Response to comments

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.

We would like to thank the reviewer for his/her useful comments and recommendations to improve the manuscript. We have addressed the specific comments in the following text.

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.

Thanks for the suggestion. We have included the citation (Sorooshian et al., 2010) as suggested.

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

Thanks for the suggestion. We have cited (Sullivan and Prather, 2007) instead of (Sullivan et al., 2007) as suggested.

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 8 µm." 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.

We agree with the comment. We have corrected the sentence to "The first one was a ground-based counterflow virtual impactor (GCVI) (Model 1205, Brechtel Mfg. Inc., USA), applied to obtain the cloud RES particles from the cloud droplets larger than 8 µm.". Please refer to Lines 133-135 of the revised manuscript.

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.

Thanks for the suggestion. Section 2.1 and 2.2 have been restructured into one section accordingly.

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?

Nfs of oxalate-containing particles for the three types shown in Fig. 1 (b) are number fractions relative to the total detected particles. We have revised the figure caption to "Fig. 1. (a) Temporal variation (in one-hour resolution) of Nfs of the oxalate-containing particles, and box-and-whisker plots of (b) the Nfs of oxalate-containing particles as shown in (a)" to make it clear. Please refer to Lines 632-635 in the revised manuscript.

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 (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.

Thanks for the comment. The sentence has been revised to "Oxalate-containing particles had higher Nfs in the cloud-free particles with $d_{va} < 0.4$ μm, indicative of primary emission or photochemical production followed by condensation (Zauscher et al., 2013). ".

We have checked the distribution of each particle type of the cloud-free oxalate-containing particles along d_{va}. The result shows that the oxalate-containing particles at the largest d_{va} (1.3-1.4 μm) they were most likely contributed by the aged biomass burning particles, as shown below. However, it shouldn't be conclusive since only 12 particles were found at this size range. Please refer to Fig. S2 in the revised manuscript.

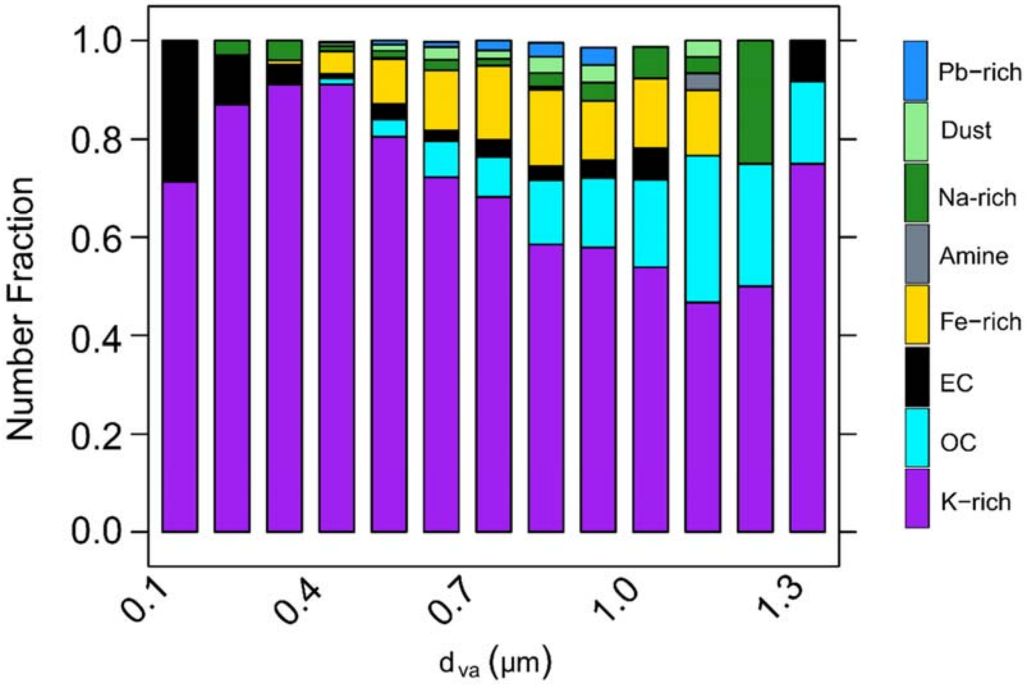

Fig S2. The size-resolved number fraction for each particle types of oxalate-containing particles.

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.

Thanks for the comment. We have revised the Fig. S4 (shown as below) by using different markers to represent the three types in addition to the wind direction, in order to support the comparison between cloud RES, cloud INT, and cloud-free particles.

