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Comment

***Interactive comment on “Size distributions of dicarboxylic acids, ketoacids,  $\alpha$ -dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in atmospheric particles over Northern Japan: implication for long-range transport of Siberian biomass burning and East Asian polluted aerosols” by S. Agarwal et al.***

**S. Agarwal et al.**

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Response on comments raised by Referee #3

(Note: The revised version of MS is attached as supplement document)

General Comments. The manuscript entitled, “Size distributions of dicarboxylic acids,

C3303

Full Screen / Esc

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Interactive Discussion

Discussion Paper



ketoacids,  $\alpha$ -dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in atmospheric particles over Northern Japan: implication for long-range transport of Siberian biomass burning and East Asian polluted aerosols” presents a comprehensive set of chemical measurements of atmospheric aerosol. The rigorous chemical analyses provide useful, accurate measurements of many aerosol components including WSOC, molecular tracers, and inorganic ions. The observed correlation between diacids and levoglucosan is an important finding, since many previous reports of diacids have not indicated a source so clearly. I do have two main concerns with the implications of this work, as presented by the authors. The first is that these results of size-resolved chemistry are presented as relevant for CCN prediction. However, all particles below 1 micron are grouped together meaning that over the 100nm-400 nm range, there is no observed difference in particle composition. More detail on this is presented below.

Response: In the manuscript, for the importance of size distribution study for understanding CCN activities, we have just stated that (see section 3.2 Size distributions of dicarboxylic acids and related compounds) “Characterizations of aerosol water-soluble organic carbon (WSOC) at molecular level are important to better understand their ability to act as CCN and estimate the hygroscopic growth factor of organics (McFiggans et al., 2005; Shilling et al., 2007).” Please see Lines 238-240 in the revised MS.

In addition to the Andersen samples, we have also collected one set of MOUDI sample during the same period, i.e. 8-11 August 2005. Following the comment and to better understand the mass and diacids concentration distributions on particle below 1  $\mu\text{m}$ , we have incorporated the MOUDI data (with a figure) and discussed briefly the MOUDI distributions in the revised manuscript as:

“It is important to state that the chemical composition associated with fine ( $< 1 \mu\text{m}$ ) and coarse ( $> 1 \mu\text{m}$ ) particles is important to better understand the atmospheric processing of the particles, while the size resolved chemical composition, especially for below 0.5  $\mu\text{m}$  sizes is very useful for constraining the CCN activity of the particles and the properties of the formed clouds. Therefore, we briefly discuss here the size resolved

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chemical composition obtained from MOUDI (Micro Orifice Uniform Deposit Impactor) sampler (MSP Corp.). During the campaign, we collected one set of MOUDI samples in parallel with the Andersen impactor sampling from 8-11 August using aluminium substrate for 10 stages and a backup quartz filter (all were pre-combusted at 450 °C for at least 12 hours). Size cut-point diameters were 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, 0.056  $\mu\text{m}$  with a flow rate of 30 litre/min. A detailed discussion on these MOUDI samples will be given elsewhere (Aggarwal et al., manuscript under preparation), however, we present the mass and total diacids concentrations in Fig 4, which were determined using gravimetric and GC methods. Aerosol mass and total diacid concentrations show almost similar pattern of distribution, with a peak at the particle size bin of 0.56 – 1.0  $\mu\text{m}$ . However, substantial concentrations of total diacids are observed in 0.32 – 0.56 and below 0.32  $\mu\text{m}$  size ranges, which are important for CCN activity of aerosol particles. Aerosol mass concentrations obtained in the particle size < 0.56  $\mu\text{m}$  is almost equivalent to that determined in particle size bin 0.56 – 1.0  $\mu\text{m}$ . In contrast, concentrations of total diacids in the particle size < 0.56  $\mu\text{m}$  are much higher than that of 0.56-1.0  $\mu\text{m}$  size bin (Fig. 4). These findings are also consistent with the hypothesis that low molecular weight diacids are the secondary oxidation products via gas-to-particle conversion in the atmosphere. This point is further discussed in section 3.6.” Please see Lines 277 to 298 in the revised MS.

