

Re-Review by the manuscript by Cheng et al.,  
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.

#### 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.

##### 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.

##### 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'  
(1. 447). These studies did not show acid catalyzed reactions.

##### 4) Trivialities

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

- 1. 302: The low percentage of NH<sub>4</sub><sup>+</sup> in oxalic acid particles in  
summer indicated the presence of oxalic acid in NH<sub>4</sub><sup>+</sup> poor particles.  
... do you want to say here that oxalic acid is rather accumulated in  
particles that do not contain NH<sub>4</sub><sup>+</sup>?

- 1. 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.

#### Minor comments

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

1. 111-112: The mechanism of oxalic acid 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.

1. 369-371: This is completely vague and does not have any observational basis. This should be accompanied by a more detailed analysis.

1. 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<sup>+</sup> concentration in this figures as mol/L(aq) so that it can help the discussion of possible acidity effects.

1. 394: replace 'due to reported studies' by 'according to previous studies' (or something similar)

1. 414: During haze periods, photochemical activity is usually reduced.

1. 429: Remove 'particles' here. 'Oxalic acid particles are prevalent in carbonaceous particles' sounds awkward.

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Below is the response by the authors to my original comment. My added comments are in red.

### Specific comments and point by point responses:

#### Major comments

1. The suggested chemical mechanism is oversimplified and contains several misconceptions and/or omissions:

a) Generally, it is assumed that direct OH uptake is the main source of OH in the aqueous phase [e.g., Ervens et al., 2003; Herrmann, 2003; Tilgner et al., 2013]. Therefore higher OH (gas) concentration will lead to higher OH concentration in the aqueous phase. Higher OH (aq) concentration will also lead to more oxidation of oxalate and therefore less SOA.

**Response:** We thank the reviewer's comments. The main sources of •OH in the aqueous phase contain both direct uptake from the gas phase and chemical sources in the aqueous phase such as Fenton reactions and photolysis of H<sub>2</sub>O<sub>2</sub> and nitrate (Ervens et al., 2014; Ervens, 2015; Gligorovski et al., 2015; Herrmann et al., 2015). Although the concentrations of H<sub>2</sub>O<sub>2</sub> and •OH in gas and aqueous phases are not available in this work, considering much higher Henry's law constant of H<sub>2</sub>O<sub>2</sub> ( $K_H=8.3\times 10^4$  M atm<sup>-1</sup>) than •OH ( $K_H=30$  M atm<sup>-1</sup>) (Hanson et al., 1992; O'Sullivan et al., 1996) and abundant fraction of transition metals in the oxalic acid particles in this work, aqueous phase chemistry likely contributes substantially to the source of •OH in the aqueous phase according to high efficiency of •OH production from Fenton type reactions (Gligorovski et al., 2015). The aqueous phase oxidation of glyoxal and methylglyoxal is the main source of oxalic acid production, and their reaction rates with •OH ( $1.1\times 10^9$  mole<sup>-1</sup> s<sup>-1</sup>) is one order of magnitude higher than oxalic acid with •OH ( $1.9\times 10^8$  mole<sup>-1</sup> s<sup>-1</sup>) as previously reported (Herrmann, 2003; Myriokefalitakis et al., 2011). Thus, the high •OH (aq) concentration would lead to the enrichment of oxalic acid in aqueous phase.

In order to clarify these points, we have changed “While the partition of •OH from gas to aqueous phase is limited by its low Henry’s law constant ( $K_{H,OH}=30 \text{ M atm}^{-1}$ ) and short lifetime of •OH in the gas phase (Hanson et al., 1992), the main sources of aqueous •OH are from the photolysis of  $\text{H}_2\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and chromophoric dissolved organic matter (CDOM) (Yu et al., 2014;Badali et al., 2015;Gligorovski et al., 2015;Tong et al., 2016). Among these sources the photolysis of  $\text{H}_2\text{O}_2$  through Fenton reactions involving the catalysis of transition metal ions like  $\text{Fe}^{2+/3+}$ ,  $\text{Cu}^{+/2+}$  and  $\text{Mn}^{2+/3+}$  is an efficient source of •OH (Deguillaume et al., 2005;Herrmann et al., 2005;Ervens et al., 2014).” to “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  $\text{H}_2\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , 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 ( $K_{H,OH}=30 \text{ M atm}^{-1}$ ) (Hanson et al., 1992) and abundant fraction of transition metal ions in the oxalic acid particles, the photolysis of  $\text{H}_2\text{O}_2$  through Fenton reactions involving the catalysis of transition metal ions like  $\text{Fe}^{2+/3+}$ ,  $\text{Cu}^{+/2+}$  and  $\text{Mn}^{2+/3+}$  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).” in lines 345-355.