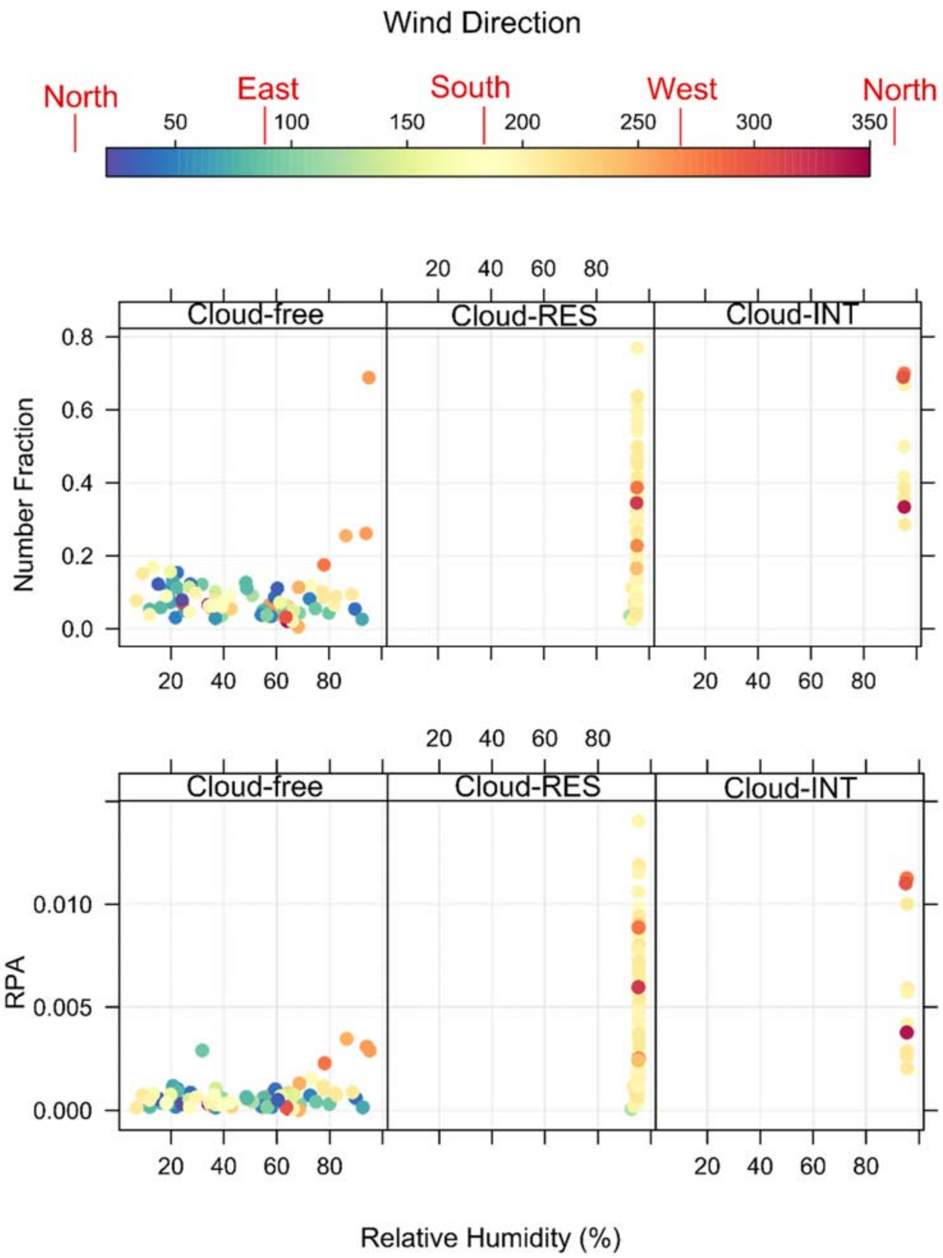

Figure S4. Scattering plots of (upper) the number fraction and (lower) the RPA of the oxalate-containing particles versus relative humidity, separated for the cloud-free, cloud RES, and cloud INT particles. The coloration indicates the wind direction.

8. Line 229: all major ion peaks in Fig. 3 show higher Nfs in oxalate-containing particles than ones in all particles, except m/z 18 (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.

