Response to comments

Anonymous Referee #2

Received and published: 30 September 2017

Review for "Insight into the in-cloud formation of oxalate based on in situ measurement by single particle mass spectrometry" by Zhang et al. submitted to ACPD

Overall comments:

This paper presents investigation of in-cloud formation of oxalate based on single particle analysis of oxalate at a remote mountain site. Size-resolved mixing state of oxalate was analyzed separately in the cloud droplet residual (cloud RES), the cloud interstitial (cloud INT), and ambient (cloud-free) particles by single particle mass spectrometry. Several reasonable results were found including the enriched aged BB aerosol was mixed with oxalate and the enhanced formation of oxalate in the cloud RES and INT particles. The investigation of the relationship between oxalate and organic acid ions also found glayoxylate as an important intermediate for the in cloud formation of oxalate. The topic is of great interest to a certain amount of readers and also proper for the scopes of the publication of this issue. However there are several general questions need to be answered before it can be considered for publication in this journal.

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.

Comments

1. *Definition: the determination of oxalate is not clear. It is according to the peak are or RPA of -89 larger than xxx? The definition of OA is also not clear. Since the*

manuscript refer to the calculation of OA intensity, the author should include the detail information in the section 2.3 or in the supporting information.

Thanks for the suggestion. We have added "The identified ion peaks have peak areas larger than 5 (arbitrary unit), whereas the noise level is lower than 1." in Lines 29-30 of the revised supplement to make it clear.

2. *Figure S7: Figure legend is not clear. No a-h is labeled, the label "cloud-free" is better on top of "cloud-RES", open circle shows all the data?*

Thanks for the comments. We have revised the Figure S7 as suggested. Open circles shows the data not included between the whiskers, which is larger than 90 percentiles or lower than 10 percentiles of the data set. Please refer to the caption of Figure S7 in the Supplement.

3. *It also can be connected with the time cloud last as it can be clearly seen the second cloud event last less time and did not have such a high mixing ratio of oxalate compared with the other events. The second event is unique. Author can investigate a little bit on this issue.*

We agree with the comment that the second event is unique. As we stated in the manuscript, air mass analysis showed that cloud II was strongly influenced by northeastern air mass, contrasting to the southwestern air mass during cloud I and III (Lin et al., 2017). However, short cloud processing time cloud not be the reason for the lower Nf of oxalate-containing particles during cloud II. As can be seen in Fig. 1, the Nf of oxalate-containing particles increased to 20% within several hours during cloud I and III. Therefore, we indicated that in-cloud production of oxalate on the aged biomass burning particles is dominantly controlled by the glyoxylate, which substantially decreased during cloud II, relative to Cloud I and III. As also suggested by the reviewer, we added some discussion on the cloud water content, as "Cloud water content plays an

important role in both the formation and scavenging of water soluble ions (Zhou et al., 2009; Wang et al., 2012), and thus might contribute to the lower fraction of oxalate during cloud II. Model simulation indicates that the formation of oxalate is as a function of cloud processing time and droplet sizes, which directly links to the cloud water content (Sorooshian et al., 2013). With visibility as an indicator (Table S3), it shows the lowest cloud water content during cloud II. However, non-significant correlation was found between the Nf of the oxalate-containing particles and visibility.". Please refer to section 3.4 of the revised manuscript.

4. *319-321 Author showed a statistics of OA for Cloud-free, RES and INC. The reviewer just curious how about the time series of these OA markers and oxalate in this campaign? Is there any good anti-trends?*

Thanks for the comments. It might be expected anti-trends between oxalate and OA markers when the total amount of OAs is constant in a close system. However, in open air, it might be expected positive correlations as analyzed in Table S1. It is reasonable since these OAs served as important precursors for the formation of oxalate. The statistics in Fig. S7 supports the conversion of OAs to oxalate via showing the decrease of the Nfs of OAs associated with the oxalate-containing particles. This only provides evidence for the conversion of OAs to oxalate during cloud events.

5. *322-325 The definition of organic acid is also one critical issue. As we all known levoglucosan also have fragment peaks in -45, -59 and -73. Biomass burning particles have abundant levoglucosan and it will also decay in the atmosphere during the aerosol aging processes. Is there possible some of these ions are partially levoglucosan? More detail discussion should be added regarding to the diagnosis of these organic acid peaks.*

We agree with the comment that levoglucosan from biomass burning also have fragment peaks in m/z -45, -59 and -73. Thus, it is also possible that some of these ions

are partly from levoglucosan. However, these ion peaks were most likely from secondary species in the present study, as discussed in the revised manuscript. This is probably explained by that their RPAs increased with increasing particle diameters (Fig. S5), consistent with that observed by Zauscher et al (2013). We indicate that these organics, most likely assigned to be formate at m/z -45[HCO_2]-, acetate at m/z -59[CH_3CO_2]-, methylglyoxal or acrylate at m/z -71[$C_2H_3CO_2$]-, and glyoxylate at m/z -73[C_2HO_3]- (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). Please refer to Lines 233-242 of the revised manuscript.

