

## Response to the comments

[Atmospheric Chemistry and Physics, MS ID: acp-2016-1081]

Title: Mixing state of oxalic acid containing particles in the rural area of Pearl River Delta, China: implications for the formation mechanism of oxalic acid

### Comments to the Author:

After the corrections/changes based on the Reviewer's comments (especially, main comment), the paper could be ready for acceptance.

**Response:** Many thanks for your reviewing and comments. We have revised our manuscript according to the reviewer's comments, and our point by point responses to the comments have been shown in the following section. We appreciate your comments and response that enable current study to meet the high quality of the journal *Atmos. Chem. Phys.*.

Anything about our paper, please feel free to contact me at [limei2007@163.com](mailto:limei2007@163.com)

Best regards!

Sincerely yours

Mei Li

July 6, 2017

## Specific comments and point by point responses:

### Main comments

Throughout the manuscript, the authors state that ‘acidic aqueous phase chemical processing’ leads to oxalic acid. I still do not understand why the authors keep emphasizing the role of acidity. In general, the rate constants of dicarboxylates (e.g. glyoxylate, pyruvate) decrease with acidity. Or are the authors saying that the LOSS PROCESSES of oxalic acid are slowed down at higher acidity and therefore oxalic acid accumulated? If so, that should be mentioned somewhere that the pH was sufficiently low that indeed oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) and not its anions ( $\text{HC}_2\text{O}_4^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ) was predominant. However, this only occurs at extremely low pH, i.e. if  $\text{pH} \sim \text{pK}_a(\text{H}_2\text{C}_2\text{O}_4) \sim 1.25$ .

**Response:** According to reported studies in field measurements, chamber experiments and model simulations (Carlton et al., 2007; Tan et al., 2009; Myriokefalitakis et al., 2011; Wang et al., 2012; Kawamura et al., 2013), oxalic acid is one of the main products from the oxidation of organic precursors like glyoxal in the aqueous phase. Although the influence of different particle acidity on the oxidation process of glyoxal still needs evaluation, the moderate acidic environment is favorable for the production of oxalic acid from the oxidation of glyoxal (Herrmann, 2003; Ervens and Volkamer, 2010; Eugene et al., 2016). In this work the general existence of nitric acid and the temporal variation of relative acidity ratio (from 7 to 114) both indicated an acidic environment of oxalic acid particles during the sampling period in winter. 98% of oxalic acid particles contained sulfate suggesting a strong connection between the aqueous phase reactions and the formation process of oxalic acid. The abundant hydrocarbon fragments and secondary ions in the mass spectra of oxalic acid particles indicated the aging process of organic precursors in oxalic acid particles. These observations suggest a possible production of oxalic acid from the oxidation of glyoxal and related precursors in the acidic aqueous phase in aerosols. Besides, the formation of organosulfate from the reaction of glyoxal and sulfuric acid requires an acidic aqueous phase environment. The robust correlation between oxalic acid and organosulfate particles in the episode suggests the formation of oxalic acid is closely associated with the oxidation of organic precursors in the acidic aqueous phase. Based on the above discussion, we believe the acidity of oxalic acid particles plays an important role in the oxidation process of organic precursors in aqueous phase.

Because the in-situ pH of oxalic acid particles was not measured in winter, and oxalic acid with its anion (oxalate) could not be characterized by the SPAMS, thus the loss process of oxalic acid through the oxidation of its anion were not discussed in winter. Several revisions have been made in the manuscript to describe the formation process of oxalic acid more clearly:

In the abstract “which suggests the formation of oxalic acid is closely associated with acidic aqueous phase chemical processing of organic precursors” has been revised to “which suggests the formation of oxalic acid is closely associated with the oxidation of organic precursors in aqueous phase” in lines 65-66.

“Several studies have reported potential production of oxalic acid from acidic aqueous phase reactions in aerosols” has been revised to “Several studies have reported the formation of oxalic acid through the oxidation of glyoxal and related precursors in acidic aqueous phase” in lines 422-423.

“Although the influence of different particle acidity on the oxidation process of glyoxal still needs evaluation, the moderate acidic environment is favorable for the production of oxalic acid from the oxidation of glyoxal (Herrmann, 2003;Ervens and Volkamer, 2010;Eugene et al., 2016).” has been added in lines 424-428.

### **Minor corrections and revisions**

1. line 55: replace ‘was’ by ‘were’

**Response:** “The HM type particles was the most abundant oxalic acid particles in summer and the diurnal variations of peak area of iron and oxalic acid show opposite trends” has been revised to “The HM type particles were the most abundant oxalic acid particles in summer and the diurnal variations of peak area of iron and oxalic acid show opposite trends” in lines 55-56.

2. line 60 – 62: This sentence seems meaningless and redundant “The strong acidity... indicated an acidic environment...”

**Response:** “The strong acidity and general existence of nitric acid in oxalic acid-containing particles indicates an acidic environment during the formation process of oxalic acid.” has been revised to “The general existence of nitric acid in oxalic acid-containing particles indicates an acidic environment during the formation process of oxalic acid.” in lines 60-62.

