentrations of the oxidants in the air was lower. Daytime ozone concentrations decreased from 30 - 50 ppb in the dry period to 10 - 20 ppb in the wet period (unpublished results), because of the decrease of VOCs concentration and of the enhanced cloud cover reducing solar radiation at the ground. Therefore, we do not expect larger artifacts in the wet period samples compared to those collected in the dry period, at least with regard to sample degradation from atmospheric oxidants.

3. Actually, after correction for the sampling biases mainly due to uncertainties in the flow measurements, the HiVol measurements provided higher WSOC concentrations than the Berner impactor during the whole campaign (see Figure 1 of the new version of the manuscript). The discrepancy is indeed larger during concentration peaks, possibly due to enhanced bouncing of the particles on the impactor plates.

4. The uncertainties in the analysis of TC, EC and WSOC were of the order of 5% of

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the TC value, therefore they were omitted from Figure 1. The accuracy of the analysis of organic compounds by GC-MS and other speciation techniques was of the order of 10 - 20% (as reported in sections 2.4 and 2.5). Sampling biases had a much bigger impact on the comparison of the concentrations of carbon fractions and organic compounds measured by the various filters and impactors. Whenever such biases could be identified and quantified they were corrected by normalization to TC (e.g., for comparison between SFU and HiVol filters) or to sulfate (e.g., for comparison between different impactor systems). The accuracy of these corrections is difficult to estimate but cannot be better than 20%. Therefore, the values in Table 4 are reported in the new version of the manuscript with only one or two significant digits.

5. Figure 2 shows the composition of the WSOC fraction speciated at the molecular level. We added to the figure the total concentration of the identified compounds together with the average OC and WSOC concentrations for the same periods. We also improved the discussion in the text in order to clarify the recovery of the molecular speciation method.

6. The EC/TC ratios found in this study are in agreement with literature data on biomass burning aerosols (e.g., Reid et al., Atmos. Chem. Phys. Discuss., 2004). We agree that the relatively low content of EC and the large fraction of (polar) water-soluble organic material of biomass burning particles indicate that char produced during the combustion represents a relatively small fraction of aerosol TC mass.

7. Indeed, with finest size range we referred to the lowest stages of the impactors, i.e., those collecting particles below 200 nm. We performed changes to the text of the manuscript version for ACP to make it clearer to the reader.

8. The 2-methyltetrols are believed to be formed from isoprene through a heterogeneous mechanism involving hydrogen peroxide as oxidant, which itself is generated by recombination of hydroperoxy radicals (Claeys et al., 2004b). The lower absolute 2-methyl-tetrols concentrations in the wet season can be explained by the lower oxi-

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dant content of the atmosphere and lower isoprene emissions during this season. This issue will be treated in more detail in an article that is mentioned in the manuscript and is in preparation (Claeys et al., in preparation). It is pointed out that Figure 3 shows % contributions of the individual compounds to the particulate mass and not absolute concentrations. As can be seen in this Figure the 2-methyl-tetrols indeed show the highest % contribution to the PM in the wet season; this is not so surprising considering that the contribution from biomass burning aerosol as reflected by the low contributions from levoglucosan, a marker for biomass burning, is very low in this season.

9. During the experiment, it was found that sampling with different collection systems produced significant discrepancies with respect of total concentrations of the chemical species. On the other hand, the chemical composition (i.e., mass ratios between the different chemical components) of the aerosol was fairly consistent between the different samplers. For example, the Berner impactor underestimated the concentrations of WSOC and sulfate in the fine fraction of the aerosol by more than 30 % compared to HiVols, but the WSOC/sulfate ratios measured by the two systems correlated well and were almost the same (slope = 1.07; $r2 = 0.80$; n = 20). We concluded that sampling biases between the samplers were mainly due to uncorrected flow measurements and to bouncing of particles on the impactor plates, rather than to volatilization of organic compounds. It is possible that the most volatile fraction of the particulate organic compounds (i.e, the fraction most subject to sampling artifacts) was collected with low recoveries by all systems.

10. Due to the compensation of the decrease of anhydrosugars concentrations with a parallel increase in concentration of natural polyols, the hygroscopic properties of the carbonaceous particles are not expected to change dramatically during the dry to wet season transition. Nevertheless, evaluating the implications of this findings for cloud formation processes and the climate system is beyond the scope of the present paper. The main objective of our study was to provide a "realistic" representation of the aerosol organic composition suitable for model applications. An example of a 1-D cloud model

employing the model compounds evaluated in this study can be found in the paper by Mircea et al. (ACP, 5, 3111-3126, 2005).

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5687, 2005.

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