Thanks for the comment. We have analyzed the Nfs of ammonium associated with different particle types in oxalate-containing particles. The result indicates that the higher Nf of ammonium in all the detected particles rather than in the oxalate-containing particles is due to uneven distribution of ammonium among the different particle types. As can be seen in Fig. 4, oxalate was dominantly distributed in the K-rich particle type, which contained lower fraction of ammonium (~40%). However, as the dominant type in all the detected particles, EC type contained higher fraction (~80%) of ammonium. Therefore, the alkali nature (larger abundance of potassium, sodium) of the K-rich might explain the lower fraction of ammonium associated with the oxalate-containing particles. The discussion on this issue has been added in Lines 254-257 of the revised manuscript and Lines 72-79 of the revised Supplement.

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.

Thanks for the suggestion. We have introduced the names of organic species with possibly representative m/a Da in Lines 233-235 of the revised manuscript. Meanwhile, we have revised the sentences to “Their RPAs increased with increasing particle sizes (Fig. S5), indicative of secondary origins (Zauscher et al., 2013). In addition, their Nfs tracked each other temporally in cloud-free particles (Table S1), supporting their similar formation mechanisms, most likely formed through photochemical oxidation followed by gas-to-particle partition (Zauscher et al., 2013).", to indicate the similar formation mechanism among the species. Please refer to Lines 233-238 of the revised manuscript.

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.

We agree with the comment. Iron might play an important role in the sink of oxalate. However, it is unlikely to be an important factor in this study, mostly with the occurrence of orographic cloud and also possibly low radiation in winter. Therefore, it is different from the observation by Sorooshian et al. (2013) and Cheng et al. (2007), which was likely associated with high radiation. We have moved the discussion to the Supplement and added some interpretations as follows: "As shown in Fig. 4, ~10% of oxalate was associated with Fe-rich particles, second only to the K-rich particles. Regarding that the Fe-rich particles only accounted for 2.5 ± 0.4% of all the detected particles (Lin et al., 2017), it might reflect that the Fe facilitated the formation of oxalate. Fenton reactions involving iron can produced more oxidants (e.g., •OH) (Nguyen et al., 2013; Herrmann et al., 2015), which would enhanced the formation of oxalate (Ervens et al., 2014). While Sorooshian et al. (2013), Zhou et al. (2015), and Cheng et al. (2017) have suggested that oxalate can be significantly lost through the photolysis of iron-oxalato complexes. The difference between these observations and this study might be attributed to the different radiation. Our observation was conducted at a mountain site in winter, mostly covered with orographic cloud, resulted in very low visibility (< 500 m), and thus low radiation was expected during sampling. With sampling conducted on an aircraft, cloud water collected by Sorooshian et al. (2013)

included the below and top of cloud water samples, and thus photolysis is expected. On the other hand, the highest fraction (> 30%) of oxalate was found to be internally mixed with metal-containing (e.g., iron, zinc, copper) particles in the Pearl River Delta region (Cheng et al., 2017). The internally mixed oxalate and iron could account for ~50% of iron particles at nighttime (Zhou et al., 2015). Additionally, oxalate was also found to be slightly enriched in amine-containing particles, which is most probably attributed to the enhanced partition of amine to wet aerosols (Rehbein et al., 2011; Zhang et al., 2012).". Please refer to the revised Supplement.

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.

Thanks for the comment. We have checked the data and confirmed the results shown in the Fig. 5. The highest R^2 of Nf for cloud INT particles is explained by the number of samples applied in the analysis, which is significantly less for cloud INT particles (N = 16 for cloud INT particles, N = 107 for cloud RES particles). R^2 in the analysis is defined as the square of the correlation between the response values and the predicted response values. Therefore, it might be inappropriate to make a comparison between R^2 for these distinctly different samples. It is also noted that statistical hypothesis testing shows that the p-value is $1.7*10^{-13}$ and 0.002 for cloud RES and INT particles, respectively. The sample number used in the analysis has been added in the caption of Fig. 5 (Line 648 of the revised manuscript) to make it clear.

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 others also have significant (positive) correlations with oxalate-containing particles?*

Thanks for the comment. In addition to the linear correlation analysis between glyoxylate- and oxalate-containing particles in the Nf and RPA in Fig. 5, we have also shown in Fig. 3 that more than half of oxalate-containing particles contained glyoxylate, in order to confirm the direct link between glyoxylate and oxalate. Besides, oxalate also shows significant correlation ($p < 0.001$) with other OAs as shown in Table S2. However, we only analyzed in detail the relationship between glyoxylate and oxalate in this manuscript, since glyoxylate is an important intermediate for the formation of oxalate, which is confirmed by the highest correlation between them, and the analysis shown in section 3.3. Please refer to Table S2 and section 3.3 of the revised manuscript.

