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

General comments:
The authors have clarified a few of my previous comments. However, several of my original concerns were not addressed at all or only very poorly. I list my main concerns below and also comment on the authors' response to my previous comments in order to highlight where more detail is needed.

Response: Many thanks for your 1st and 2nd round reviewing and comments. Indeed, it will be great to give a comprehensive and quantitative discussion on the contributions of various source •OH radicals especially that formed through Fenton reactions to the formation of liquid phase oxalic acid. However, the SPAMS could only detect the peak area of iron element, and the concentration of $Fe^{2+/3+}$ ions as well as H_2O_2 could not be obtained in the current work. Here, we prefer to cut down the Fenton reaction discussion to minimum as a possibility according to the literature, and the proposed mechanism has also been completely removed from the whole manuscript along the advice of the referee. Furthermore, we have also extended the discussion of the potential sink of oxalic acid via the photolysis of iron oxalato complexes corresponding to the diurnal variation of peak area of iron and oxalic acid in HM type particles. Finally we appreciate your comments and response that enable current study to meet the high quality of the journal *Atmos. Chem. Phys.*, and our point by point response to your comments as well as our revisions have been shown in the following section.

Anything about our paper, please feel free to contact me at limei2007@163.com

Best regards!

Sincerely yours
Mei Li
May 24, 2017

Specific comments and point by point responses:

Major comments

1) Role of Fenton chemistry

I still find the discussion of the role of iron chemistry in SOA formation confusing. It is possible that Fenton chemistry enhances OH concentration. However, there are many other radical sources that are not discussed.

Response: According to the referee's 1st and 2nd round comments, we think that more field measurements and data are needed to comprehensively and qualitatively discuss the contribution of Fenton reaction source •OH radicals to oxalic acid formation. This is out of the interest of this work. Thus we prefer to remove the discussion of the contribution of Fenton reaction in the formation process of oxalic acid and the proposed mechanism along the suggestion of the referee. Fenton reaction is only mentioned as a possibility according to the literature in a very cautious expression.

"The favorable in-situ pH (2-4) and the dominance of transition metal ions in oxalic acid particles can be plausibly explained by the enhanced production of •OH from Fenton like reaction, which can promote the oxalic acid production from the oxidation of precursors by •OH in HM type particles." has been removed from the abstract in line 55.

"Furthermore, suitable in-situ pH is favorable for Fenton like reactions to produce •OH in HM type particles, and might promote the oxalic acid production from the oxidation of precursors by •OH in HM type particles." has been removed from the conclusion in line 480.

"The high abundance of metal ions in oxalic acid particles may be an indication of possible Fenton reactions in the acidic aqueous phase of acidic particles (pH<5, Figure S3), although we cannot exclude the possibility of gas phase condensation of oxalic onto HM particles.

The oxidation of glyoxal and glyoxylic acid by •OH has been identified as an important pathway of oxalic acid production by field and laboratory studies (Ervens et al., 2004;Ervens and Volkamer, 2010;Wang et al., 2012;Wang et al., 2015). The modeling studies from Ervens et al. (2014) suggest that oxalic acid production from glyoxal and glyoxylic acid in aqueous phase significantly depends on •OH availability (Ervens et al., 2014). The main sources of •OH in the aqueous phase contain both direct uptake from the gas phase and the chemical sources in the aqueous phase such as Fenton type reactions and photolysis of H_2O_2, NO_3^-, NO_2^-, and chromophoric dissolved organic matter (CDOM) (Yu et al., 2014;Badali et al., 2015;Ervens, 2015;Gligorovski et al., 2015;Herrmann et al., 2015;Tong et al., 2016). Considering the low Henry's law constant of •OH ($K_{H,OH}$=30 M atm^{-1}) (Hanson et al., 1992) and abundant fraction of transition metal ions in the oxalic acid particles, the photolysis of H_2O_2 through Fenton reactions involving the catalysis of transition metal ions like $Fe^{2+/3+}$, $Cu^{+/2+}$ and $Mn^{2+/3+}$ likely contributes substantially to the source of •OH in the aqueous phase in this work (Deguillaume et al., 2005;Herrmann et al., 2005;Ervens et al., 2014). The •OH formation process through Fenton reactions can be expressed as

