

[Interactive
Comment](#)

Interactive comment on “Diurnal variations of total carbon, dicarboxylic acids, ketoacids and α -dicarbonyls in aerosols in the northern vicinity of Beijing” by N. He et al.

Anonymous Referee #2

Received and published: 5 July 2013

This study presents results of dicarboxylic acids and related compounds collected at site North of Beijing. The data set is quite unique since due to varying wind directions during day and night time different emission sources were captured. One of the main results is that during night time more oxalate (C2) is found than during night time, as compared to trends in all other compounds investigated. Other results include correlations of various acids whose ratios might point to differences in emission sources and/or processing. Overall, the data interpretation is very poor and conclusions are not sufficiently supported by the data. This lack of confidence in the data interpretation is reflected at numerous places where terminology as ‘we suppose’, ‘likely’, ‘species may

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



be produced', . . . are used. Throughout the text it is often unclear which conclusions are based on the current study and which are taken from previous literature. I admit that such complex meteorology and transport patterns as encountered at the sampling site make data interpretation difficult; however, this caveat cannot be used as a reason to justify such vague statements. In summary, I do not support publication of the paper in its current form since it does not add any substantial and supported new evidence on organic aerosol processing. Specific comments are listed below. In addition, the manuscript should be carefully checked for language; e.g., in several sentences articles ('a', 'the') are missing.

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.

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?

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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

a convincing and quantitative interpretation of contributions of the different sources to WSOC mass.

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?

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.

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 this values in order to clarify this.

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?

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.

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

p. 16707, l. 20: This paragraph is very hard to read and should be reordered. It might

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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.

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

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

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?

p. 16709, l. 24: Not clear what ‘they’ refers to: Is it C2, C9, wC8 and wC9 or ‘most organic species’?

p. 16710, l. 14: Do you mean that C3 has likely more sources than just C4?

p. 16710, l. 16 and Figure 5: The largest difference between day and night time samples in C3/C4 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?

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.

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

discussion?

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

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

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).

Figure 7: It seems that the data form two regimes and not necessarily form two slopes: At lower concentrations ($< \sim 500$ 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?

Technical comments

p. 16701, l. 9: mega-cities p. 16702, l. 25: composition p. 16707, l. 19: 'were similar' instead of 'became equivalent' p. 16708, l. 6: What is meant by 'less polluted'? p. 16710, l. 20: 'under the strong sunlight conditions' should be moved after 'daytime'. p. 16714, l. 22ff: Please add standard deviations here. I expect that doing so, the digit after the comma becomes redundant. p. 16715, l. 6: Please structure of sentence. Figure 10: Please number the sites and add these numbers to the appropriate references in the caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 16699, 2013.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