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.

Thanks for the comment. We have corrected the Fig. S7 to make it clear. Fig. S7 is shown as followed in the revised Supplement.

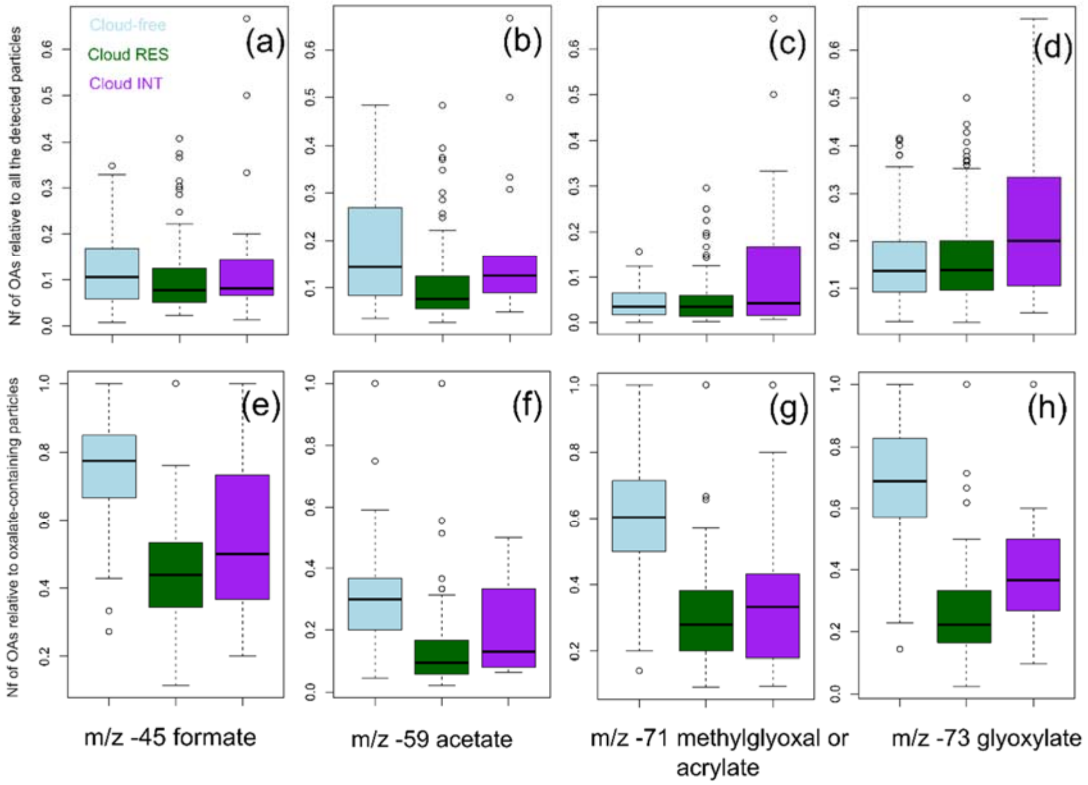

Fig. S7. Box and whisker plot of the variations of number fractions for four OAs in (a-d) all the detected particles, and (e-h) oxalate-containing particles, separated for cloud-free, RES, and INT particles, respectively.

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 glyoxylate and oxalate based on previous context (Line 322 – Lin 326). Better interpretations are required.

Thanks for the comment. We have revised the sentence to "Assuming that the in-cloud formation of oxalate was dominantly contributed from the volatile organic compounds, glyoxylate and oxalate would be evenly formed in all the particle types," to make it clear. We also explain in the following text that "This is inconsistent with our observation that oxalate was predominantly associated with the aged biomass burning particles (Fig. 3). It indicates that a certain amount of glyoxylate should be directly produced in cloud from the organics formed before the cloud events and associated with aged biomass burning particles.”. Please refer to Lines 325-330 of the revised manuscript.

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.).

They have been corrected accordingly.

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

It has been corrected accordingly.

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

It has been corrected accordingly.

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

It has been corrected accordingly.

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

It has been corrected accordingly.

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.

We have added the corresponding specie names with each m/z Da in the figure as suggested.