(Ervens, 2015):

$$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + \bullet OH \ \ (\text{or } Fe^{3+} + OH^- + \bullet OH) \qquad (R1)$$

$$FeOH^{2+}/Fe^{3+} + HO_2^{\cdot}/O_2^{\cdot -} \rightarrow Fe^{2+} + O_2 + H_2O/OH^- \qquad (R2)$$

The actual chemical process is far more complex and involves iron oxides and iron-complexes, thus in the current work we focus on the potential availability of •OH from Fenton reactions and the impact on the oxidation process of organic precursors.

In order to investigate the photochemical aqueous phase formation of oxalic acid in summer, the diurnal variations of O_3, oxalic acid particles, HM group particles and pH_{is} of ambient particles averaged from July 28 to August 1, 2014 are shown in Figure 7. The concentration of O_3 increased after 9:00 and peaked at 17:00, while oxalic acid particles and HM group particles both increased after 10:00 and showed two peaks at 15:00 and 19:00. The prominent photochemical feature of oxalic acid particles suggested a close association of photochemical reactions with oxalic acid production. Although •OH production from Fenton reactions can both occur under dark and light radiation conditions, photo-Fenton reactions may have more contribution to the enhancement of oxalic acid particles in the current work. This was possibly due to the diurnal variation of pH_{is}, since Fenton reactions strongly depend on the pH of the aqueous phase (Gligorovski et al., 2015). When pH<1, Fe^{2+} is directly oxidized by H_2O_2 to Fe^{3+} with no production of •OH (Barb et al., 1951;Kremer, 2003), and the most favorable pH value for Fenton reaction is between 2.5 and 5 (Deguillaume et al., 2005). In the current work the pH_{is} of ambient particles ranged from -1.42 to 4.01, and the influences of pH_{is} from RH and inorganic ions are discussed in Figure S5. Strongly acidic particles were observed during the whole day with high pH_{is} at 6:00 and after 12:00. Although pH_{is} was around 2 at 6:00, only a few oxalic acid-containing particles were observed during this period due to low abundance of HM particles. Oxalic acid-containing particles were found to increase from 12:00 to 21:00, which was attributed to increased organic precursors from VOCs oxidation and enhanced •OH production from Fenton reactions under pH_{is} at 1-4. The number concentration of oxalic acid particles peaked at 19:00 instead of during the strong photochemical activity period in the afternoon; this was possibly due to the efficient degradation of oxalic acid from the complex with iron (Sorooshian et al., 2013;Zhou et al., 2015). Furthermore, photolysis of $Fe(oxalate)_n^{3-2n}$ can contribute to 99% of the overall degradation of oxalic acid (Weller et al., 2014). Although the enhanced •OH production from photo-Fenton reactions was favorable for the formation of oxalic acid from 12:00 to 18:00, we speculate that a high degradation rate of oxalic acid by iron complexation resulted in a lower net production of oxalic acid than at 19:00. In addition to the contribution from Fenton reactions after 12:00, the precursors of oxalic acid such as glyoxylic acid have higher reaction rate with •OH in high pH solutions due to reported studies(Ervens et al., 2003;Herrmann, 2003;Cheng et al., 2015), thus the increase of pH not only enhances •OH production from photo-Fenton reactions, but also promotes the oxidation process of oxalic acid's precursors by •OH.

