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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.

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Reply to Referee 2.

General comments: The main concerns of the Referee are about the quality of the presentation of the results and about the unclear links between the model compounds and the outcomes of the chemical analysis presented in the Results section. In this respect, the Referee believes that the discussion focuses too much on data presented in another paper (i.e., the 1HNMR data) and on the model compounds. We acknowledge the Referee for his thorough review of the manuscript and the useful comments.

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Interactive Discussion
Discussion Paper

We have tried to address all the points raised by the Referee in the new version of the manuscript prepared for publication on Atmos. Chem. Phys., with a particular care in improving the discussion about Figure 2, Table 4, and especially section 4.2, which was fully revised. Above all, we would like to avoid the misconception that the results of the chromatographic techniques are not useful for the evaluation of the model compounds. The categorization of WSOC into the three major classes separated by the IC-UV technique (neutral compounds, mono-/di-acids and polyacids) was used as a frame for the model compounds. A direct representation of the classes of individual compounds identified by GC-MS, IC and IEC techniques was also included in the model. In fact, despite the low recovery of the speciation techniques with respect of OC or WSOC, they were fairly efficient in analyzing the most polar fraction of WSOC (i.e., carrying the most part of COOH and hydroxyl groups), as indicated by the comparison with the 1HNMR data. Since the SMOCC project focused on the hygroscopic properties of the aerosol, we retained as much information as possible on the most polar fraction of OC in the model compounds. On the other hand, we agree with the Referee that the 1HNMR data are central for the discussion and must be introduced in the preceding sections of the paper. The Experimental and the Results sections have been implemented accordingly, providing details on the types of samples which underwent 1HNMR characterization and reporting a brief presentation of the main results. A full discussion of the 1HNMR measurements is included in the paper by Tagliavini et al. (2005), now published (ACPD, 5, 9447-9491). By making these changes to the original manuscript, we have attempted to clarify the links between the results of the chemical analysis and the model compounds. We do not believe that the paper focuses too much on the latter, and that both aspects are essential in this study and are consistent with the title of the paper.

Specific comments

- Section 2.5 has been reduced in length, but not cut substantially. One of the GC-MS(UA) methods, i.e., method 2 followed for the determination of carboxylic compounds, has not been previously reported and therefore had to be presented in more detail. The UA laboratory used more sophisticated methods compared to MPIC and especially adopted internal recovery standards extensively. Since the two protocols of analysis provided different recovery with respect to various classes of compounds identified (see Table 2), the reader might be interested in the details of the two methodologies. We agree with the Referee that a clearer reference of the data to the original laboratories involved in sampling and analysis was desirable. In the new version of the manuscript, the origin of the samples, the corrections for sampling biases, as well as the laboratories involved in the chemical analysis are now always indicated in the text and/or in the captions of the figures and tables, whenever the concentrations of chemical compounds or carbon fractions are presented. Explanation of the abbreviations for the analytical techniques (e.g., “GC-MS”) are now systematically reported in the Experimental section. The number of samples analyzed with each technique for molecular speciation of the organic compounds is indicated in Table 2 of the manuscript.

- In the new version, we avoided the term “chemical classes” when referring to the classes of compounds identified at the molecular level, as suggested by the Referee.

- The final part of section 3.3 (dealing with TC/PM ratios in MOUDI samples) was removed, since it was not essential for the following discussion.

- The sampling times of the IFUSP MOUDI and Berner (BI) impactor samples, collected “approximately in parallel”, are now reported in the text. As the Referee can easily check, the difference between the sampling times of the two impactors is within 10% of the total duration, with the exception of the third couple of samples, for which BI sampled 8 hours more than MOUDI on 46 and 38 h total sampling times for the two impactors, resulting in ca. 20% of difference. The significant effects on collection of some organic species due to large differences (i.e., of a factor of five) in the sampling time investigated by Mochida et al. (2003) do not apply to samples discussed in section 4.1. The observed discrepancies in the measurements performed by different impactor and SFU systems were mainly attributed to differences in the sampling efficiency, because some of the samplers (i.e., the Berner impactor) systematically provided lower concentrations. It was also found that the same sampling artifacts were observed in the same size range for all inorganic ions and WSOC. For this reason, normalization to sulfate concentrations was introduced to correct for the sampling biases between the two impactor systems used to provide the concentrations of the organic compounds identified at the molecular level (the MOUDI) and the IC-UV classes and WSOC (the Berner). IFUSP MOUDI samples were used for these purposes instead of UGent MOUDI samples because sulfate was determined only on the former. We agree with the Referee that the accuracy implicit in some data reported in the original Table 4 cannot be reached by the applied procedure. The values in Table 4 are now reported with only one or two significant digits.

- The discussion referring to Figure 5 has been thoroughly revised and the reference to each panel of the figure was clarified in the text. Two impactor stages of the BI sample in Figure 5a are missing because they were not subjected to 1HNMR analysis due to the low concentrations in the extracts. This was clarified in Section 2.9.

- A new table (now Table 5) was included in the paper, reporting the details of the evaluation of model compounds for the WSOC composition characteristic of the dry period in daytime conditions. The explanation included in the text illustrates the input information and constraints (namely the concentrations of total WSOC, of the IC-UV chemical classes, and of the classes based on individual compounds identified) and the data set used for validation (the 1HNMR composition). The mixture of model compounds is not produced by any algorithm, but it is simply obtained heuristically by changing the structure and relative concentrations of the model compounds representing the unidentified WSOC, until a reasonable agreement with all the available 1HNMR composition is reached. To avoid misconceptions, the term “chemical model” was omitted in the text. Despite their small contribution to total WSOC mass, the individually identified compounds were treated as distinct model compounds, since they include the most water-soluble species with the lowest molecular weight. Therefore, they are be-

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lieved to have a particular importance with respect to the hygroscopic properties of the aerosol, which are a function of the solubility of the aerosol chemical components in subsaturated conditions and of the molality of the aqueous phase formed on the particles (Mircea et al., Atmos. Chem. Phys., 5, 3111-3126).

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

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