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Atmospheric
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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.

Anonymous Referee #1

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General comments

The paper focuses on the very interesting and highly relevant subject of cloud droplet activation probabilities of organic aerosols originating from the tropical rainforest and the impact of biomass burning. Various methods have been used to elucidate the water soluble organic fraction at different aerosol particle sizes during the three periods

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‘dry season’, ‘transition period’ and ‘wet season’ in a field experiment in the Brazilian tropical rain forest. Moreover, single organic compounds were identified by GC-MS, IC and IEC as well as the total and elemental carbon was investigated at the different conditions. On average, it was found that about two third of the fine organic aerosol mass and one third of the coarse aerosol mass are water soluble, thus capable to act as nuclei for cloud droplet formation. The very interesting outcome of this experiment was the fact that the water soluble organic compound fraction remains fairly constant during all the investigated periods, independent on the origin of the organic compounds, either of photooxidation of VOC or of pyrogenic formation during biomass burning. The paper is written well and presents the results clearly. Nevertheless, there are some remarks to be made and some questions to answer for the results shown.

Specific comments and questions

1. Has anyone performed laboratory experiments or simulations concerning VOCs released during biomass burning and their reactions in the gas-phase or their pyrolysis. I would guess none of the usual rate constants obtained at e.g. room temperature can be used because of a much higher diffusivity of the compounds thus, a higher probability to react. This would be of interest for understanding the production of the compounds found, in case they are not emitted directly. From the results presented with the water-solubility independent on the present conditions it does not matter if the compounds are pyrolyzed or oxidized in the gas-phase. However, I would suspect a difference, but I might be wrong.
2. You might allow one question concerning the compounds analysis and the long sampling period. I am aware of the huge amount of material needed for performing the analysis, but what is actually going on at the collector surface during this long time (> 1 day), passing the gas-phase oxidants continuously along and allowing a faster

reaction because of a ‘pre-concentration’ on the collectors surface. Is this able to affect the results presented?

3. Figure 1 is quite interesting including the good match between Berner Impactor and High-Volume sampling results. Why do both not match between approximately the 19^{th} and the 22^{nd} of September? Did anything special occur or is there any reason for that?

4. I miss the uncertainty range in the plot as well as for some other results, to claim a reasonable conclusion, although I assume it to be done already.

5. What about unidentified compounds In Figure 2? Pie charts etc. are nice to view, but the amount of unidentified should be included here.

6. Elemental carbon seems to be of minor importance in this study at least in the fine fraction (Table 1). So pyrolysis impact only on the coarse mode and the production of fine particle mass is mainly due to gas-phase oxidation? This would explain you observation of the good correlation of water soluble compounds in the gas-phase and the total carbon as well as the particulate matter. Since the compounds with the highest amount of functionalities (-OH, -COOH etc) possess the lowest saturation vapour pressure forming most likely secondary organic aerosol mass.

7. What is meant by the sentence ‘In all periods, the carboxylic acids are less abundant in the finest size range, as well as in the coarse fraction.’ on page 5710? Since the fine particle size range is usually defined from 0.01 - 1 μm in diameter and the coarse particle size range from 1 - 10 μm. Do you mean the fine aerosol range below 100 nm (ultra-fine and Aitken mode) and the coarse mode above 1 μm, so that the maximum is highest in the accumulation mode? Please specify more clearly.

8. Why are 2-methyltetrols less abundant in the fine fraction during the wet period? From Table 2 it looks so, but using Figure 3, which is referred to it seems that 2-methyltetrols are highest in the fine aerosol size range during the wet period. If only the smallest section is meant, the maximum occurs during the transition period. As stated in the previous comment a definition of names and size ranges, e.g. the latter in brackets, will help in understanding, at least myself. However, the maximum at larger particle sizes is not surprising, since the partitioning is favoured with larger or-

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ganic aerosol masses present (see Pankow, 1994) and the increase of the saturation vapour pressure at smaller sizes due to the Kelvin effect. Because of the sufficiently high water solubility of 2-methyltetrol, it cannot constitute a large fraction of the largest particles, since these have been removed by previous clouds and rainfall, with only the insoluble particles remaining. Therefore, the meteorological history of the air including the studied particles gets important, which is unfortunately not treated in here.

9. The authors state on page 5714 that they used sulfate sampling efficiencies for organic compounds for obtaining the organic concentrations. Do they actually behave exactly similarly? I know that performing field measurements can be a tough job and sometimes rough approximations are done to get the dataset interested in. But as pointed out earlier, the aerosol samples were collected for more than a day, which is reasonably long to allow any processing of the compounds on the impactor stages, when passing all the ambient oxidants through the sampler once the compound has attached. I would expect it different to the sulfates. Have you checked it with other compounds if available? Do they behave similar?

10. Finally, your main conclusion is that the water soluble fraction remains constant independent of the conditions present, i.e. biomass burning or not, wet or dry. Would you conclude that probably the individual compounds contribution might change, but the general solubility is constant with time and can thus be treated in a climate model on a regional scale or a local scale? Do you expect this to change once the global temperature is rising according to the expectations of climate change causing an increase in individual biogenic VOC emissions? I do not know about the exact link between higher temperatures and biomass burning activities (anthropogenic and natural), but would the individual ratio change or is every reactive organic compound processed sufficiently fast to the described equilibrium between water-soluble and insoluble ones?

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Typos and small corrections

1. p. 5696: ‘Hoffer et al., 20051’ should be ‘Hoffer et al., 2005[1]’.
2. Figure 1: use ‘sep’ and ‘oct’ instead of ‘set’ and ‘ott’ to abbreviate September and October.
3. Figure 3: although the present figure is correct, it might help the reader to add ‘dry’, ‘transition’ and ‘wet’ to the time given, to allow an easier understanding of the differences between the different seasons.

References

Pankow, J., 1994, An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. Atmos. Environ., 28, 189-193.

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

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