

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 #1

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This study uses filter measurements of organic acids and dicarbonyls north of Beijing to make speculations of production mechanisms. The topic is of interest to this journal. The authors have experience with such measurements and thus they are of good quality. The data are from many years ago (2007) and are based on 58 bulk aerosol samples that were weighed and analyzed via various chemical techniques. The paper could be written/structured better (in light of comments below) and the tables/figures are illustrated well, although as noted below I think a couple of the figures are quite unnecessary.

As the paper currently stands, I cannot support its publication for many reasons pro-

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vided below. Most importantly, the analysis is too superficial (conclusions are not supported well) and no significant insight is provided currently. Major improvements and revisions are required before this manuscript should be considered again for publication.

General Comments:

A very simple dataset and analysis (basic calculations of averages, ranges, standard deviations, and ratios) is used to make very lofty speculations about aqueous-phase processing, biogenic versus anthropogenic emissions, and transport of air masses. The authors fail to provide this reviewer a convincing explanation for their conclusions. Major issues are that bulk aerosol samples are used and it is difficult to unravel the role of coarse particles (e.g. direct emission of particle types such as dust or primary biological particles) versus fine particles. The authors have no measurements or records of gas-phase concentrations to back up assertions of the impact of anthropogenic versus biogenic vapors in explaining their organic aerosol concentrations. No transport modeling is used to support the air parcel trajectories coming to the sample site. Not much discussion at all is provided for sources in the Mangshan itself and how important those may be. Factors such as filter artifacts, volatilization (will affect daytime vs nighttime), and mixing height effects are ignored in the manuscript, which is problematic as such factors are critical to explain concentrations. Section 3.6 needs to be merged with Section 3.5, but the problem is that the discussion about oxalic acid loss processes is highly superficial without any analysis to back up conclusions. All of a sudden Fe is introduced without any discussion of its sources, concentrations, and diurnal variability.

Section 3.5 is not very convincing so none of the analysis or figures probe deeply to examine how concentrations (and relative concentrations) change with relative humidity. But even if concentrations did change with RH, this has been established thus far and the reader is left to wonder what new substance or insight the authors are providing for oxalic acid.

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Specific comments:

Section 2.1: Would be helpful here to say what size particles were sampled.

General comment: what is the characteristic transport time from Beijing to the sample site using wind data? it would be useful to include this somewhere. Similarly, what is the transport time from the forested area to the sample site during the time of day when air comes from that direction?

Pg 16707-16708: The paper would be richer if the authors compared concentrations to places in other regions outside China and Japan. Or if the authors have a reason to only compare to their specific region, they should say why.

Pg 16709, Line 9-11: Do the authors mean to say that rain is the ONLY control of the concentrations? I think not, so the authors should relax their wording here. Furthermore, what about scavenging of gases too? the authors should mention the possibility of this effect.

General comment: How sensitive are the results to the lack of gas-phase denuder in the measurements. For instance, if certain concentrations of species are higher during the night, maybe positive artifacts of non-diacid precursor gases such as nitric acid, ammonia, and sulfuric acid were more abundant during the day which made the denominator (bulk aerosol mass) larger. Or perhaps diacid precursor gas concentrations may have been higher at night, especially with the biogenic VOCs that may have been transported to the sample site. The authors need to address this issue about whether this potential artifact effect can influence their measurements and interpretations of the data.

General comment: Building on the previous comment, how sensitive are the results to volatilization since during the daytime higher temperatures will promote aerosol-phase species to go to the gas-phase, unlike night-time. How would such an effect, which seems very likely, alter the results of this study?

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Section 3.5: Since the measurements are of bulk aerosol, could not the oxalic acid be associated with coarse matter such as dust or primary biological particles? The authors should address this issue and give a feel for how important coarse particles were in the measurements. I find it difficult to speculate so much about oxalic acid sources without even having addressed first order issues such as the importance of coarse particles which would dominate the aerosol mass. Could diacids be enriched in primary biological particles?

Page 16712, Line 22-27: the authors need to also consider sinks of oxalate and how those affect the relationship between oxalate and other diacids. I see this comes up in Section 3.6, but that seems too late to come into the discussion.

Figure 2: This figure would be better represented in a table to also provide actual fraction values.

Figure 6: It seems to be too large of a stretch to devote an entire figure to this mechanism when it isn't very convincing in the manuscript that such processes actually took place. Such figures already exist in numerous other papers already and it isn't needed again here. I would remove the figure and summarize main points in text.

Figure 9: Previous comment applies also to this figure. Too large of a stretch with this dataset to make such connections.

Technical corrections:

Pg 16709, Line 16: "built" should be "build"

Pg 16709, Line 2-4: I encourage the authors to re-write this sentence since the meaning is not very clear to me of what the authors intend to say.

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

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