6. *Section 3.4 Line354: K-rich and oxalate showed really low R^2 really surprised me. Is that really fresh biomass burning aerosol in the cloud-free case?*

Thanks for the comment. In this study, the K-rich particles were highly aged, and heavily internally mixed with sulfate and nitrate (Lin et al., 2017). As analyzed in section 3.4, it is shown the higher correlation between the Nfs of oxalate-containing and glyoxylate-containing particles, relative to that between the Nfs of oxalate-containing particles and the aged biomass burning particles (Table S1). The result suggests that the formation of oxalate is more dependent on the amount of glyoxylate rather than the amount of biomass burning aerosol, which might be influenced by the burning condition and meteorological conditions during the transport.

Lin, Q., Zhang, G., Peng, L., Bi, X., Wang, X., Brechtel, F. J., Li, M., Chen, D., Peng, P., Sheng, G., and Zhou, Z.: In situ chemical composition measurement of individual cloud residue particles at a mountain site, southern China, Atmos. Chem. Phys., 17, 8473-8488, doi:10.5194/acp-17-8473-2017, 2017.

7. *Line 354-358 cloud water content is not discussed in this manuscript, is there*

possible that the cloud water content influenced the process, or other factors? Cloud can promote formation of oxalate but it can also scavenge water soluble ions (Zhou et al. 2010; Wang et al. 2012). More discussion can be added.

Y. Zhou, T. Wang, X. Gao, L. Xue, X. Wang, Z. Wang, J. Gao, Q. Zhang, W. Wang. Continuous observations of water-soluble ions in PM2.5 at Mount Tai (1534 m a.s.l.) in central-eastern China, Journal of Atmospheric Chemistry, 2010, 64, 107-127

Z. Wang, T. Wang, J. Guo, R. Gao, L. Xue, J. Zhang, Y. Zhou, X. Zhou, Q. Zhang, W. Wang, Formation of secondary organic carbon and cloud impact on carbonaceous aerosols at Mount Tai, North China. Atmospheric Environment, 2012, 46, 516-527

We agree with the comment that cloud water content might be an important factor that influences the oxalate formation in the droplets. Such discussion has been added in this section as "Cloud water content plays an important role in both the formation and scavenging of water soluble ions (Zhou et al., 2009; Wang et al., 2012), and thus might contribute to the lower fraction of oxalate during cloud II. Model simulation indicates that the formation of oxalate is as a function of cloud processing time and droplet sizes, which directly link to the cloud water content (Sorooshian et al., 2013). With visibility as an indicator (Table S3), it shows the lowest cloud water content during cloud II. However, non-significant correlation was found between the Nf of the oxalate-containing particles and visibility.".

8. *Figure 2. It is quite ingesting that the cloud-free oxalate showed a peak with such a small size. If the data is correct, it might be fresh emitted biomass burning aerosols. Is there any other evidence to support this phenomena?*

We agree with the comment that the peak at such a small size might be contributed from the freshly emitted biomass burning aerosols. However, this peak is most likely attributed to the photochemical production, since these smaller particles (0.1 - 0.3 μm) were extensively (nearly 100%) internally mixed with secondary species, such as sulfate and nitrate. The discussion has been included in Lines 202-204 of the

revised manuscript.

Others

1. *Figure 1, Cloud-free is better on top of other two labels.*

It has been revised as suggested.

2. *Figure 3, color coded digital data with peak area information of oxalate can include more information.*

Figure 3 was shown to illustrate the predominant association of the major OAs with the oxalate-containing particles, rather than all the detected particles. We agree with the comment that peak area information of oxalate would provide some useful information. Actually, this information is shown in Fig. S1, and thus we only showed the number fraction in Fig. 3 for simplicity. In addition, we also compared the variation of the peak area distribution of oxalate, glyoxylate, and the major OAs in Fig. 6 to investigate the transformation of OAs to oxalate. Please refer to Fig. S1 and Fig. 6 of the revised manuscript.

3. *Figure 5, regression method should be included. The author can refer the software made by Wu et al. 2017 https://www.atmos-meas-tech-discuss.net/ amt-2017-300/*

Thanks for the suggestion. We have included the method. The caption of Fig. 5 has been revised to "Simple linear regression (with least-square method) between (a) the Nfs and (b) The RPAs of the oxalate-containing and glyoxylate-containing particles, separated for the cloud-free, cloud RES, and cloud INT particles, respectively.". The least-square approach is applied in this work, although Wu et al. (2017) recommended other regression methods (such as DR, WODR and YR). It is because (1) simple linear regression with F-test allows for the testing on the correlation of our data, (2) we did not attempt to quantify the slope from the analysis, and (3) the recommended

regression methods need appropriate weighting, which would complicate the analysis for the single particle data since it is hard to provide appropriate uncertainties.

4. T*able S1, K.rich should be K-rich; Table S2 what's 41 for? Table S3 what's 45 for?*

We have corrected the mistake in Table S1. In Table S2 and S3, the ion peaks at m/z -45, -59, -71, and -73 stands for formate, acetate, methylglyoxal or acrylate, and glyoxylate, respectively. Please refer to Lines 233-235 of the revised manuscript.

5. *Table S3 normalized by ???*

We did not normalized the data in Table S3. We only showed the normalized data in Fig. S3, which is normalized by the largest number over the size bins.