The second concern pertains to the extremely limited sample size of this measurement set (6 samples). Although air was sampled from a variety of source regions, it seems like a stretch to say that the composition of 1 or 2 samples can represent “biomass burning” while just 1 other sample can represent “pollution.”

Response: Regarding small no. of samples, we have 6 sets (total samples 24 = 6 x 4) of Andersen samples for the study period. These samples were analyzed for different species at bulk and molecular level (i.e., OC, EC, WSOC, inorganic ions and molecular compound classes such as, diacids and sugars). The sample types are designated according to backward trajectory analyses, and by the chemical tracers. These tech-

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niques are very powerful to designate the samples whether they are biomass burning-, pollution- or marine- influenced samples. Therefore, we believe that categorization of the samples is reasonable and we had a good chance to receive 3 different air masses within a short period of study time. These points are briefly mentioned in the revised MS. Please see Lines 192 to 206.

The authors should consult a native English speaker for grammatical corrections. After making more than 11 grammatical corrections to the abstract alone, I have not attempted to provide further text editing. However, the authors do make clear points and do provide adequate motivation for their work. Once the many small mistakes are corrected, the paper will communicate their findings clearly.

Responses: We have checked and corrected all the English grammatical errors in the revised version of this manuscript carefully.

I recommend this paper for publication with major grammatical correction and the following itemized corrections.

Specific Comments 1. Pg. 6715, lines 16-21: add standard deviations to mean values to indicate the range of observed variability.

Response: This is a mean of two samples. For a particulate designated sample types (i.e., biomass burning, pollution, marine influenced) there are only two samples for a particular size bin. However, in the text and figures, we have presented concentration of all 24 samples (6 sets of Andersen samples). Thus, we did not give standard deviations in the revised MS.

2. Pg. 6716, lines 4-6: This sentence is awkward, and it's unclear whether the authors intend to state that primary sources outweigh secondary sources, or whether they simply wanted to say that both primary and secondary sources exist. Not all sources can be "major" sources.

Response: Following the comments, we have corrected the sentence as

Full Screen / Esc

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Interactive Discussion

Discussion Paper



“Important sources recognized for organic aerosols are primary emissions from biomass burning and bio- and fossil-fuel combustions as well as secondary productions from biogenic and anthropogenic emissions (Claeys et al., 2004; Koch et al., 2007; Schichtel et al., 2008; Venkataraman et al., 2005; Wang et al., 2006a).” Please see Lines 51 to 53.

3. Pg. 6716, line 27: Please add a reference for the uptake of acidic gases onto alkaline dust components. Krueger et al. 2004 can be used.

Response: As suggested, the reference has been incorporated. Please see Line 72.

4. Pg. 6718, line 17: The measurements of size-segregated chemical composition are relevant to understanding chemical transformation pathways (e.g. photochemical and cloud processing). However, with respect to cloud condensation nuclei activity, it is necessary have size resolved composition below 1 micron since particles larger than 1 micron are likely to activate with only a small amount of soluble material. This point is particularly important since this paper is reporting measurements of aged aerosol that is more likely to contain some soluble material. Therefore, the implications of this work for future CCN studies are quite limited.

Response: As responded above, in addition to the Andersen samples, we had also collected one set of MOUDI sample during the same period, i.e. 8-11 August 2005. Following the comment and to better understand the mass and diacids concentration distributions on particle below 1  $\mu\text{m}$ , we have incorporated the MOUDI data (with a figure) and discussed briefly the MOUDI distributions in the revised manuscript. Please see Lines 277 to 298.

5. Pg. 6718, line 20: The small number of samples collected means that sampling statistics are poor, so the authors should be careful about drawing too many conclusions from the differences in the composition related to difference back trajectories. Wherever possible, the authors should add error or variability bars to help readers understand that the measured differences are real, and not within the noise. This com-

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ment applies to the text in Section 3.1 as well, where the composition of each type of aerosol is discussed.