Reviewer, 2<sup>nd</sup> round: The Fenton reaction is NOT a photolysis of  $\text{H}_2\text{O}_2$ . A photolysis would yield two OH radicals, whereas Fenton reaction leads to  $\text{OH} + \text{OH}^-$

b) Higher iron concentration might lead to more OH. However, more importantly is the effect of the loss of oxalate due to the photolysis of the iron-oxalato complex. While this reaction is mentioned in the manuscript, its predominating role in oxalate loss [Sorooshian et al., 2013] is not discussed in a balanced way.

**Response:** The degradation of oxalic acid from the complex with iron has been discussed in the manuscript to explain the diurnal change of oxalic acid particles. Indeed, it would be more specific to evaluate the net production of oxalic acid from photochemical process if we could calculate the production and loss of oxalic acid. Unfortunately, we have no real time data about the ambient concentrations of oxalic acid and iron, so the exact amount of oxalic acid loss from the photolysis of the iron complexes cannot be obtained for now.

Reviewer, 2<sup>nd</sup> round: 1. 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?

c) At low pH, it can be expected that reaction rates are lower since in general the undissociated acids (glyoxylic, glycolic) react more slowly than their dissociated

counterparts. Oxalate has a very low pKa (1.23) so that even at low pH a substantial fraction is still present as oxalate. Could changes in pH and therefore reaction rates explain some of the temporal trends?

**Response:** Indeed, the reaction rate of glyoxylate with  $\bullet\text{OH}$  ( $k=2.8\times 10^9 \text{ mole}^{-1} \text{ s}^{-1}$ , pH=8) is one order of magnitude higher than glyoxylic acid ( $k=3.6\times 10^8 \text{ mole}^{-1} \text{ s}^{-1}$ , pH=1), so the aqueous phase with high pH value is more favorable for the production of oxalic acid from the oxidation of precursors. The SPAMS can only detect the ion peak of oxalate ion (m/z -89) in single particles, so the percentage of oxalate in total oxalic acid cannot tell from the data of SPAMS. We believe the diurnal change of pH also has influence on the oxidative process of organic precursors in addition to provide a proper environment for Fenton like reactions. We have added the related discussion in the manuscript. “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  $\bullet\text{OH}$  at high pH based on previous studies(Ervens et al., 2003;Herrmann, 2003;Cheng et al., 2015), thus the increase of pH not only enhances  $\bullet\text{OH}$  production from photo-Fenton reactions, but also promotes the oxidation process of the precursors of oxalic acid by  $\bullet\text{OH}$ .” has been added in lines 392-397.

Reviewer, 2<sup>nd</sup> round: The same is true for the loss of oxalic acid by OH reactions. This should be mentioned here.

d) At very low pH (< 1.23), it is expected that oxalic acid is present in undissociated form and therefore not able to make salts or complexes that „trap“ it in the particle phase. This fact contradicts the trend of increased oxalate concentrations at low pH. This should be discussed.

**Response:** Oxalic acid is predominantly enriched in particle phase due to its low vapor pressure ( $3.5\times 10^{-5}$  Torr) (Prenni et al., 2001) and high water solubility. Several studies have indicated that more than 70% of oxalic acid could exist in particle phase (Limbeck et al., 2001;Mochida et al., 2003a;Mochida et al., 2003b). The salt and complex formation of oxalate with ammonium, potassium, sodium and metal ions have been considered as the main behavior of oxalic acid in the particle phase (Yao et al., 2002;Moffet et al., 2008;Furukawa and Takahashi, 2011), and a higher pH condition would be more favorable for the salt and complex formation. Due to the abundant signals of potassium, sodium and metal ions in this work, oxalic acid can react with these anions and stay in the particle phase. Besides, the oxalic acid particles and in-situ pH both exhibited an increase in the afternoon, which was in accordance with the announcement of more oxalate at higher pH.

