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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.

Anonymous Referee #2

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This paper presents a comprehensive study of organic aerosol during the LBA-SMOCC 2002 experiment. Several analytical techniques were used for the molecular speciation and characterization of functional classes. The combination of several analytical techniques and different sampling systems is the only way to get a comprehensive picture of ambient organic aerosol and should be applied in more field campaigns. However, the wealth of different data sets (different samplers, size ranges, measurements, meteorological periods) requires a structured presentation and thorough dis-

cussion of the results. Here I see the major problem of this paper: in several cases it is hard to follow the reasoning of the authors, because of an unclear structure of the text and/or missing/incorrect references to tables and figures (especially Figure 5, see detailed comment below). The labeling of figures should be improved in order to help the reader navigate through the complex data structure. It might be helpful to indicate the metrological period, size range, sampler for each figure (e.g. Figure 2).

I have the impression that the discussion (4.2) focuses very much on the 1HNMR measurements and the chemical model. However, the 1HNMR measurements were not part of the experimental and results section. They are to be published in a separate paper by Tagliavini et al., which was not yet available at the time of this review, so I cannot assess potential conflicts. The authors should be careful not to have too much overlap. Could the authors please give a short overview of what will be presented in that paper. Also the chemical model, which is the basis for the model compounds, is not described at all in this paper. On the other hand, the main part of the data presented in the results section (individual compounds identified and chemical classes characterized by IC-UV) seem to be of minor importance in the discussion. Maybe this is a misconception that can be clarified by the authors.

If these issues can be resolved, this paper is a very valuable contribution to the understanding of the organic aerosol composition. The proposed model compounds are an interesting approach to reduce the complexity of organic aerosol and make it accessible for atmospheric chemistry models.

Specific comments

2. Experimental: The experimental section should be more coherent. For example section 2.4 is very short and 2.5 (which admittedly consists of two subsections) is much more detailed, although both methods are based on published methods. No information on standard compounds is given in 2.4 whereas they are extensively discussed for 2.5. On the other hand, details on the silylation are given in 2.4, but not in 2.5. I realize

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that the measurements were performed in different labs, but a more uniform structure of this section would be desirable. For readers not familiar with all analytical techniques it would be helpful to include the full name of each method (not only abbreviations as in the headers) in the first sentence of each paragraph (see 2.7). It would also be useful to indicate the laboratory involved in the analysis. GC-MSUA measurements were presumably performed at the University of Antwerp, but this laboratory is not mentioned at all in the whole text (except for title and acknowledgements). Could you indicate how many samples were measured with each technique, as done for TOC analysis.

Page 5702, line 9: What was the duration of the gradient? Why do you refer to Table 1?

Page 5706, line 8: "...relative concentrations of the different identified chemical classes..." It would be better not to talk about “chemical classes”, but about “classes based on individual compounds identified” OR “fraction characterized at the molecular level” (as in the caption for Figure 2). Otherwise they might be mistaken for the chemical classes characterized by IC-UV.

Page , line 11: “However, the available TC size-distributions indicate a relatively constant TC/PM ratio for submicrometer aerosols, which are essentially carbonaceous particles (Fuzzi et al., 20052). Therefore, the fraction of TC speciated at the molecular level is also expected to be higher for particles with diameter larger than 0.4 μm than for those in the finest size range.” Could you explain the reasoning/motivation behind these two sentences? Does this statement/assumption have any relevance for further discussion?

Section 4.1: The MOUIDI and Berner samples were “collected approximately in parallel”. What was the (relative) overlap in sampling time? Could you give detailed sampling times? Were the samplers located directly next to each other? Huge discrepancies have been reported for sampling systems operated in parallel (eg. Mochida et al.). This would be even more pronounced for different flow rates, which were presumably

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used in this case (details are not given in experimental section). The normalization to sulphate concentrations might compensate for some differences, but will very likely not resolve all problems. Was it not possible to split samples from one of the samplers? In view of these limitations, the discussion in section 4.1 should be a little bit more cautious. The figures given in Table 4 (e.g. 12.1%) imply an accuracy that can certainly not be achieved by the applied procedure.

Figure 5: Figure 5 and the corresponding discussion should be thoroughly revised. It is difficult to relate the discussion in the text to the graphs. There are several inconsistencies. Page 5716, lines 24-29: "Figure 5 shows ... . The functional group compositions of the IC-UV classes isolated from the PM2.5 HVDS sample collected on 25-26 September is also reported." The caption for Figure 5 gives the impression that only functional group compositions as determined by 1HNMR are displayed. Furthermore, it would be helpful to indicate which specific graph (5a,b,c,...) you are referring to in the text, presumably 5c in this case. Page 5721 , lines 2-7: "Figure 5 shows ... . In contrast, the representation of the composition of the NC fraction, of the coarse and fine aerosol samples from the wet period is not as good." This sentence should be rephrased, e.g. "... fine aerosol from wet period, NC fraction and coarse aerosol ". Otherwise one might get the impression that the NC fraction and the fine aerosol samples originate from the wet period as well (which is not the case for the samples shown in Figure 5). Again, referring to specific graphs would make reading much easier. Indicating wet, transition and dry period for each graph might also be helpful (otherwise the reader has to go back to the experimental section to find out which graph/date corresponds to the period mentioned in the text). Caption of Figure 5 - What about the coarse fractions (1.2-3.5μm and 3.5-10μm) for "23Sept Day" in Figure 5a? Were they not measured or calculated? Those size ranges are shown in Figure 5b. - The last part of the caption for Figure 5 ("(d) one coarse HVDS sample from the transition period.") does not relate to any graph.

Page 5718, line 26: No description or direct reference to the "chemical model" is given.

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A short explanation would be useful. What role, if any, do the individually identified compounds play in this model?

Page 5271, line 16: In my opinion the word “explicitly” should be omitted, as each fraction is only represented by one model compound.

Technical comments:

Page 5696 L6/18: TC is not explained in/before line6 (except for abstract), but it is explained in line 18; why not on page 5695 line 7, where the abbreviations OC and EC are introduced?

Page 5699 L13: Should be 0.25μm film thickness (in 0.25mm ID column!)

Page 5700, lines 6-7: should be "...part of the quartz filter sample (1/4 of the whole filter area) was used..."

Page 5708 line 25: "...levoglucosan and potassium sulfate (Maenhaut et al., 2005, in preparation)". "(" missing

Page 5271, line 5: The size range should be 0.42-1.2 μm as given in Figure 5a,b (not 0.42-1.42 μm)

Table 3: label first column as particle diameter (μm); give unites of concentrations in table

Figure 2: according to the text Figure 2 refers to fine aerosol, but no indication is given in the caption or legend of Figure 2 (would make understanding the figure easier)

Figure 4: axis label of Transition (Day) should be 10 not 0

References: Mochida, M., A. Kawabata, K. Kawamura, H. Hatsushika and K. Yamazaki (2003). “Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific - art. no. 4193.” Journal of Geophysical Research-Atmospheres 108(D6): 4193.

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Interactive Comment