Response: Following the comment, we have added error bars in Fig. 2. This figure (for marker species) and the air mass backward trajectory analyses are the basis of the categorization of samples (as responded above). Please see Lines 192 to 235 and new Fig. 2.

6. Pg. 6721, line 22: Add appropriate month after “8 August and 8-9” or, since both are in August, rewrite it as “8 and 8-9 August.” This pattern should be applied to all instances where dates are listed.

Response: As suggested, corrections have been made in the revised manuscript.

7. Pg. 6724, lines 12-13: The authors state that diacids are higher in samples 1-3 than in 4-6. Perhaps a better measure would be diacid fraction of OC. It's difficult to argue that biomass burning contributes significantly more diacid in absolute terms.

Response: Concentration of diacids is found to be higher in biomass influenced samples as follows:

“The biomass burning (samples #1 and #2) or biomass burning + pollution (#3) aerosols showed higher concentrations of total diacids in PM<sub>1.1</sub> than those of pollution (#4), marine (#5) or marine + mixed sourced (#6) aerosols (Fig. 3).” Please see Lines 299 to 301.

However, we also discussed the diaicid-C fraction in OC (see section 3.6, last paragraph).

“In contrast, size distributions of diacids and OC are not parallel in most of the samples (Figs. 3 and 9b). We found enhanced ratios of C<sub>2</sub>-C/OC and total diacid-C/OC in PM<sub>1.1</sub>, except for #5 and #6 samples (being similar to C<sub>2</sub>-C/WSOC and total diacid-C/WSOC ratios), where the atmospheric particles were influenced by marine sources (Figs. 10d and 10e). This can be interpreted by secondary photochemical production of

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Full Screen / Esc

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Interactive Discussion

Discussion Paper



diacids in the atmosphere. In the above two sets of samples, a shift of the mode peak towards larger size ranges was found, again suggesting that oxalic acid and other semi-volatile species could have been adsorbed on alkaline sea-salt particles. The C2-C/OC and total diacid-C/OC ratios are highest in the aerosol samples influenced by pollution sources (#4). Because WSOC accounted for more than 50% of OC in fine aerosols (except marine-influenced aerosols), this study indicates that a considerable fraction of OC in fine mode is likely formed by the secondary processes that occur in the atmosphere during long-range transport of organic precursors.” Please see Lines 548 to 559.

In addition to this, now in the revised manuscript we have also incorporated one set of MOUDI data collected during the same period. This also shows that diacids are peaked in fine mode (section 3.2).

“A detailed discussion on these MOUDI samples will be given elsewhere (Aggarwal et al., manuscript under preparation), however, we present the mass and total diacids concentrations in Fig 4, which were determined using gravimetric and GC methods. Aerosol mass and total diacid concentrations show almost similar pattern of distribution, with a peak at the particle size bin of 0.56 – 1.0  $\mu\text{m}$ . However, substantial concentrations of total diacids are observed in 0.32 – 0.56 and below 0.32  $\mu\text{m}$  size ranges, which are important for CCN activity of aerosol particles. Aerosol mass concentrations obtained in the particle size  $< 0.56 \mu\text{m}$  is almost equivalent to that determined in particle size bin 0.56 – 1.0  $\mu\text{m}$ . In contrast, concentrations of total diacids in the particle size  $< 0.56 \mu\text{m}$  are much higher than that of 0.56-1.0  $\mu\text{m}$  size bin (Fig. 4). These findings are also consistent with the hypothesis that low molecular weight diacids are the secondary oxidation products via gas-to-particle conversion in the atmosphere. This point is further discussed in section 3.6.” Please see Lines 287-298.

8. Pg. 6724, lines 15-18: What are the correlation coefficients between sulfate and oxalic acid (and sulfate with total diacids)? To show that biomass burning is a stronger source of diacids than fossil fuel combustion, the authors must provide a comparison

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of the correlation coefficients. It may be that many components increase their concentration simultaneously, but this does not mean they are from the same source.