Based on above discussions of the mixing state of oxalic acid with secondary ions and transition metals, a plausible explanation to the formation process of oxalic acid in the HM type oxalic acid particles is proposed (Figure S6). In summer strong photochemical activity and high O_3 concentrations in the afternoon lead to more production of reactive radicals such as •OH and $HO_2^{\bullet}$, which promote the oxidation of VOCs to dicarbonyls and aldehydes (e.g. glyoxal and methylglyoxal), followed by a subsequent partitioning into the aqueous phase of particles (Myriokefalitakis et al., 2011). Acidic particles containing transition metals like Fe and Cu potentially yield more •OH in acidic aqueous phase, then hydrated dicarbonyls and aldehydes can be oxidized by •OH to glyoxylic acid and finally to oxalic acid (Wang et al., 2012) (Figure S6). Recently Ma et al. (2015) had studied the Fe-containing particles in the PRD and found Fe-containing particles are more efficient at generating •OH in summer than winter (Ma et al., 2015), which supports the enhanced •OH production in HM type particles in this work. A large amount of Fe related particles are emitted from steel industries in the North China Plain and metals like V, Zn, Cu and Pb from electronic manufacturing (Cui and Zhang, 2008;Dall'Osto et al., 2008). These metals contribute significantly to haze episodes (Moffet et al., 2008;Li et al., 2014), which possibly increases the formation of SOA by yielding more •OH participating the heterogeneous and aqueous reactions."

has been revised to

"In order to investigate the photochemical formation of oxalic acid in summer, the diurnal variations of O_3, oxalic acid particles, HM type particles and pH_{is} of ambient particles averaged from July 28 to August 1, 2014 are shown in Figure 7. The concentration of O_3 increased after 9:00 and peaked at 17:00, while oxalic acid particles and HM type particles both increased after 10:00 and showed two peaks at 15:00 and 19:00. 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. The oxidation of glyoxal and glyoxylic acid by •OH has been identified as an important pathway of oxalic acid production by field and laboratory studies (Ervens et al., 2004;Ervens and Volkamer, 2010;Wang et al., 2012;Wang et al., 2015). In summer strong photochemical activity and high O_3 concentrations in the afternoon lead to more production of dicarbonyls and aldehydes (e.g. glyoxal and methylglyoxal) from VOCs (Myriokefalitakis et al., 2011), which increases the precursors of oxalic acid. While the aqueous phase oxidation of glyoxal can both take place in clouds and wet aerosols (Lim et al., 2010), the lower yield of oxalic acid from glyoxal in wet aerosols compared to clouds has been reported in chamber experiments due to the significant formation of higher molecular weight products such as oligomers in aerosols-relevant concentration (Carlton et al., 2007;Tan et al., 2009), which helps to explain the lower peak of oxalic acid particles at 15:00 compared to 19:00. Besides, the precursors of oxalic acid such as glyoxylic acid have higher reaction rate with •OH in high pH solutions according to previous studies(Ervens et al., 2003;Herrmann, 2003;Cheng et al., 2015), and in this work the increase of pH_{is} was observed as the enhancement of oxalic acid particles in the afternoon (Figure 7), which suggests an efficient oxalic acid production from the oxidation of precursors.

The similar photochemical pattern of HM type particles with O_3 and total oxalic acid particles implies a possible participation of metal ions in the formation process of oxalic acid. The modeling studies from Ervens et al. (2014) suggest that oxalic acid production from glyoxal and glyoxylic acid in aqueous phase significantly depends on •OH availability (Ervens et al., 2014). The main sources of aqueous phase •OH in cloud droplets include direct uptake from the gas phase(Jacob, 1986), ozone photolysis by UV and visible light at the air-water interface (Anglada et al., 2014), and also aqueous phase chemical reactions(Gligorovski et al., 2015). For the last kind of source, •OH radicals could be generated through Fenton or Fenton like reactions and photolysis of H_2O_2, NO_3^-, NO_2^-, and chromophoric dissolved organic matter (CDOM) (Badali et al., 2015;Ervens, 2015;Herrmann et al., 2015;Tong et al., 2016). Given that SPAMS cannot be used to quantify the concentrations of iron ions and H_2O_2, we will investigate the relative contribution of different source •OH radicals to the formation of oxalic acid and show results in our follow up studies." in lines 335-373.

2) Role of metal in decreasing SOA

Neither in the abstract nor in the conclusions, have the authors discussed the significant role of Fe-oxalato complexes as a sink of oxalate. Instead, the only modified slightly a couple sentences in the main parts of the manuscript without discussing in detail the balance between oxalate formation and loss.

