

Responses to Anonymous Referee #1

The authors thank the referee's valuable comments. The comments are helpful to improve the quality of the paper greatly. Before revision of the paper, we would like to response to the referee's comments.

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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 provided 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.

Response to General Comments:

In our study, bulk aerosol samples were collected and aerosol-phase concentrations of organic acids and dicarbonyls were measured. This method of sample collection is commonly used for analysis of organic compounds in atmospheric aerosols.

We conducted air mass back trajectories at the sampling location, most of which showed a consistency with the local wind data. This result indicates the wind came from the south in daytime and from the north in nighttime. But some trajectories suggest that the wind hovers around the sampling site, therefore, anthropogenic and biogenic WSOC could have been mixed in some samples.

Mangshan site is located at the top of a mountain, where no pollution source existed and local influence could be insignificant. We have added some descriptive sentences to the sampling site as the referee suggested.

Quartz fiber filters may adsorb organic vapors which would contain or form the speciated organic compounds, causing positive artefacts. On the other hand, some of the measured organics especially dicarbonyls and ketoacids may partially evaporate from aerosol particles on the filters, resulting in negative artefacts. Mixing height effects are important factors to the concentrations. Concentrations of all the compounds should show consistent changing pattern in a day due to this factor. However, in this study, concentrations of C2, C9, C11 diacids, etc. are lower in daytime and higher in nighttime, showing an opposite changing pattern with other organic compounds. So mixing height effects are not considered as an important factor to explain the differences in the concentrations of the Mangshan aerosols.

Previous studies reported that Iron(III)-oxalato complexes exist in the atmosphere, and

an iron(III) catalyzed photochemical process in aqueous phase serves as a major removal pathway for atmospheric oxalic and α -keto acids, resulting in CO₂ (Zuo and Hoigne, 1992, 1994; Ervens et al., 2003; Pavuluri and Kawamura, 2012). Iron(III) is commonly emitted by both natural and anthropogenic sources, and it can be present in aerosol filter samples (Zhu et al., 1993). Though the concentrations of Iron(III)-oxalato complexes in samples were not measured in the study, we expect the samples from the southern polluted region might have higher Iron(III) concentrations than the northern biogenic samples. This assumption corresponds to the higher concentrations of most organic compounds in daytime than nighttime. In other words, Fe-oxalato complex of higher concentrations were emitted with other organic compounds from the southern polluted region in daytime, and photolysis occurred during the transport from the south to the northern sampling site. By the photochemical process, oxalic acid is partly destroyed. In contrast, although the Fe-oxalato complex also existed in nighttime, due to the lack of sunlight, the iron(III) catalyzed photochemical process did not happen and oxalic acid could be accumulated in nighttime. This is a possible reason of the higher concentrations of oxalic acid in nighttime. We will add these to the discussion of loss processes of oxalic acid, and Section 3.6 will be merged with Section 3.5.

In Section 3.7, high relative humidity is a favorable condition for aqueous phase reaction, and higher relative humidity in nighttime supports a possibility of aqueous phase reactions, resulting in the production of C₂ in nighttime.

The above points will be added in the revised manuscript.

Response to Specific Comments on Page C4115:

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?

Response: Thanks. We collected TSP samples. This point is mentioned in abstract and experimental section. Please see the revised MS. Based on the air mass trajectory analysis, we calculated transport time, which is added in the revised MS. Please see Line 118 and Line 439.

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.

Response: Thanks. We have added one sentence in the revised MS to explain the reason why we compared the concentrations among the sites in East Asia. See Lines 483-485 in the revised MS.

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.

Response: Thanks. We admit that scavenging of gases might also lead to low concentrations of gas phase compounds. We have added these points in the revised MS. Please see Lines 260-262.

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.

Response: Thanks. We admit the possibility that biogenic VOCs in gas phase might have been transported to the sampling site in nighttime and resulted in C_2 via a series of reactions. We have addressed this issue in the revised MS in Lines 423-426.

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?

Response: We could think about volatilization in order to interpret the unique diurnal variations of C_2 . However, this process is not important, because most of the organic compounds, except for oxalic acid, showed higher concentrations in daytime samples. This explanation is against the result we expected considering volatilization. In other words, if higher temperatures will promote aerosol-phase species to go to the gas-phase in daytime, not only C_2 , but also other compounds (e.g., C_3) should have a similar trend

and have lower concentrations in daytime. These points are discussed in the revised MS. Please see Lines 390-395.

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?

Response: Thank you for the comment. Now, we briefly discussed on the presence of diacids in the coarse fraction with addition of two references. Please see Lines 338-353 in the revised MS.

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.

Response: Thanks. Some descriptions on the sinks of oxalate and how they affect the relationship between oxalate and other diacids have been added in Line 67 and Lines 429-455.

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

Response: Thanks. It has been presented as Table 1 in the revised MS.

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.

Response: Following the comment, we have deleted this figure in the revised MS.

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

Response: Thanks. We made some modifications in the figure and decided to keep it in the revised MS.

Technical corrections:

Pg 16709, Line 16: “built” should be “build”.

[Response: Corrected.](#)

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.

[Response: Thanks. This sentence has been re-phrased in the revised MS. Please see Line 248.](#)