

Responses to Anonymous Referee #2

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

Anonymous Referee #2

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General comments

1) The structure of the manuscript should be carefully revised. The discussion section switches back and forth between presentation of current results and previous data and it is often not clear what new information and context is.

Response: Thanks. The discussion section has been carefully revised as the referee suggested.

2) I had mentioned in my initial quick report that a much more likely explanation for the lower day time oxalate values as compared to night time ones, might be different oxalate losses under photochemical conditions. The authors chose to include an additional sentence in the abstract and a Section 3.6 where in a very general manner Fe-oxalato complexes are discussed. This section seems out of place and poorly connected to the rest of the text. The reader has to understand why such chemistry is not efficient for other compounds. Is it likely that Fe was present in samples? In general, I would expect that samples from the South might have higher Fe concentrations than the biogenic ones. Does the time scale for Fe-oxalato complex photolysis approximately agree with the processing/ transport time scales?

Response: Thanks. We have made revision according to referee's comments in the revised MS. Please see Line 67 and Line 429. We also added on sentence on the decomposition rate of malonate-Fe(III) complex, which is ca. 20 times lower than that of oxalate-Fe(III) complex. Please see Lines 453-455 in the revised MS.

3) The authors do not present any trace gas measurements beyond Ox. Could the differences between day and night time samples simply be explained by different trace gases? While typical oxidation products of biogenic and anthropogenic WSOC precursors are discussed in a very qualitative way, only levels of WSOC precursors will allow a convincing and quantitative interpretation of contributions of the different sources to WSOC mass.

Response: Thanks for the reviewer's suggestion. We added data of O₃ in the revised MS and discussed relations of diacids with ozone. Please see Lines 123, 368-385 and Section 3.6.

4) The attribution of anthropogenic and biogenic WSOC contributions relies solely on the 'predominant wind directions'. How long were typical processing times? Could other air masses have been mixed with those that were assumed? How do back trajectories look like for the sampling location?

Response: Thanks. A description about transport time and the relevant discussions

have been added in the revised MS. Please see Line 118.

5) It is implied that correlations as shown in Figures 7 and 8 indeed support mechanisms as shown in Figures 6 and 9. While to my knowledge Figure 6 is indeed based on laboratory experiments under controlled conditions (an appropriate references should be added to the Figure caption), Figure 9 is solely based on observed correlations using ambient data and thus is rather speculative. – The discussion of the mechanisms has to be written in a much less definite form, e.g. that the current correlations ‘suggest’ that previously identified mechanisms might occur.

Response: Thanks. We have rewritten the sentences in discussion section as the referee suggested. Please see Lines 422-423. Figure 6 is deleted in the revised MS based on the comment of Reviewer #1.

6) In the text, measured data are only given as their average values (e.g. p. 16706, l. 13: TC values; p. 16710 C₃/C₄ ratios and C₆/C₉ ratios). Are the day/night samples significantly different? Ranges and/or standard deviations should be added to these values in order to clarify this.

Response: Following the comment, we have added range and standard deviations for C₃/C₄ and C₆/C₉ ratios in the revised MS. Please see Line 289 and Line 306.

7) Overall, what can we learn from the current data set? What are the contributions to WSOC from (i) day vs night time processing, (ii) biogenic vs anthropogenic precursors, (iii) sources vs sinks?

Response: Thanks. We have made the related revisions in the conclusion section. Please see Lines 511-524.

Specific comments:

p. 16702, l. 9ff: The authors’ group is not the only one that has identified dicarboxylic acids as aerosol constituents. The reference list should be somewhat more balanced.

Response: Based on the comment, other references have been added. Please see Line 64.

p. 16703, l. 1213: This sentence is out of place. Results should not be included in the introduction.

Response: Thanks. We have deleted the results in the introduction section.

p. 16707, l. 20: This paragraph is very hard to read and should be reordered. It might be easier to follow if first the results are reported and then these are put into context with possible sources. In addition, 1) Is the attribution of C₂ sources always the same? The sources listed here seem to be not specific to the current data set but are very general. 2) The text implies that C₂ is either formed by gas or aerosol phase processes (l. 24) or by aqueous phase processes (l. 25). Is there any study that shows major C₂ contributions from gas phase processes? Do not the aerosol processes referred to include aqueous phase processing? Some reference to laboratory studies might be

useful here.

Response: Thanks. We have reordered this paragraph as the referee suggested. Please see Lines 210-225.

p. 16708, l. 21: What is meant by ‘more aged’? Higher concentrations in ketocarboxylic acids might also originate from higher emission sources.

Response: Thanks. “more aged” means the aerosols have undergone more photochemical processes. We have added one sentence “higher concentrations of ketocarboxylic acids in daytime might suggest higher emission sources” in Line 230.

p. 16709, l. 3: what is meant by ‘more altered’?

Response: It means the aerosols have undergone more photochemical processes. We reworded this phrase in the revised MS. See Line 248.

p. 16709, l. 6ff: Did the rain alter the bulk composition of particles (which might point to size dependent composition) or did all aerosol constituents decrease evenly?