Response: The sink of oxalic acid via the photolysis of iron oxalato complexes has been discussed through the diurnal variation of peak area of iron and oxalic acid in HM type particles.

"The number concentration of oxalic acid particles peaked at 19:00 instead of during the strong photochemical activity period in the afternoon; this was possibly due to the efficient degradation of oxalic acid from the complex with iron (Sorooshian et al., 2013;Zhou et al., 2015). Furthermore, photolysis of $Fe(oxalate)_n^{3-2n}$ can contribute to 99% of the overall degradation of oxalic acid (Weller et al., 2014). Although the enhanced •OH production from photo-Fenton reactions was favorable for the formation of oxalic acid from 12:00 to 18:00, we speculate that a high degradation rate of oxalic acid by iron complexation resulted in a lower net production of oxalic acid than at 19:00." has been revised to "The oxalic acid loss through the photolysis of iron oxalato complexes is a significant sink according to field measurements and model simulations (Sorooshian et al., 2013;Weller et al., 2014;Zhou et al., 2015). Considering the high abundance of iron in oxalic acid particles in the current work (Figure 6), the photolysis of iron oxalato complexes could have played important role in the diurnal variation of oxalic acid particles. Because the mass concentration of Fe (III) and oxalic acid could not be obtained through SPAMS, the diurnal variations of peak area of iron (m/z=56) and oxalic acid (m/z=-89) were used to investigate the role of iron on the net production of oxalic in the HM type particles from July 28 to August 1, 2014 (Figure 8). Interestingly, the peak area of iron likely anti-correlated with the peak area of oxalic acid from 4:00 to 11:00. As the peak area of Fe increased from 1565 to 29920 from 4:00 to 7:00, the peak area of oxalic decreased from 6052 to 3487 accordingly. From 8:00 to 11:00, the peak area of Fe had a very low value of 1168, but the peak area of oxalic had a very high value of 5538. In addition, the peak area of iron exhibited a high value of 138199 at 14:00, while the peak area of oxalic acid showed a lower peak of 7687 at 14:00 and a higher peak of 11879 at 19:00 with an extreme low abundance of iron. 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." in lines 374-393.

"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, which suggest a possible loss of oxalic acid through the photolysis of iron oxalato complexes during the strong photochemical activity period." has been added in the abstract in lines 55-58.

"The diurnal variations of peak area of iron and oxalic acid in HM type particles indicate a net production of oxalic acid at 15:00 lower than at 19:00, likely due to a significant loss of oxalic acid through the photolysis of iron oxalato complexes during the strong photochemical activity period." has been added in the conclusion in lines 480-483.

