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Atmospheric Chemistry and Physics Discussions

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.

S. Kundu et al.

kundu@pop.lowtem.hokudai.ac.jp

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Dear Editor, Here are the point-by-point responses to the comments of the second reviewer. Two figures (Figure 4 and Figure 7) which will be added in the revised manuscript are attached as well. Sincerely, Shuvashish Kundu

Anonymous Referee #2

Received and published: 5 December 2009

In this work the authors measure the abundance of carboxyilic acids and dicarbonyls

in biomass burning plumes. Filter samples are obtained from the LBA-SMOCC campaign in the Amazonia and the water-soluble components are analyzed. Oxalic acid is confirmed to be the most abundant of the detected acids. Results indicate that oxalic acid may be formed from the degradation of dicaroboxylic species in the daytime. However, the abundance of dicarboxylics samples in daytime samples compared to biomass burning tracers suggest additional dicarboxylics are formed via photochemical production. The findings regarding the degradation pathways of biomass burning plumes are novel. The paper provides further evidence that biomass burning is a significant source of dicarboxylics and carbonyls. Furthermore it presents concentrations, ratios, and values that are relevant and of use to the atmospheric community. The authors do a nice job of citing relevant papers. This reviewer has only a few concerns and they are as follows:

MAJOR CONCERNS

Comment 1. The definitions of Low molecular weight (LMW) and high-molecular weight (HMW) compounds are somewhat ambiguous. Compounds less than 500 g mol-1 are commonly considered LMW, however C5 molecules that may be less than 500 g mol-1 are defined as HMW in this paper. It would be beneficial to the larger scientific community to report the findings in comparable terms to already published molecular weight literature. Perhaps the simple modification to Smaller-MW and Larger-MW compounds would suffice?

Response 1: We will replace low molecular weight (LMW) by smaller-MW and high molecular weight (HMW) by larger-MW in the revised manuscript.

Comment 2. Have the authors considered temperature effects on the rates of formation/degradation? The authors suggest photochemical pathways to explain their observations but the difference in daytime and nighttime temperatures may also affect acid formation rates.

Response 2: Based on the comment, we explored our data to find whether there is

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any relation between temperature and concentrations of dicarboxylic acids and related compounds for both day and night samples. We have not observed any systematic and statistically significant relations. But, we have found that the ratios of oxalic acid to some other dicarboxylic acids and related compounds are positively correlated with temperature in the daytime samples (see the attached Figure 7). Such relations were not observed in the nighttime samples. These results indicate that the degradation of dicarboxylic acids and related compounds is characteristic in daytime. These points will be added in the revised version.

Comment 3. Were the fires more prominent in the day versus night? If so, it could also explain observations; in other words, a decrease in carboxylics would be expected for less biomass burning particles at night when sunlight was not present. Furthermore correlations with EC/OC/K+ are systematically weaker at night, suggesting biomass plumes are not prevalent. How did the total particulate matter vary diurnally? Were changes in boundary height (i.e. changes in ambient concentrations) accounted for in the analysis?

Response 3: Thank you so much for raising this important issue. Fuzzi et al. (2007) reported the diurnal pattern of PM2.5 aerosol mass with the maximum concentrations at night during our sampling period. Higher concentrations at night were mostly explained by very compact boundary layer height. In order to offset the effect of boundary layer height, we have normalized the aerosol mass (PM2.5) by biomass burning tracers (levoglucosan and K+). The ratios of aerosol mass to biomass burning tracers show a diurnal cycle with maximum concentrations in the daytime (see the attached Figure 4). These points will be added in the revised manuscript.

Diurnal patterns of dicarboxylic acids and related compounds in the Figures 2-5 are discussed by normalizing their concentrations by biomass burning tracers (levoglucosan and K+). So, we already considered the difference in boundary layer height between day and night in the text (see lines 21-23 of section 3.4 in the page 19792 and lines 6-8 of section 3.5 in the page 19795.

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MINOR CONCERNS

Comment: P 19785L26. Asa-Awuku et al. 2008 also present data of CCN activity of WSOC from Biomass Burning Aerosol. Furthermore (P19786 L3) they show that the "hydrophobic-long chained" species and inorganic components in the biomass sample have CCN activity greater than that of ammonium sulfate. The CCN activity also correlates with the ability of WSOC to significantly depress surface tension in the presence of salts.

Response: We would like to add the good findings of Asa-Awuku et al. 2008 in the introduction section.

Comment: P 19786 L26. Replace "Sapporo" with "Sapporo, Japan"

Response: The comment will be taken.

Comment: P19793 L11. The sentence beginning with "Alternatively,. . .. . .." is very long and confusing. The authors should consider revising it.

Response: We will modify this sentence to make it more understandable 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.

Comment: PL19795 L26. What is meant by normal?

Response: By "normal chain" we wanted to mean "straight chain". To avoid this confusion, we will replace "normal chain" by "straight chain".

Comment: REFERENCES: Asa-Awuku, A., A. P. Sullivan, C.J. Hennigan, R. J. Weber and A. Nenes, Investigation of Molar Volume and Surfactant Characteristics of water-soluble Organic Compounds in Biomass Burning Aerosol, Atmospheric Chemistry and

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Physics, 8, 799-812, 2008

Response: We will add this reference in the revised manuscript.

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

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Interactive Comment

Figure 7.

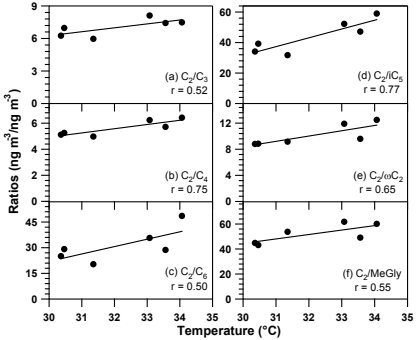

Fig. 1. Figure 7. Correlations of the ratios of oxalic acid to other selected dicarboxylic acids and related compounds with temperature. See Table 1 for abbreviations.

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Figure 4.

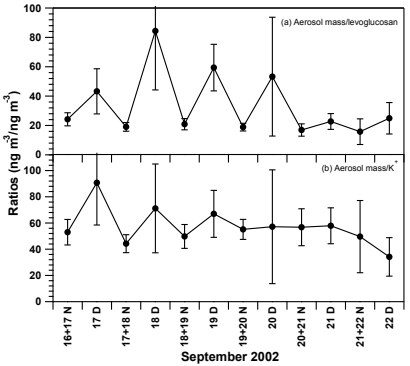

Fig. 2. Figure 4. Diurnal variations in the ratios of (a) aerosol mass to levoglucosan and (b) aerosol mass to K+. PM2.5 concentrations were determined every 30 min using a Tapered Element Oscillating Microba

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