Reviewer, 2<sup>nd</sup> 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.

e) The proposed mechanism is by no means new or detailed (l. 360). It does not include any sinks of oxalate, nor complex formation. It is one possible formation mechanism of oxalic acid from glyoxal. The generalization to dicarbonyls and aldehydes is not correct since only small compounds (C2) will follow the suggested reaction pathways.

**Response:** The photochemical production of oxalic acid has been studied in many field researches due to a similar diurnal pattern with O<sub>3</sub> (Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005; Aggarwal and Kawamura, 2008; Miyazaki et al., 2009), but the detailed photochemical formation process of oxalic acid has not been comprehensively discussed. While the oxidation of glyoxal and glyoxylic acid has been proposed and discussed in many field, laboratory and model studies (Myriokefalitakis et al., 2011; Wang et al., 2012; Kawamura et al., 2013; Ervens et al., 2014; Wang et al., 2014), the influential factors of their oxidation reactions with •OH still needs to be ascertained from the field studies. Based on a comprehensive discussion of the mixing state of oxalic acid with secondary ions and transition metals, we propose a plausible explanation to connect among the diurnal pattern of O<sub>3</sub>, oxalic acid, iron and in-situ pH. (Sorooshian et al., 2013; Zhou et al., 2015). However, without the direct measurement of the concentrations of •OH, iron ions, and oxalic acid, the proposed photochemical formation mechanism of oxalic acid in the original manuscript is difficult to be confirmed. Thus, we have changed the expression about the oxalic acid production in HM type particles into a plausible explanation instead of a proposed formation mechanism, and have softened our tone in the discussions. The schematic diagram to explain the formation process of oxalic acid in the HM type particles has been moved to the supplement material in Figure S6.

The related discussion has been revised as follows:

In the abstract “Furthermore, favorable in-situ pH (2-4) conditions were observed, which promote Fenton like reactions for efficient production of •OH in HM type particles. A mechanism in which products of photochemical oxidation of VOCs partitioned into the aqueous phase of HM particles, followed by multistep oxidation of •OH through Fenton like reactions to form oxalic acid is proposed.” has been changed to “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.” in lines 55-58.

“Based on above discussions, detailed mechanism for oxalic acid formation in acidic aqueous phase of particles is proposed for our field observations (Figure 8).” has been changed to “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 lines 398-400.

In the conclusion “The favorable in-situ pH and the dominance of transition metal ions in oxalic acid particles suggests an enhanced production of •OH from Fenton like reactions. A mechanism involving the photochemical production of VOCs via efficient aqueous phase reactions with enhanced •OH to oxalic acid was proposed.” has been

changed to “Furthermore, suitable in-situ pH is favorable for Fenton like reactions to produce  $\bullet\text{OH}$  in HM type particles, and might promote the oxalic acid production from the oxidation of precursors by  $\bullet\text{OH}$  in HM type particles.” in lines 504-506.

To address the referee’s concern, we have revised the description of dicarbonyls and aldehydes in Figure S6. The “dicarbonyls and aldehydes” has been changed to “Low molecular weight dicarbonyls (e.g. glyoxal)”, and “Hydrated dicarbonyls and aldehydes” has been changed to “Hydrated dicarbonyls (e.g. glyoxal)” in Figure S6:

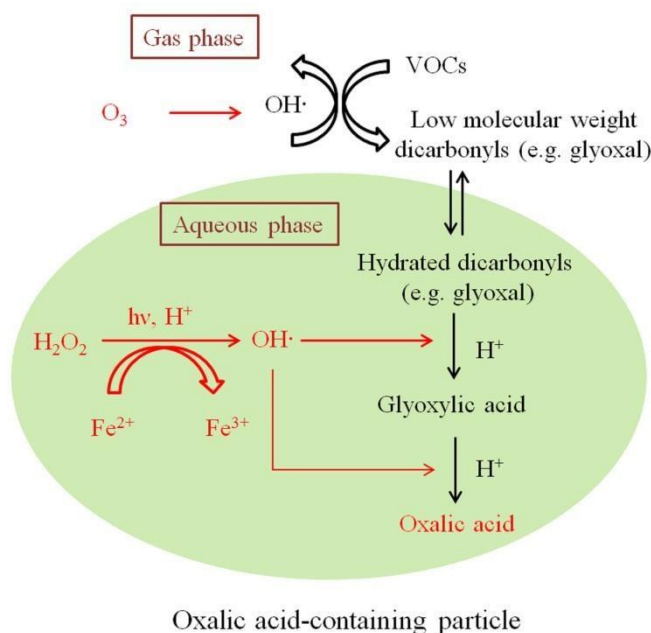


Figure S6. A schematic diagram to explain the formation process of oxalic acid in the HM type particles: the red steps are enhanced by photochemical activities in the current study.