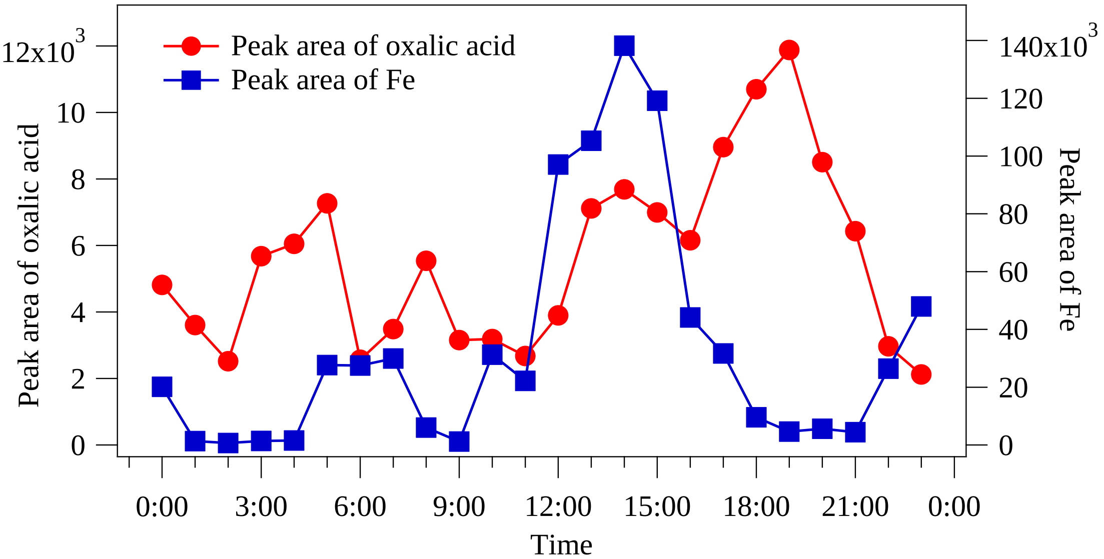

Figure 8. The diurnal variations of peak area of iron (m/z=56) and oxalic acid (m/z=-89) in the HM type oxalic acid particles from July 28 to August 1, 2014.

3) Acid catalysis

By definition, a catalysis is a process where a compound (a catalyst) is involved in the reaction but will be recycled and not be consumed.

The authors refer to 'acid-catalysed oxalate formation from glyoxal' (l. 447). These studies did not show acid catalyzed reactions.

Response: In the abstract "which suggests the formation of oxalic acid is closely associated with acid-catalyzed reactions of organic precursors." has been changed to "which suggests the formation of oxalic acid is closely associated with acidic aqueous phase chemical processing of organic precursors." in lines 65-66.

"Several studies have reported potential production of oxalic acid from acid-catalyzed aqueous phase reactions in aerosols" has been changed to "Several studies have reported potential production of oxalic acid from acidic aqueous phase reactions in aerosols" in lines 422-423.

"which can be used as an indicator of acid-catalyzed ageing process of organic compounds." has been changed to "which can be used as a marker of acidic aqueous phase aging process of organic compounds" in lines 453-454.

"Based on the above discussion, the degradation of carbonaceous species associated with acid-catalyzed reactions may have an important contribution to the formation of oxalic acid during the episode in winter." has been changed to "Based on the above discussion, the degradation of carbonaceous species associated with acidic aqueous phase chemical reactions may have an important contribution to the formation of oxalic acid during the episode in winter." in lines 462-465.

"which suggest the acid-catalyzed oxidation of organic precursors as a potential source for oxalic acid." has been changed to "which suggests the acidic aqueous phase chemical processing of organic precursors as a potential source for oxalic acid." in lines 467-468.

"Nitric acid and organosulfate were found to co-exist in oxalic acid-containing particles in the winter, which suggests a close association with acid-catalyzed reactions. Acid-catalyzed oxidation of organic precursors is a potential contribution for the formation of oxalic acid in winter." has been changed to "Nitric acid and organosulfate were found to co-exist in oxalic acid-containing particles in the winter, which suggests a close association with acidic aqueous phase reactions. Acidic aqueous phase chemical processing of organic precursors is a potential contribution for the formation of oxalic acid in winter." in lines 486-489.

4) Trivialities

At several places, the authors include sentences that do not add to the discussion but are circular and trivial. Examples include

- l. 302: The low percentage of NH4+ in oxalic acid particles in summer indicated the presence of oxalic acid in NH4+ poor particles.

… do you want to say here that oxalic acid is rather accumulated in particles that do not contain NH4+?

- l. 438: Nitrate, sulfate and oxalic acid showed very similar variation patterns in winter, indicating a close connection of their coexistence.
… what is meant by 'connection of coexistence'? – it seems redundant.

<u>Response</u>: "However, the percentage of NH_4^+ with oxalic acid was only 18% in summer but increased to 71% in winter. Linear correlations between NH_4^+-containing oxalic acid particles (C_2-NH_4^+) and total oxalic acid particles are depicted in Figure 3, with better linear regression (r^2=0.98) in winter than summer. The low percentage of NH_4^+ in oxalic acid particles in summer indicated the presence of oxalic acid in NH_4^+-poor particles." has been changed to "However, the NH_4^+-containing oxalic acid particle (C_2-NH_4^+) only accounted for 18% of total oxalic acid particles in summer but this fraction increased to 71% in winter, and linear correlation between C_2-NH_4^+ particles and total oxalic acid particles showed better linear regression (r^2=0.98) in winter than summer, indicating a general mixing state of NH_4^+ with oxalic acid in winter." in lines 300-304.