Response: Although concentrations of all aerosol constituents decreased evidently during the rain event, α -dicarbonyls seems preferentially removed. This point is briefly added in the revised MS. See Lines 256-257.

p. 16709, l. 24: Not clear what ‘they’ refers to: Is it C_2 , C_9 , ωC_8 and ωC_9 or ‘most organic species’?

Response: “They” refers to “these species”. We reworded it in the revised MS. Please see Line 272.

p. 16710, l. 14: Do you mean that C_3 has likely more sources than just C_4 ?

Response: We have deleted the sentence “Further, malonic acid is probably more produced in the air by photochemical process (Kawamura and Ikushima, 1993)” to avoid misunderstanding.

p. 16710, l. 16 and Figure 5: The largest difference between day and night time samples in C_3/C_4 seems to occur during the period of lowest WSC concentrations (cf. Figure 4). For the rest of time, the day/night samples exhibit very similar ratios. How significant is the difference if only values after the 18th are considered?

Response: Though the differences between day and night time samples are not large, there does exist a trend that the ratios went up in daytime and fell in nighttime in a day. Following the reviewer’s comment, we added two sentences in the revised MS to discuss the high peaks of C_3/C_4 ratios after the rain event. Please see lines 290-293.

p. 16711, l. 4: What are the approximate yields and resulting SOA masses from typical precursors? A simple rough estimate based on WSOC (e.g. glyoxal, methylglyoxal) mass = ‘biogenic or anthropogenic precursor concentration’ times ‘yield’ (from lab studies) would be much more convincing in order to interpret the different WSOC levels during day and night time as a function of emission source.

Response: Thanks. We admit it would be much more convincing if we could provide the calculated SOA masses. Unfortunately, we did not measure the biogenic or anthropogenic precursors. However, we could use this method to explain the SOA masses resulted from typical precursors in future studies by analyzing SOA tracers.

p. 16712, l. 6 – 14: This paragraph is out of place here. What does it add to the discussion?

Response: Thanks for the comment. But, we would like to keep this paragraph here because it describes the formation mechanism of C₂ from Megly and Gly in aqueous phase in nighttime.

p. 16712, l. 23: Here would be a place where not only C₂ sources but also C₂ (and others') sinks should be discussed!

Response: Thanks. We have added the discussion about sinks of C₂ in Lines 429-455.

p. 16712, l. 26: Not clear why different slopes can point to different sources.

Response: Thanks. We have revised the sentence in Lines 459-461.

Figure 6: This figure lacks a reference (e.g. Tan et al., ACP, 2012) and includes several mistakes: 1) Glyoxal and methylglyoxal are in equilibrium with their hydrated forms (double arrow), 2) does acetic acid only produce non-hydrated glyoxylic acid?, 3) the caption suggests that these products are formed in an aerosol aqueous phase. However, several studies have suggested that in the aqueous phase associated with aerosol particles, these compounds rather form oligomers and the processes as shown here rather occur in more dilute aqueous phase (e.g. cloud droplets).

Response: Thanks. We have deleted this figure in the revised MS. Referee #1 suggested to delete Figure 6.

Figure 7: It seems that the data form two regimes and not necessarily form two slopes: At lower concentrations ($< 500 \text{ ng m}^{-3}$ oxalic) all points fall on the same line whereas only at higher concentrations there is a clear split between day and night time samples. Is there any explanation for this?

Response: Points of lower concentrations are crowded together that makes the split not clear, but we believe the data form two slopes. We agree with the reviewer's point on a non-split between day and nighttime for low concentration samples. Following the comment, we added few sentences to discuss the point for lower concentration samples. "Although a clear split was found between day and nighttime samples with high concentrations, it is not clear for the samples with oxalic acid concentrations of $< 500 \text{ ng m}^{-3}$ (Figure 8), which are associated with wet scavenging of pre-existing aerosols (Figure 3). It is likely that after the wet removal of aerosol particles, the back and forth movement of air masses does not cause a contrast of organic acid concentrations." Please see lines 464-468.

Technical comments:

p. 16701, l. 9: mega-cities

Response: Corrected.

p. 16702, l. 25: composition

Response: Corrected.

p. 16707, l. 19: 'were similar' instead of 'became equivalent'

Response: Corrected.

p. 16708, l. 6: What is meant by 'less polluted'?

Response: It means the Mangshan aerosols are less influenced by anthropogenic pollutants than Beijing aerosols. We deleted the sentence with "less polluted" in the revised MS.

p. 16710, l. 20: 'under the strong sunlight conditions' should be moved after 'daytime'.

Response: Corrected.

p. 16714, l. 22ff: Please add standard deviations here. I expect that doing so, the digit after the comma becomes redundant.

Response: Thanks. Added.

p. 16715, l. 6: Please structure of sentence.

Response: Thanks. We reorganized the conclusion section.

Figure 10: Please number the sites and add these numbers to the appropriate references in the caption.

Response: Thanks. Corrected.