Reviewer, 2<sup>nd</sup> round: In this figure, the loss of oxalate due to the photolysis of the iron-oxalato complex is missing.

2. The number fraction of oxalate containing particles seems very low. Is this comparable to other measurements? What was the mass fraction of oxalate (a) in the particles and (b) related to the total aerosol loading?

**Response:** Yang et al. (2009) has measured the oxalic acid-containing particles in the urban area of Shanghai by ATOFMS and found 15,789 oxalate-containing particles, accounting for 3.4% of the total collected particles. In this work 13,109 and 20,504 of oxalic acid-containing particles were obtained in summer and winter separately, accounting for 2.5% and 2.7% of the total detected particles. The abundance of oxalic acid-containing particles in this work was lower than the reported studies in the urban area of Shanghai (3.4%), which was possibly due to less anthropogenic precursors for oxalic acid at the rural sampling site in Heshan. Higher abundance of oxalic acid particles (1-40%) was observed in the much cleaner western Pacific Ocean by Sullivan et al. (2007), which corresponded to higher ambient concentration of DCAs

(19±4.8%) in total particulate organic matter. From the reported studies in PRD (Yao et al. 2004; Ho et al. 2011), the abundance of DCAs was 1-3.5% in total organic matter, which was much lower than those in the western Pacific Ocean, leading to lower percentage of oxalic acid-containing particles in this work. We have added the comparison between this work and the study in Shanghai in the manuscript. “The percentage of oxalic acid-containing particles in total particles in this work was comparable to the reported value in the urban area of Shanghai (3.4%) (Yang et al., 2009). However, these percentages are in general much lower than those reported in cleaner environments such as the western Pacific Ocean where oxalic acid was found in up to 1-40% of total particles due to little anthropogenic influences (Sullivan and Prather, 2007).” is added in lines 192-198.

For the second question, the relative fraction of oxalic acid particles in total detected particles was accounting for 2.5% and 2.7% of the total detected particles in summer and winter (Figure 1a). However, because we didn’t collect filter samples during the sampling period, we cannot calculate the relative mass fraction of oxalic acid in ambient PM<sub>2.5</sub>.

Reviewer, 2<sup>nd</sup> round: Thanks for clarifying.

3. Was all iron in the particles in form of soluble iron, i.e. available for reaction?

**Response:** Indeed, it would be more convincing to discuss the role of Fenton reactions in the formation of oxalic acid particles if we could obtain the concentration of Fe<sup>2+/3+</sup> ions. However, we didn’t collect filter samples during the sampling period, so the concentration of Fe<sup>2+/3+</sup> ions were not measured. Besides, the SPAMS could only detect the peak area of iron element, and the different valence state of iron could not be distinguished. Therefore, the discussions between Fenton reactions and oxalic acid production have been revised to a plausible explanation instead of a proposed formation mechanism.

Reviewer, 2<sup>nd</sup> 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.

4. Oxalate and the other DCAs usually represent only a very small fraction of the total organic aerosol mass. Therefore the title is misleading as it talks about SOA in general.

**Response:** Based on the comments from you and other reviews, the title “Mixing state of oxalic acid containing particles in the rural area of Pearl River Delta, China: implication for seasonal formation mechanism of Secondary Organic Aerosol (SOA)” has been changed to “Mixing state of oxalic acid containing particles in the rural area of Pearl River Delta, China: implications for the formation mechanism of oxalic acid”.

Reviewer, 2<sup>nd</sup> round: I appreciate this change.

5. It seems based on Figure S5, that RH was always < 100% (except a very brief period). Therefore, the discussed aqueous chemistry will have to take place in aqueous



aerosol. There are many studies that have discussed different reaction pathways in aqueous aerosol vs cloud [e.g., Tan et al., 2009; Lim et al., 2010] with less efficient oxalate formation in the former. In addition, it seems likely that iron ions might be less dissolved in the rather highly concentrated aqueous aerosol solutions. All discussion is about chemistry as it happens in cloud droplets. These two regimes should be differentiated.