"Nitrate, sulfate and oxalic acid showed very similar variation patterns in winter, indicating a close connection of their co-existence." has been changed to "Nitrate, sulfate and oxalic acid showed very similar variation patterns in winter, suggesting a close connection of the formation of oxalic acid with the existence of nitrate and sulfate." in lines 412-414.

Besides, we have examined the whole manuscript and revised the following sentence due to same problem. "The prominent photochemical feature of oxalic acid particles suggested a close association of photochemical reactions with oxalic acid production." has been removed in line 340.

Minor comments

1. line 60: 'relative acidity ratio' should be defined here (or simply called 'acidity')

<u>Response</u>: "The general existence of nitric acid and high relative acidity ratio in oxalic acid-containing particles indicates an acidic environment during the formation process of oxalic acid." has been changed to "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." in lines 60-62.

2. line 111-112: The mechanism of oxalic acid as described in the manuscript is not uncertain. The main uncertainty are the oxidant levels - as correctly stated in the response to the reviews, but is should be added here.

<u>Response</u>: "However, the detailed formation mechanisms of oxalic acid from photochemistry and aqueous phase chemistry in ambient aerosols are still not comprehensively understood and need to be further studied." has been changed to "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.” in lines 111-114.

3. line 369-371: This is completely vague and does not have any observational basis. This should be accompanied by a more detailed analysis.

Response: We have removed these sentences in the manuscript due to the uncertainty of the role of Fenton reactions in the formation process of oxalic acid. Please see the detailed discussion and revisions in the major comment 1.

4. line 378: The figure merely shows RH and some inorganic compounds etc. The figure does not ‘discuss’ anything but only shows time traces.

In addition, I suggest showing the H+ concentration in this figures as mol/L(aq) so that it can help the discussion of possible acidity effects.

Response: The concentration of H$^+$ has been changed from nmol/m to mol/L in Figure S5.

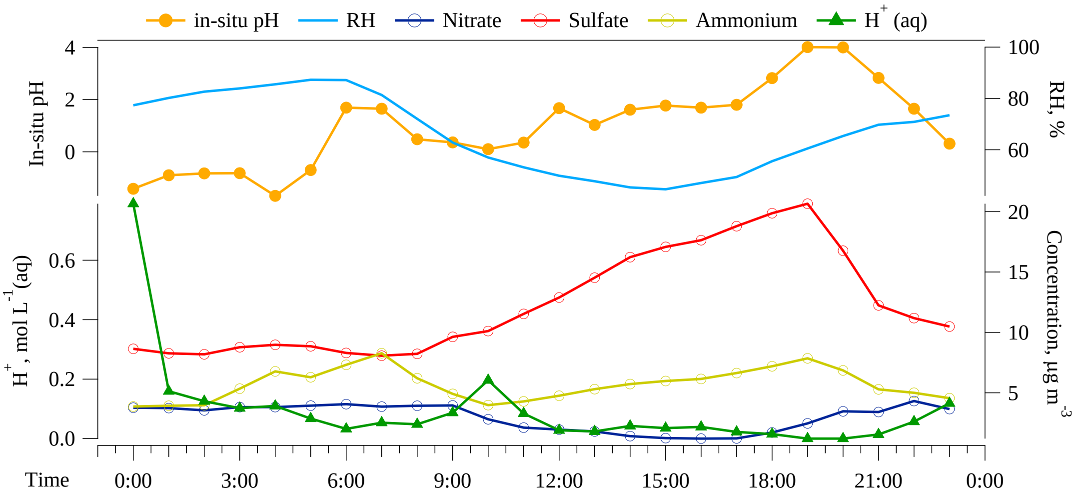

Figure S5. The diurnal variations of in-situ pH (pH_{is}), RH, nitrate, sulfate, ammonium and the aqueous phase concentration of H$^+$ (mol L^{-1}) in aerosols from July 28 to August 1 in 2014.

