Atmos. Chem. Phys. Discuss., 13, C4088–C4093, 2013
www.atmos-chem-phys-discuss.net/13/C4088/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the mountain aerosols over the North China Plain during wheat burning season" *by* K. Kawamura et al.

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Received and published: 23 June 2013

Authors' Responses to Ref. #1

Thank you for the careful reading and valuable comments on our paper.

Comments on "High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and a-dicarbonyls in the mountain aerosols over the North China Plain during wheat burning season" by K. Kawamura, E. Tachibana, K. Okuzawa, S. G. Aggarwal,

Y. Kanaya, and Z. F. Wang

Referee #1 General comments: This paper discusses the bulk composition of (TC, WSOC, OC and TN) and molecular level composition of diacids, ketoacids and dicarbonyls in atmospheric aerosols collected over the summit of Mount Tai in Central East China. Higher loadings of organics in atmospheric aerosols were explained by the open field burning of agricultural waste in the North China Plain. Agricultural waste burning as an important source of organic aerosols was claimed by fire spot analysis, backward trajectory analysis and organic tracer compounds. Although the molecular level composition of diacids and ketoacids and dicarbonyls are well studied in atmospheric aerosols, this study has showed how air quality in China is deteriorated by the agricultural waste burning. This study also finds that air masses over Mount Tai is less aged than air masses of remote marine aerosls and oxalic acid could be generated by the oxidations of C3-C10 diacid, glyoxylic and glyoxal. All these results will add to the knowledge base of air quality, sources, formation processes and chemical evolution of organic aerosols in the atmosphere. I definitely support the publication of this paper after the revisions following the comments listed below.

Major Comments 1. P3697, lines 24-26 "the subsequent photochemical oxidation of volatile and semi-volatile organic precursors emitted from field burning": This statement is partially true. Because, in addition to the photochemical oxidation of VOCs and semi-VOCs, SOA can also be generated by other mechanisms including a) dark ozonolysis of VOCs, semi-VOCs and involatiles, b). accretion reactions where no oxidation occurs (Kroll and Seinfeld, 2008) and c) oxidation of involatile organics (e.g., oxidation of unsaturated fatty acids and their derivatives; Hung et al., 2005 and Kockritz et al., 2008). Please make the statement keeping in mind all of the possible pathways of SOA production. I think authors need to generalize the comments. Response: Those points raised by the reviewer were briefly added in Abstract section as "as well as dark ozonolysis of volatile organic compounds and other organics, accretion reactions and oxidation of non-volatile organics such as unsaturated fatty acids". Please see lines

40-42.

2. P3701, section 2.2: I was trying to understand which analytes were quantitated with respect to the authentic standards and which analytes were quantitated with respect to surrogate standards. However, I could not retrieve it. This is very important as the response depend a lot on the structure and nature of compounds. Please mention this point explicitly. Response: Based on the reviewer's comment, one paragraph was added. Please see lines 149-154.

3. Some steps of analytical uncertainty of chemical measurments have been mentioned in the manuscript. For example, uncertainty associated with the recovery has been mentioned for diacids, dicarbonyls and ketoacids (line 21-25, p 3701); and measurement reproducibility has been described for TC and TN measurements (p 3702, line 6-7). It is not understandable how did you calculate the analytical uncertainty of WSOC measurements. Please note that in addition to recovery and reproducibility, analytical errors are emerged from detection limit, calibration equation and other steps. Please try to give an estimation about the overall analytical uncertainty of your measurements. You can do that by the propagation of error which is widely used in analytical chemistry. This uncertainty will be very helpful to understand whether the variability in your data is within or beyond analytical uncertainty. To me, it looks that chemical data (TC, WSOC, total diacids, and total ketoacids) in the end of the campaign (June 7 to July 2) and just before the first biomass buring event on June 7 are variable within analytical uncertainty. Response: We were sorry that we made a big mistake in the expression of concentration unit in the sentence of analytical uncertainties. "0.1 mgC m-3" should be read as "0.1 μgC m-3" for WSOC. Thus, we believe that the temporal variations of WSOC for June 7 to July 2 are not within the analytical uncertainties. The concentration unit has been corrected in the revised MS. Please see line 173. Some sentence on analytical uncertainties has been modified to clarify based on the reviewer's comment. Please see lines 168-170.