**Response:** While the aqueous phase formation of oxalic acid from organic precursors has been found both in cloud droplets and aerosols water, the more efficient production in cloud droplets than aerosols water has been reported by several studies (Tan et al., 2009; Lim et al., 2010; Myriokefalitakis et al., 2011). In this work, the well internally mixing state between oxalic acid and sulfate in summer and winter suggests a common production route of oxalic acid and sulfate, likely aqueous phase reactions. The strong photochemical pattern of oxalic acid particles with O<sub>3</sub> under the condition of RH below 100% implies a less influence from cloud-processing of oxalic acid particles. Thus we speculate the oxalic acid formation process in HM type particles is related to aqueous phase reactions in aerosols, and this point has been stated in the manuscript: “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<sub>3</sub> concentrations in the afternoon lead to more production of reactive radicals such as •OH and HO<sub>2</sub>•, 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” in lines 398-404.

Although the reviewer has pointed out that iron ions might be less dissolved in the rather highly concentrated aqueous aerosol solutions, the low in-situ pH of aerosols is also favorable for the dissolved of iron. Because we didn't collect filter samples during the sampling period, the concentration of Fe<sup>2+/3+</sup> ions were not measured, so the ratio of Fe<sup>2+/3+</sup> ions to total iron element could not be evaluated for now, and we will further discuss this issue in our next study.

Reviewer, 2<sup>nd</sup> 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.

6. While briefly discussed, it is not clear to what extent different air masses cause different oxalate levels. How much of the measured oxalate is background material? Did other meteorological conditions affect the concentrations such as changes in boundary layer?



**Response:** The different air masses arriving in sampling site in summer and winter had substantial impact on the amount of organic precursors from anthropogenic emissions. More carbonaceous signals were found in the oxalic acid particles in winter since oxalic acid is mainly derived from secondary oxidation of VOCs and subsequent intermediates. However, it is still difficult to quantify exactly the increase of oxalic acid concentration in winter based on the SPAMS data. The sampling site in this work is a rural site and the aerosols are influenced by the regional transport in PRD. Although we cannot obtain the exact background level of oxalic acid, the lowest percentage of oxalic acid particles in total detected particles is used to evaluate the approximate background level of oxalic acid particles. The lowest hourly percentage of oxalic acid particles in total detected particles were 0.1% and 0.5 % in summer and winter, which were much lower than the average value in summer (2.3%) and winter (2.8%), suggesting a small impact of the background distribution to the measurements of oxalic acid particles.

The wind speed was from 0.3 to 4.0  $\text{m}\cdot\text{s}^{-1}$  with an average of 1.6  $\text{m}\cdot\text{s}^{-1}$  during the sampling period in winter, which indicated a rather stagnant atmospheric condition. The stagnant atmospheric condition in winter was favorable for the aging process of aerosols and might have contributed to the broader size distribution of oxalic acid particles. Unfortunately the height of boundary layer was not available in this work. Nevertheless, the relative abundance of oxalic acid particles had no obvious increase at night and the lower mixing height may not be an important factor during the formation process of oxalic acid in the winter. We will further examine their relationships in our next study.

The diurnal variations of meteorological factors such as temperature, RH and wind speed have been discussed in Figure S7.