“LWC is strongly dependent on the ambient RH and affected by water-soluble composition in the aerosols. Thus we investigate the diurnal patterns of RH, major inorganic ions and the free amount of H$^+$ in Figure S5. Although RH increased from 00:00 to 07:00, H$^+$ had higher concentration during this period than the other time, which resulted the lower value of pH_{is} (between -1.42 and 0) from 00:00 to 05:00. Thus more acidic aerosols with pH_{is} below 0 were observed due to the combined effects of the RH and relative abundance of H$^+$ in aerosols.” has been changed to “LWC is strongly dependent on the ambient RH and water-soluble inorganic salts like sulfate, nitrate and ammonium in the aerosols. The aqueous phase concentration of H$^+$ was lower from 12:00 to 21:00 compared to other time, which suggests a less acidity effect on the photochemical production of oxalic acid during this period." under the Figure S5.

5. line 394: replace 'due to reported studies' by 'according to previous studies' (or something similar)

Response: "the precursors of oxalic acid such as glyoxylic acid have higher reaction rate with •OH in high pH solutions due to reported studies" has been changed to "the precursors of oxalic acid such as glyoxylic acid have higher reaction rate with •OH in high pH solutions according to previous studies" in lines 354-356.

6. line 414: During haze periods, photochemical activity is usually reduced.

Response: Because we have removed the discussion of the role of Fenton reactions in the formation process of oxalic acid, the implication of metals in the formation of SOA has also been deleted in the manuscript. "A large amount of Fe related particles are emitted from steel industries in the North China Plain and metals like V, Zn, Cu and Pb from electronic manufacturing (Cui and Zhang, 2008;Dall'Osto et al., 2008). These metals contribute significantly to haze episodes (Moffet et al., 2008;Li et al., 2014), which possibly increases the formation of SOA by yielding more •OH participating the heterogeneous and aqueous reactions." has been removed in line 370.

7. line 429: Remove 'particles' here. 'Oxalic acid particles are prevalent in carbonaceous particles' sounds awkward.

Response: "oxalic acid particles were still prevalent in carbonaceous particles" has been changed to "oxalic acid was still prevalent in carbonaceous particles" in lines 403-404.

Below are the responses to the reviewer's 2nd round comments.

1. (a) Reviewer, 2nd round: The Fenton reaction is NOT a photolysis of H_2O_2. A photolysis would yield two OH radicals, whereas Fenton reaction leads to OH + OH^-

Response: We are sorry for this mistake. The discussion of Fenton reaction has been removed from the manuscript. "the photolysis of H_2O_2 through Fenton reactions involving the catalysis of transition metal ions like $Fe^{2+/3+}$, $Cu^{+/2+}$ and $Mn^{2+/3+}$ likely contributes substantially to the source of •OH in the aqueous phase in this work" has been removed.

(b) Reviewer, 2nd round: l. 383-392: While the authors add some text about the significant loss of oxalic acid due to the photolysis of the iron-oxalato-complex, this discussion is neither balanced nor well connected with the rest of the discussion. If iron is indeed abundantly available for Fenton reaction, why doesn't it show an impact on oxalic acid during day time when – according to literature – up to 99% of oxalic acid might be reduced?

Response: The sink of oxalic acid via the photolysis of iron oxalato complexes has been discussed through the diurnal variation of peak area of iron and oxalic acid in HM type particles. Please see the major comment 2.

(c) Reviewer, 2nd round: The same is true for the loss of oxalic acid by OH reactions. This should be mentioned here.

Response: It is true that the higher pH is favorable for the dissociation of oxalic acid to oxalate, however, the kinetic coefficient for oxalate with OH reaction is $(1.9\pm0.6)\times10^8$ at pH=3 and $(1.6\pm0.6)\times10^8$ at pH=8 according to Herrmann's work (Herrmann, 2003). Thus it is difficult to say the higher pH is favorable for the loss of oxalic acid via •OH reactions without further quantitative result.

(d) Reviewer, 2nd round: At low pH, when oxalic acid is not dissociated, the Henry's law constant is 9000 M/atm. That means only a very small fraction (<<1%) of all oxalic acid is expected to be in the aqueous phase of particles. Therefore, the authors' arguments here are not convincing.

