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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Insight into the in-cloud formation of oxalate based on in situ measurement by single particle mass spectrometry" *by* Guohua Zhang et al.

Anonymous Referee #1

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The manuscript "Insight into the in-cloud formation of oxalate based on in situ measurement by single particle mass spectrometry" provides in-situ observations of oxalate-containing particles using single particle mass spectrometry combined with ground-based counterflow virtual impactor. This study aims to quantify single particle mixing sate and formation path of oxalate in cloud droplet residuals (cloud RES), the cloud interstitials (cloud INT), and ambient particles (PM 2.5) (cloud-free) at remote mountain site, in southern China during winter time in 2016. It concludes that oxalate-containing particles are highly correlated to aged biomass burning (potassium-rich) particles during the study period. In addition, enrichment of various organic acids in aged biomass burning particles is a control factor for oxalate formation. The results suggest that cloud

processing is the regional dominant formation mechanism for oxalate production with glyoxylate as a major intermediate.

The topic of this paper is relevant to the journal and has importance scientifically. The experiment design and data analysis presented are well done. However, in discussion section, the authors need to provide more sufficient in-depth scientific interpretation and discussion rather than make simple comparisons and draw conclusions in a rush by citing previous studies. Prior to publication, the authors should address the specific comments below.

1. Line 86: For the sake of completeness, authors can include the following study based on aircraft data:

Sorooshian, A., S. M. Murphy, S. Hersey, R. Bahreini, H. Jonsson, R. C. Flagan, and J. H. Seinfeld (2010). Constraining the contribution of organic acids and AMS m/z 44 to the organic aerosol budget: On the importance of meteorology, aerosol hygroscopicity, and region, Geophys. Res. Lett., 37, L21807, doi:10.1029/2010GL044951.

2. Line 99 and Line103: Shouldn't the appropriate reference be Sullivan and Prather, 2007 instead of Sullivan et al., 2007?

3. Line 134- 136: "The first one was a ground-based counterflow virtual impactor (GCVI) (Model 1205, Brechtel Mfg. Inc., USA), applied to collect the cloud RES particles with a diameter greater than 8μm."

Is the 8 micron in reference to droplets or the actual particle size? I believe it is the droplet size, and so more careful wording is required here to not say it is the particles that have diameters above 8 micron.

4. Suggest restructuring section 2.1 and 2.2 into one section, since currently section 2.2 doesn't provide many details about instrumentation for the study.

5. Line 183- Line186: Nfs of oxalate-containing particles for the three types shown in Fig. 1 (b) are number fractions relative to total oxalate-containing particles or total

detected particles?

6. Line 200-201: "Oxalate-containing particles had higher Nfs in the smaller cloud-free particles, indicative of primary emission or photochemical production followed by condensation (Zauscher et al., 2013)."

It likely would be more clear to indicate the specific particle size range as it is shown in the Fig. 2, instead of using the word "smaller".

In Fig 2., Nfs of cloud-free particles show two peak Nf values ($\sim$0.1) at the very first and last point. What are the interpretations for the peak at largest dva? Previous studies have shown oxalic acid found in aged sea salt and mineral dust particles in both sub- and super-micron size range.

7. Line 209- 217: Improvement of Fig. S4 is required in order to support the comparisons between cloud RES and cloud-free particle types.

The current figure shows the trends of Nfs and RPA for all particles instead of straightforward comparisons among the different particle types and especially, it is hard to distinguish Cloud RES and Cloud INT. Wind direction is not helpful to separate them, since the two types might have same air mass origins (i.e. cloud event III). Suggest using different markers to represent the three types in Fig. S4.

8. Line 229: all major ion peaks in Fig. 3 show higher Nfs in oxalate-containing particles than ones in all particles, except m/z18 (ammonium). It is necessary to add discussion here for the difference between m/z 18 and the rest of the species, since it is an important message delivered by Fig 3.

9. Line 234- 237: It is better to first introduce organic species names along with their possibly representative m/z Da at Line 230.

It is unclear how the correlation matrix (Table S1) can indicate the similar formation mechanism among the species. More interpretations are expected here.

10. Line 271 – 276: It is inappropriate to state Fe facilitated the formation of oxalate.

Sorooshian et al. (2013) has observed anti-correlation between Fe and Oxalate in cloud water vertical profiles over California coastal region. Similarly, oxalate is significantly lost through the photolysis of iron oxalato complexes as shown by the study over the rural area of PRD in China (Cheng et al., 2017). Thoughtful interpretations are required here.

11. Line 292- 294: For results of Nf, Cloud INT yields the highest R2 for instead of Cloud RES. Any interpretation for this? In addition, Fig. 5 shows identical linear fitting result for Nfs and RPA of Cloud INT particles, which is suspicious. Please check and confirm.

12. Line 302 -303: "To our knowledge, it is the first report on the direct link and the internally mixing state between glyoxylate and oxalate during in-cloud processing with high time resolution. "

The conclusion is not convincing by only using simple linear correlation analysis of Nf (and RPA) for glyoxylate- and oxalate-containing particles. Although, it indicates highest linear correlation is found between glyoxylate and oxalate, what are the results for the other major OAs shown in Fig. 3 and table S2? Do the authors also have significant (positive) correlations with oxalate-containing particles?

13. Line 313- 321: it is unclear what the (major) OAs referred to are, as they are not shown in Fig. S7. Plots are not labeled in the figure, and therefore it is difficult to follow the context here. Improvement is required.

14. Line 326- 327: "If this pathway dominated in this study, glyoxylate and oxalate should be evenly distributed in all the particle types…" It is unclear to have such expectation for glycoylate and oxalate based on previous context (Line 322 – Lin 326). Better interpretations are required.

Minor Comments

1. References should be cited in order of publication year from the oldest to the latest. Corrections are required through out the current manuscript (i.e. Line 58-59; Line 63; Line 67; Line 86-87; Line 324, etc.).

2. Line 86: appropriate preposition is “over” instead of “above”

3. Line 186: “Figure 1” should be “Fig. 1”

4. Line 190: typo, “a species”, should be singular not plural.

5. Line 224: there is an extra single space between “39” and “Da”.

6. In Fig. S5, plots on left don’t have corresponding specie names with each m/z Da as ones on the right. Consistency is required.

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