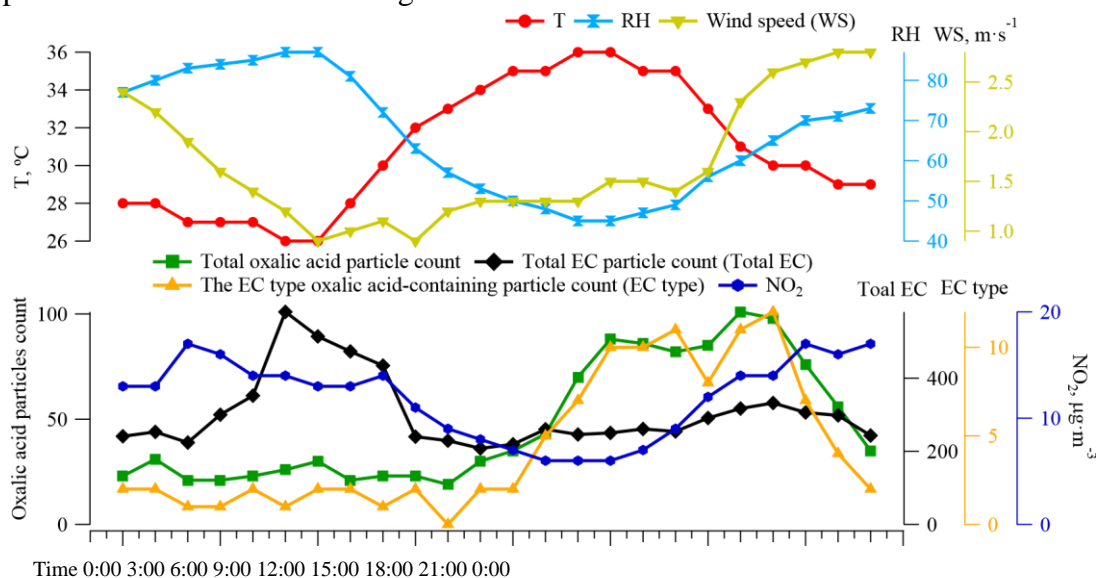


Figure S7. The diurnal variations of temperature (T), RH, wind speed (WS), oxalic acid particles, total EC particles, the EC type oxalic acid-containing particles and ambient  $\text{NO}_2$  concentrations from July 28 to August 1 in 2014.

We have added the related discussion in the manuscript. “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. The influence from traffic emission was investigated through the diurnal variations of total EC type particles and NO<sub>2</sub> (Figure S7). The EC type particles increased from 12:00 to 21:00, which had same variation as total oxalic acid, but NO<sub>2</sub> followed the rush hour pattern with two peaks from 5:00 to 8:00 and from 18:00 to 21:00. Traffic emission is not expected to have a large contribution to oxalic acid in this study.” has been added in lines 417-426 in the manuscript.

Reviewer, 2<sup>nd</sup> 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.

7. I am not sure what Figure S6 is really showing. Does it show a correlation of organosulfur particles and oxalate or does it simply show that more particles cause higher concentrations of „everything“? How about the mixing state of organosulfur compounds and oxalic acid particles? The fact that they are in the same particle class, does not necessarily mean that they are internally mixed and therefore their formation pathways are related.

**Response:** The original Figure S6 (now Figure S8) presented the temporal variation of total organosulfate (m/z=-155) containing particles during whole sampling periods in Heshan, China. The temporal trend of organosulfate-containing oxalic acid particles in winter has been added in Figure S8, which exhibited a similar pattern as the total oxalic acid particles. The percentage of organosulfate-containing oxalic acid particles in total oxalic acid particles ranged from 0 to 16.4% with the highest ratio observed on February 8. The linear regression between oxalic acid particles and organosulfate particles in Figure 9b has been replaced by the correlation between organosulfate-containing oxalic acid particles and total oxalic acid particles, and the robust correlation ( $r^2=0.81$ ) between them supports a possible production of oxalic acid from acid-catalyzed reactions.

We also believe more evidence and discussion are needed to support the connection between oxalic acid formation process and acidic aqueous phase chemistry. So the related discussions have added as follows:

“Despite lower O<sub>3</sub> concentrations and photochemical activity in winter, oxalic acid particles were still prevalent in carbonaceous particles, especially BB type particles. While oxalic acid was found to be internally mixed with sulfate and nitrate both in summer and winter, the nitric acid was only observed in oxalic acid particles in winter, indicating a strongly acidic nature of oxalic acid particles in winter. Considering a possible connection of oxalic acid production with the acidic environment, the temporal concentrations of oxalic acid, sulfate and nitrate were investigated through their peak areas in the carbonaceous type oxalic acid particles including EC, OC, ECOC and BB