5. I am positively intrigued by the Figure 11. Figure 11a suggests that C3-C10 could

be a precursor of oxalic acid. For further evaluation you can draw a figure C2/C2-C10 versus C3-C10/TC. If there is a negative correlation, then the idea that C3-C10 are precursors of oxalic acid would be emboldened. If there are any paper which observed the formation of oxalic acid from C3-C10 diacids in the laboratory could be referred here. Figure 11c-d suggests that pyruvic acid and Meglyoxal are not the precursor of oxalic acid or oxidation of pyruvic acid and methylglyoxal to oxalic is slower than their replenishment in the atmosphere. What do you see if you draw the figure as Pyr/C2 versus C2/C2-C10 and Megly/C2 versus C2/C2-C10? The y axis is normalized by TC in the Figure 11a-d, but in the Figure 11e-f the y axis has been normalized by C2. Please rationalize why the species in the y-axis in Figure 11e-f was normalized by C2. Do you see the similar results if wC2 and glyoxal were normalized by TC in the Figure 11e-f. Response: The authors appreciate for the very helpful comments. Following the comment, we drew the figure C3-C10/TC vs. C2% and found that they showed a negative relation. This point has been briefly added in the revised MS (see lines 501-504). We added new reference on laboratory experiment (Charbouillot et al., 2012) in the revised MS (see line 495). A new sentence on the plots for pyruvic acid and methylglyoxal was added in the revised MS following the reviewer's comment (see lines 506-508). I draw pyruvic acid/C2 vs. C2% and methylglyoxal/C2 vs. C2%. The former plots did not show any correlation whereas the latter plots showed a weak positive correlation (r=0.20). These points were briefly mentioned in the revised MS (see lines 528-535).

Minor comments: 1. Aerosol samples were collected on the summit of Mount Tai (elevation 1534 m asl) where aerosol masses are transported from sources regions and fine particles are produced during transport. It could have been better to study the PM2.5 composition. So, please rationalize why were TSP sampling carried out. Response: We collected TSP samples in order to obtain the information of pollen and fungal spores whose particle sizes are larger than 2.5 μm. This point has been briefly added in the revised MS (see lines 117-118).

2. The more than 50% of the cited papers are from the same group. If it is possible, the selfcitations should be reduced. Response: It is not easy to delete the papers on dicarboxylic acids from our group because all the cited paper are important in the discussion in this manuscript. However, we added five references from other groups and thus the rate of self-citations is smaller in the revised MS than before.

3. p36699 line 21 “many outcomes” Please write the outcomes very shortly. This will make this paper relativelyl independent. Response: One sentence was added to briefly describe the outcomes of the project as; e.g., high concentrations of ozone, volatile organic compounds including glyoxal and methylglyoxal, inorganic ions, black carbon, satellite observation of tropospheric NO2, etc.. See lines 93-95.

4. P3699, line 3, insert the citation after “hygroscopicity of particles” Response: We added two citations in the revised MS (see lines 75).

5. Page 3702, line 9, replace “cm” with cm2. Response: replaced with cm2. See line 172.

6. Page 3704, lines 23-25, “During 22–23 June the winds came from the east or southeast (Fig. 2), suggesting that contributions of marine organic matter enriched with organic nitrogen may result in the lower C/N ratios” Instead of surface wind directions, air mass trajectory is better to understand sources of oceanic air masses. How is about air mass trajectory on this time period;. are air masses being originated from the oceans on this date. Please confirm it. You also see higher concentration of azelaic acid in this period (Figure 6e). It should be mentioned here. Response: Information of air mass trajectory was added in the revised MS together with additional discussion on the source region. Please see lines 241-247.

7. P3702 Lines 22 “direction shifted to south or southwest”. I think you want to say that wind direction shifted to north or northwest. The direction in the Figure 2 says so. Response: Yes the reviewer is right. We corrected the mistakes. Please see lines 186-187.

8. P3703 line 15 “showed a good relation”. Please write down the r2 value. Response: We added the value of r2=0.63. Please see line 204.

9. Page 3705, line 12 “However, the WSOC/TC ratios significantly dropped in 8–12 June when wind direction shifted to south with minimum value of 0.2.”. I think you want to say wind direction shifted to north. Response: Thank you. Corrected.

10. Figure 2: Please name the primary and secondary y axis. Probably, you can abbreviate, e.g., temperature as “T” in the legend. Then, use “T” to name the secondary axis. Response: One sentence was added in the legend of Fig. 2 to explain the primary and secondary y-axis.

11. Figure 3: The name of the y axis should be “concentration ratios”. Response: Corrected.

12. Figure 4: Please write down duration and arrival height of the air masses. Response: The information of the duration and arrival height was given in the legend of Fig. 4.

13. p3715, lines 7-8“Although atmospheric photochemical processing over Mt. Tai is not as serious as remote marine aerosols”. The “serious” is not a proper wording here. Please change it. Response: It was changed to “strong”. Please see line 559.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 3695, 2013.