

Interactive comment on “Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers” by S. Kundu et al.

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Dear Editor, Here are the point-by-point responses to the comments of the first reviewer. Sincerely, S. Kundu

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This article provides novel insights into the formation of oxalic acid and other low molecular-weight dicarboxylic acids in biomass burning aerosols that were collected in the Amazon during the dry period of the 2002 SMOCC campaign. A better understanding has been achieved of sources and formation processes of dicarboxylic acids through detailed analysis of their molecular distributions and that of related compounds in day-and nighttime samples. Convincing data are presented that biomass burning is an important source of dicarboxylic acids in the atmosphere, and that low-molecular-weight dicarboxylic acids have mainly a secondary origin in biomass smoke. Some minor revisions are suggested as detailed below.

Specific comments:

Comment: Page 19787–line 5: it is not clear how the quantitative determinations were made the quantitation/calibration procedures should be briefly included in the experimental section.

Response: According to the suggestion, we have clarified the quantification as well as identification procedure by modifying and adding few sentences: Peak identification was carried out by comparison of the GC retention times with those of authentic standards (derivatives of C2-C11 dicarboxylic acids, glyoxylic acid, 4-oxobutanoic acid, pyruvic acid, glyoxal and methylglyoxal). Identification of esters and acetals was also confirmed by mass spectral analysis using a GC/MS instrument (Thermoquest, Trace MS) with similar GC column conditions. The quantification of the compounds was performed in comparison to the GC response factors with those of authentic standards. The GC peak areas were calculated with Shimadzu C-R7A Plus integrator. These points will be added in the revised manuscript.

Comment: Page 19789–line 19 and places elsewhere: it is hard to consider the C5-C10 compounds as high-molecular-weight compounds. I still consider these compounds as low-molecular-weight compounds; a better term would be medium-chain compounds.

Response: Similar ambiguity about the definition of low-molecular-weight (LMW) and

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high-molecular-weight (HMW) was raised by another reviewer. We will replace LMW by smaller-MW and HMW by larger-MW in the revision.

Comment: Page 19792–line 21: I do not consider it a striking phenomenon that the concentrations of dicarboxylic acids and related compounds normalized to the biomass burning tracer levoglucosan are higher in the daytime than in the nighttime. The highest atmospheric concentrations of levoglucosan are found during nighttime when smoldering combustion takes place; hence, even in the case that the concentrations of the dicarboxylic acids would not reveal day/night differences, the concentrations normalized to levoglucosan would be higher in the daytime. I suggest to simply write: “We have observed that the concentrations of dicarboxylic acids and related compounds normalized by the.”

Response: We will take this comment in the revision.

Comment: I think it could also be informative to calculate the percentage contributions of the dicarboxylic acids and related compounds to the OC and to evaluate their day/night differences.

Response: Actually we have already reported the relative abundances of the carbon component of diacids and related compounds to OC and WSOC in another paper using the same set of samples (Kundu, Kawamura, Andreae, Hoffer and Andreae, *Journal of Aerosol Science*, in press, 2009). I would quote the results: “The mean contribution of total diacids-carbon to OC was 1.7% in the daytime versus 1.4% in the nighttime, while its contribution to WSOC was similar (2.3%) in the day- and night-time. The average percentage of total oxoacids to OC was 0.15% in the daytime versus 0.11% in the nighttime, while the percentage of total oxoacids to WSOC was 0.19% in the daytime and 0.18% in the nighttime. The average contribution of total dicarbonyls accounted for 0.07% and 0.09% to OC and WSOC, respectively, in the daytime versus 0.05% and 0.08% in the nighttime”. These points will be concisely added in the revised manuscript.

Technical corrections:

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Comment: Page 19784–line 7.gas chromatography (GC) and

Response: It will be corrected.

Comment: Page 19784–line 11: and 56 ng m⁻³, (insert a space after ng)

Response: It will be corrected.

Comment: Page 19787–line 15: a capillary GC instrument (the abbreviation GC denotes “gas chromatography” and not the instrument)

Response: It will be corrected.

Comment: Page 19787–line 21: a GC/MS instrument

Response: It will be corrected. Comment: Page 19791–line 10: aromatic hydrocarbons,

Response: It will be corrected.

Comment: Page 19792–line 9: Table 2 compares concentration data of

Response: It will be taken in the revised manuscript.

Page 19793–line 14: heterogeneous degradation reactions

Response: Based on the comment and the comment of other reviewer, we will rewrite this sentence as: Alternatively, Gao et al. (2003) suggested that large organic molecules emitted from biomass burning might be degraded in the daytime to smaller molecules due to heterogeneous oxidation reactions. They invoked this logic based on the enrichment of oxalate, glutarate and succinate with respect to K⁺ by an order of magnitude when fresh biomass burning plumes from savanna fires age for about 40 min.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 19783, 2009.

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