Response: "Oxalate has a very low pKa (1.23) so that even at low pH a substantial fraction is still present as oxalate." has been mentioned by the referee in the 1st round comment (c), and in this work the pH_{is} of ambient particles ranged from 1.5 to 4.01 from 12:00 to 21:00, which is suitable for the oxalic acid to dissociate to oxalate.

(e) Reviewer, 2nd round: In this figure, the loss of oxalate due to the photolysis of the iron-oxalato complex is missing.

Response: Thanks for your suggestion, and we have removed this figure and related discussion from the manuscript and supplement.

2. Reviewer, 2nd round: Thanks for clarifying.

Response: Thank you for your comment.

3. Reviewer, 2nd round: Given all these uncertainties and the fact that the authors do

not have any measurements on iron availability, I suggest to word the role of Fenton chemistry much more carefully throughout the whole manuscript.

Response: According to the referee’s 1^{st} and 2^{nd} round comments, we think that more field measurements and data are needed to comprehensively and qualitatively discuss the contribution of Fenton reaction source •OH radicals to oxalic acid formation. This is out of the interest of this work. Thus we prefer to remove the discussion of the contribution of Fenton reaction in the formation process of oxalic acid and the proposed mechanism along the suggestion of the referee. Fenton reaction is only mentioned as a possibility according to the literature in a very cautious expression. Please see the revisions and changed in major comment 1.

4. Reviewer, 2nd round: I appreciate this change.
Response: Thank you for your comment.

5. Reviewer, 2nd round: The studies by Tan et al., Lim et al. and other by the Turpin group and others, have shown that oxalic acid is not efficiently formed in aqueous aerosol particles. – as I had pointed to in my previous comment.
Either the authors need to clarify that despite of RH < 100% (i.e. no clouds) at the study location, the observed oxalic acid was likely formed in clouds prior to arriving at the study location (what data is available to prove cloudiness) or they should at least briefly mention the more significant formation of oligomers as shown in the cited references.
Response: “The aqueous phase oxidation of glyoxal can take place in both of clouds and wet aerosols (Lim et al., 2010). However, the lower yield of oxalic acid from glyoxal in wet aerosols compared to in clouds has been reported in previous chamber experiments due to the formation of substantial amount of high molecular weight products such as oligomers in aerosols-relevant concentrations (Carlton et al., 2007;Tan et al., 2009). These findings may explain the lower peak of oxalic acid particles at 15:00 compared to that at 19:00.” has been added in the manuscript in lines 348-354.

6. Reviewer, 2nd round: Why is higher temperature favorable for more SOA formation? Rate constants usually increase. However, they do so for both formation rates and loss rates of oxalic acid. In addition, higher temperature also favor higher evaporation of volatile gases, including water.
Response: We believe this expression “The high temperature between 9:00 and 19:00 was favorable to the secondary processing of organic precursors.” is vague and ambiguous. Since the diurnal pattern of temperature is routine and the mixing state of oxalic acid with major chemical species has been discussed in the manuscript, we decide to remove this sentence.

“The diurnal patterns of temperature, wind speed are presented in Figure S7. The high temperature between 9:00 and 19:00 was favorable to the secondary processing of organic precursors. The wind speed was low during the whole day, especially between 9:00 and 18:00, which provided a stagnant environment for the increase in oxalic acid produced from photochemical process.” has been changed to “The wind speed was low during the whole day (Figure S6), especially between 9:00 and 18:00, which provided a stagnant environment for the increase in oxalic acid produced from photochemical process.” in lines 399-401.

7. Reviewer, 2nd round: Thanks for clarification.

Response: Thank you for your comment.

References:

Anglada, J. M., Martins-Costa, M., Ruiz-López, M. F., and Francisco, J. S.: Spectroscopic signatures of ozone at the air–water interface and photochemistry implications, Proceedings of the National Academy of Sciences, 111, 11618-11623, 10.1073/pnas.1411727111, 2014.

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