Response: Oxalic acid and total diacids show no significant correlation with sulfate in fine particles. This point is added in the revised manuscript.

“We found a strong correlation between oxalic acid and levoglucosan (a biomass burning tracer, the concentrations are given in section 3.3) ( $r = 0.94$ ), and between total diacids and levoglucosan ( $r = 0.86$ ) in fine particles (PM<sub>1.1</sub>). In contrast, both oxalic acid and total diacids showed no correlation against fine particle sulfate ( $r = 0.07$  and  $0.11$ , respectively). This suggests that biomass burning is a potential source of diacids and their precursors.” Please see Lines 301 to 306.

9. Pg. 6728: Could some of the sugars be attributed to marine aerosols? There has been recent work (Russell et al., 2010) showing the prevalence of sugar compounds in primary marine aerosol. Either way, the authors should address this issue, as other readers will be likely to have a similar thought.

Response: Following the comment, a possible source of sugars and OM from ocean bubble bursting is briefly added in revised manuscript, as follows.

In section 3.3 Size distributions of sugar compounds “Recently, Russell et al. (2010) reported the prevalence of sugar compounds in ocean aerosols via bubble bursting processes.” Please see Lines 389 to 390.

In section 3.5 Size distributions of WSOC, OC and EC “A considerable amount of WSOC is also observed in marine influenced samples (#5 and #6), indicating that ocean bubble bursting may be a potential source of polar organics in marine aerosol (Russell et al., 2010).” “As discussed above, possible source of sugars is soil resuspension (microorganisms and plant debris) and ocean bubble bursting (especially in marine influenced samples)” Please see Lines 493 to 496, 501 to 503.

References listed: Krueger, B.J., V.H. Grassian, J.P. Cowin, and A. Laskin (2004), Het-



erogeneous chemistry of individual mineral dust particles from different dust source regions: the importance of particle mineralogy, *Atmospheric Environment*, 38, 6253-6261. Russell L.M., L. N. Hawkins, A. A. Frossard, P. K. Quinn, and T. S. Bates (2010), Carbohydrate-Like Composition Submicron Atmospheric Particles and their Production from Ocean Bubble Bursting. *Proceedings of the National Academy of Sciences*, doi:10.1073/pnas.0908905107

Response: Both references have been cited in the revised manuscript. Please see Lines 704 to 706, 750 to 753.

Technical Comments. 1. Pg. 6715, line 4: insert “an” before “Anderson”

Response: corrected. Please see Line 27.

2. Pg. 6715, line 8: pluralize “trajectory” to “trajectories”

Response: corrected. Please see Line 31.

3. Pg. 6715, line 9: insert “the” before “campaign”

Response: corrected. Please see Line 31.

4. Pg. 6715, line 9: omit “the” before “air masses” and omit “were”

Response: corrected. Please see Line 32.

5. Pg. 6715, line 10: insert “a” within parentheses before “biomass burning region” and insert “from” before “China” and insert “an” within parentheses before “anthropogenic”

Response: corrected. Please see Lines 32 to 33.

6. Pg. 6715, line 11: insert a comma after “9-10 August”

Response: corrected. Please see Line 33.

7. Pg. 6715, line 13: put “i.e. SO<sub>4</sub> [ . . . ]” in parentheses

Response: corrected. Please see Line 35.

8. Pg. 6715, line 18: replace “maximized” with “were highest”

Response: corrected. Please see Line 40.

9. Pg. 6715, line 22: replace “is abundant” with “are abundant” to match “biomass burning products”

Response: corrected. Please see Line 44.

10. Pg. 6715, line 22: replace “that” with “of”

Response: corrected. Please see Lines 44 to 46.

11. Pg. 6715, line 23: replace “in Siberian region have” with “illustrating that the Siberian region has”

Response: corrected. Please see Lines 44 to 46.

12. Figure 2 needs vertical error bars to clearly show that one point is statistically higher than another.

Response: Error bars are added. Please see revised Fig. 2.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C3303/2010/acpd-10-C3303-2010-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 6713, 2010.

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