type in Figure 8. The peaks of  $m/z$  -62[NO<sub>3</sub>]<sup>-</sup> and - 97[HSO<sub>4</sub>]<sup>-</sup> represent nitrate and sulfate, respectively. Nitrate, sulfate and oxalic acid showed very similar variation patterns in winter, indicating a close connection of their co-existence. Although nitric acid was found in the oxalic acid particles, the acidity of the oxalic acid particles was not estimated since the real-time concentration of inorganic ions was not available during the sampling period in winter. Instead the relative acidity ratio ( $R_{ra}$ ), defined as the ratio of total peak areas of nitrate and sulfate to the peak area of ammonium ( $m/z$  18[NH<sub>4</sub>]<sup>+</sup>), was used (Denkenberger et al., 2007;Pratt et al., 2009). The  $R_{ra}$  of carbonaceous type oxalic acid particles ranged from 7 to 114 with an average value of 25 (Figure 8), indicating an intensely acidic environment of carbonaceous type oxalic acid particles in winter. Several studies have reported potential production of oxalic acid from acid-catalyzed aqueous phase reactions in aerosols (Carlton et al., 2006;Carlton et al., 2007;Tan et al., 2009). In this work the acidic environment of the carbonaceous type oxalic acid particles and similar variation patterns among oxalic acid, sulfate and nitrate may suggest a relationship between the degradation of organic precursors and the acidic chemical process. However, the temporal change of  $R_{ra}$  did not follow a similar trend as the peak area of oxalic acid in most particles, possibly due to the multi-step formation of oxalic acid influenced by many factors such as precursors, liquid water content and ion strength (Carlton et al., 2007;Cheng et al., 2013;Cheng et al., 2015).” has been added in lines 428-455.

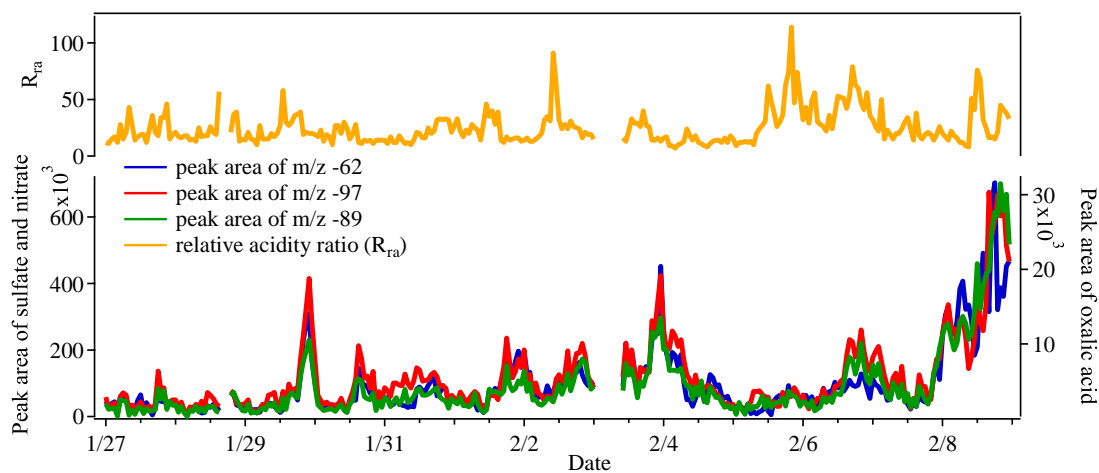


Figure 8. The temporal variations of peak area of nitrate, sulfate and oxalic acid, and the relative acidity ratio ( $R_{ra}$ ) in carbonaceous type oxalic acid particles in winter.

The related discussions about Figure 9 and Figure S8 have been revised: “The organosulfate derived from glyoxal requires acidic aqueous environment of particles, and herein is used as an indicator of acid-catalyzed ageing process of organic compounds. The temporal variation of organosulfate ( $m/z=-155$ ) containing particles during the entire sampling period in Heshan, China is shown in Figure S6. During the episode, oxalic acid particles had moderate linear correlation with organosulfate particles (Figure 9b).” has been changed to “The formation of organosulfates from glyoxal requires an acidic aqueous environment, which can be used as an indicator of acid-catalyzed ageing process of organic compounds. The temporal trend of

organosulfate-containing oxalic acid particles in winter is shown in Figure S8, which exhibited a similar pattern as the total oxalic acid particles during the whole sampling period in winter. The percentage of organosulfate-containing oxalic acid particles in total oxalic acid particles ranged from 0 to 16.4% with the highest ratio observed in the episode (February 8). The linear regression between total oxalic acid particles and organosulfate-containing oxalic acid particles in the episode is exhibited in Figure 9b, and the robust correlation ( $r^2=0.81$ ) between them suggests that oxalic acid and organosulfate may share similar formation process.” in lines 476-486.