3. line 111: The formation MECHANISM of oxalic acid is relatively well constrained, i.e. the facts that glyoxal is oxidized to glyoxylic acid and further to oxalate. However, the oxidation RATES are associated with uncertainties as they are the product of the reactants (organics and oxidants) and the rate constants.

**Response:** “However, the detailed formation mechanisms of oxalic acid from photochemistry and aqueous phase chemistry in ambient aerosols are still not comprehensively understood due to the great uncertainty of oxidant levels, and need to be further studied.” has been revised to “However, the formation process of oxalic acid in ambient aerosols is still associated with great uncertainty due to the oxidation rates of precursors and oxidant levels in photochemistry and aqueous phase chemistry, which needs to be further studied.” in lines 111-114.

4. line 342: As mentioned in my previous comments, the figure does not DISCUSS the influence of the pH. A discussion would include a line of arguments on the various processes that include RH, inorganic ions etc and how and to what extent they affect pH. Since this information cannot be gathered from Fig. S5, it is not a discussion but merely the representation of temporal trends of pH, RH, inorganic ions etc.

**Response:** “The  $pH_{is}$  of ambient particles ranging from -1.42 to 4.01 indicated an acidic environment, and the influences of  $pH_{is}$  from RH, inorganic ions and  $H^+$  (aq) in aerosols are discussed in Figure S5.” has been revised to “The  $pH_{is}$  of ambient particles ranging from -1.42 to 4.01 indicated an acidic environment, and the temporal trends of RH, inorganic ions and  $H^+$  (aq) in aerosols are shown in Figure S5.” in lines 340-342.

5. line 349: Remove ‘of’

**Response:** “in both of clouds and wet aerosols” has been revised to “in both clouds and wet aerosols” in line 349.

6. line 352: replace ‘aerosols-related’ by ‘aerosol-related’

**Response:** “oligomers in aerosols-relevant concentrations” has been revised to “oligomers in aerosol-related concentrations” in line 352.

7. line 383: Why ‘likely correlated’? There are robust statistical methods that can be applied to confirm (or refuse) a statistical correlation.

**Response:** “Interestingly, the peak area of iron likely anti-correlated with the peak area of oxalic acid from 4:00 to 11:00.” has been revised to “Interestingly, the peak area of iron exhibited opposite trend with the peak area of oxalic acid from 4:00 to 11:00.” in lines 383-384.

8. line 389: replace ‘extreme’ by ‘extremely’

**Response:** “an extreme low abundance of iron” has been revised to “an extremely low abundance of iron” in lines 389-390.

9. line 390: What do you mean by ‘above asynchronous variation’? I suggest replacing it by a more common expression.

**Response:** “Above asynchronous variation of iron and oxalic acid in iron rich HM type particles during the photochemical activity period from 5:00 to 19:00 strongly indicated that photolysis of iron oxalato complexes could be an efficient sink of oxalic acid.” has been revised to “Above opposite variation patterns of iron and oxalic acid in iron rich HM type particles during the photochemical activity period from 5:00 to 19:00 strongly indicated that photolysis of iron oxalato complexes could be an efficient sink of oxalic acid.” in lines 390-393.

#### References:

- Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H. J., and Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, *Atmospheric Environment*, 41, 7588-7602, 10.1016/j.atmosenv.2007.05.035, 2007.
- Ervens, B., and Volkamer, R.: Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles, *Atmospheric Chemistry and Physics*, 10, 8219-8244, DOI 10.5194/acp-10-8219-2010, 2010.
- Eugene, A. J., Xia, S. S., and Guzman, M. I.: Aqueous Photochemistry of Glyoxylic Acid, *Journal of Physical Chemistry A*, 120, 3817-3826, 10.1021/acs.jpca.6b00225, 2016.
- Herrmann, H.: Kinetics of aqueous phase reactions relevant for atmospheric chemistry, *Chem Rev*, 103, 4691-4716, Doi 10.1021/Cr020658q, 2003.
- Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S. G., Kanaya, Y., and Wang, Z. F.: High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and alpha-dicarbonyls in the mountaintop aerosols over the North China Plain during wheat burning season, *Atmospheric Chemistry and Physics*, 13, 8285-8302, 10.5194/acp-13-8285-2013, 2013.
- Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, *Atmospheric Chemistry and Physics*, 11, 5761-5782, 10.5194/acp-11-5761-2011, 2011.
- Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Effects of Precursor Concentration and Acidic Sulfate in Aqueous Glyoxal-OH Radical Oxidation and Implications for Secondary Organic Aerosol, *Environmental Science & Technology*, 43, 8105-8112, 10.1021/Es901742f, 2009.
- Wang, G. H., Kawamura, K., Cheng, C. L., Li, J. J., Cao, J. J., Zhang, R. J., Zhang, T., Liu, S. X., and Zhao, Z. Z.: Molecular Distribution and Stable Carbon Isotopic Composition of Dicarboxylic Acids, Ketocarboxylic Acids, and alpha-Dicarbonyls in Size-Resolved Atmospheric Particles From Xi'an City, China, *Environmental Science & Technology*, 46, 4783-4791, 10.1021/es204322c, 2012.