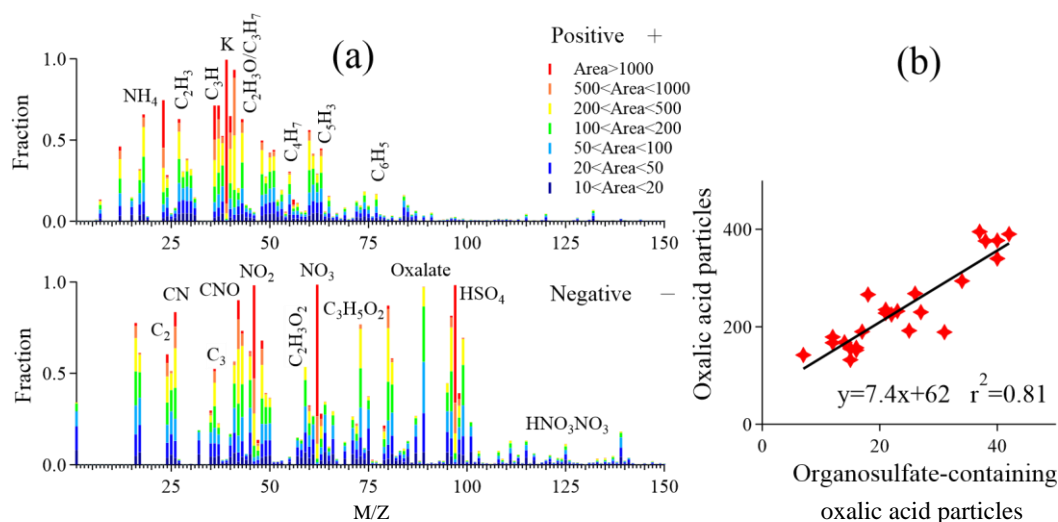


Figure 9. The comprehensive study of oxalic acid particles increase on Feb 8, 2015: (a) The digitized positive and negative ion mass spectrum of oxalic acid particles during the episode; (b) Linear regression between total oxalic acid particles and organosulfate-containing oxalic acid particles (m/z -155).

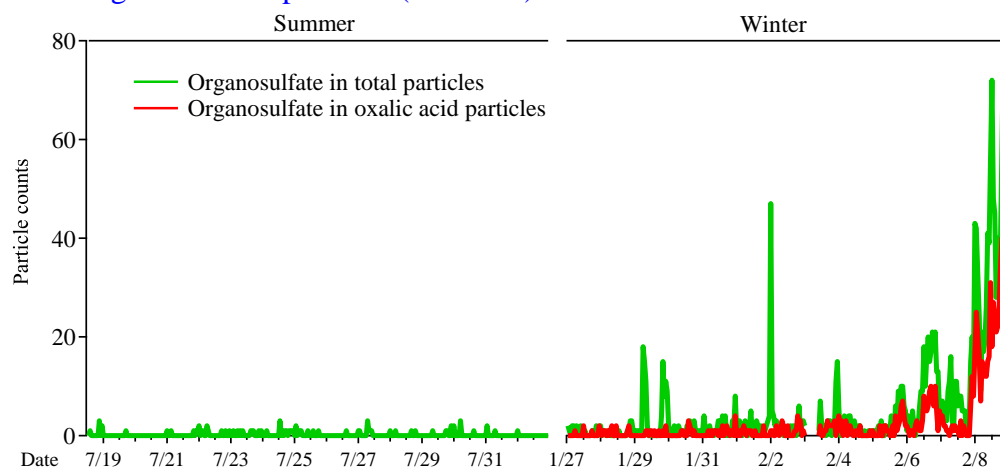


Figure S8. Temporal variation of organosulfate (m/z=-155) containing particles in total particles and in oxalic acid particles in Heshan, China.

“The temporal trend of organosulfate-containing oxalic acid particles in winter is also shown in Figure S8, which exhibited a similar pattern as the total oxalic acid particles. The percentage of organosulfate-containing oxalic acid particles in total oxalic

acid particles ranged from 0 to 16.4% with the highest ratio observed on February 8. ”  
has been added in the supplement material.

Reviewer, 2<sup>nd</sup> round: Thanks for clarification.