

Response to the comments of Anonymous Referee #1

[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: implication for seasonal formation mechanism of Secondary Organic Aerosol (SOA)

General comments:

This paper reports the observation results of abundances and mixing states of oxalic acid containing particles using a single particle aerosol mass spectrometer in the summer and winter of 2014 in Heshan, an atmospheric measurement supersite of PRD region, China. Based on the difference in mass spectrometry, the authors proposed two different seasonal formation mechanisms for oxalic acid. This work presented interesting results, which is helpful for improving our understanding on SOA formation. After addressing the questions below, this paper could be accepted for a final publication in the journal.

Response: Thank you for your comments. These comments are all valuable and very helpful for revising and improving our paper, as well as the important guiding significance to our researches. We have studied these comments carefully and have made corrections. Our responses to the comments are itemized below.

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

Best regards!

Sincerely yours

Mei Li

April 6, 2017

Specific comments and point by point responses:

1. Page 3, line 84-91, these statements are confusing. On one hand, the authors claimed that primary emissions of DCA are minor. On the other hand, however, they stated that high concentrations of DCA have been observed in biomass burning plumes and the primary sources are still unclear. So, the authors should clarify if the primary source of DCA is important or not.

Response: The primary emissions of DCAs from anthropogenic sources in urban areas are minor according to reported studies (Huang and Yu, 2007; Stone et al., 2010). As for the biomass burning emission, research work from biomass burning plume showed less than 23% of oxalic acid had strong connection with direct emission from biomass burning (Kundu et al., 2010), so the primary source of DCAs is less important compared to secondary sources. We have changed “Even though high concentrations of DCAs have been observed in air masses influenced by biomass burning (Kundu et al., 2010; Kawamura et al., 2013), the primary source of DCAs is still not clear (van Pinxteren et al., 2014).” to “High concentrations of DCAs have been observed in biomass burning plume (Kundu et al., 2010; Kawamura et al., 2013) with more than 70% of DCAs produced from photochemical oxidation of water-soluble organic compounds, and only a small contribution from direct biomass burning emission (van Pinxteren et al., 2014).” in lines 89-92.

2. Page 7, line 189-193, what principle here is used for the particle type definitions? It is hard to understand what are the differences between the ECOC type, EC and OC. In Table S1, the authors presented the criteria for particle type identification, is there any references to support such definitions?

Response: We have added the classification rules for oxalic acid particles in the manuscript and explain the differences among the EC, OC, ECOC type, and several literature publications are cited in the manuscript to support these classification rules. “All oxalic acid particles are classified into eight types: elemental carbon (EC), organic carbon (OC), elemental and organic carbon (ECOC), biomass burning (BB), heavy metal (HM), secondary (Sec), sodium-potassium (NaK) and dust.” has been changed to “The oxalic acid containing particles are classified into eight types in the following order: elemental carbon (EC), organic carbon (OC), elemental and organic carbon (ECOC), biomass burning (BB), heavy metal (HM), secondary (Sec), sodium-potassium (NaK) and dust. Different type particles are identified according to characteristic ion markers and dominant chemical species (Table S1): (1) particles containing abundant carbon clusters like $\pm 12[\text{C}]^{+/-}$, $\pm 24[\text{C}_2]^{+/-}$, $\pm 36[\text{C}_3]^{+/-}$ with relative peak area more than 0.5% are classified as EC type, (2) any remaining particles containing abundant signals of $27[\text{C}_2\text{H}_3]^+$, $43[\text{C}_2\text{H}_3\text{O}]^+$ and hydrocarbon clusters with relative peak area more than 0.5% are classified as OC type, (3) any remaining particles containing signals of $\pm 12[\text{C}]^{+/-}$, $\pm 24[\text{C}_2]^{+/-}$, $37[\text{C}_3\text{H}]^+$ and $43[\text{C}_2\text{H}_3\text{O}]^+$ with relative peak area more than 0.5% are classified as ECOC type, (4) any remaining particles containing abundant signals of $39[\text{K}]^+$ (peak area > 1500) with relative peak area of $-59[\text{C}_2\text{H}_3\text{O}_2]^-$ and $-73[\text{C}_3\text{H}_5\text{O}_2]^-$ simultaneously more than 0.5% are classified

as BB type, (5) any remaining particles containing signals of $55[\text{Mn}]^+$, $56[\text{Fe}]^+$, $63/65[\text{Cu}]^+$, $64[\text{Zn}]^+$ and $208[\text{Pb}]^+$ with relative peak area more than 0.5% are classified as HM type, (6) any remaining particles containing abundant signals of $18[\text{NH}_4]^+$ (peak area>50), $-62[\text{NO}_3]^-$ (peak area>100) and $-97[\text{HSO}_4]^-$ (peak area>100) are classified as Sec type, (7) any remaining particles containing abundant signals of $23[\text{Na}]^+$ (peak area>1500) and related species are classified as NaK type, (8) any remaining particles containing signals of $40[\text{Ca}]^+$, $56[\text{CaO}]^+$ and related species are classified as dust type. The rules for oxalic acid particles classification in the current work have been reported in previous studies (Sullivan and Prather, 2007; Yang et al., 2009; Zhang et al., 2013; Li et al., 2014).” in lines 199-221.

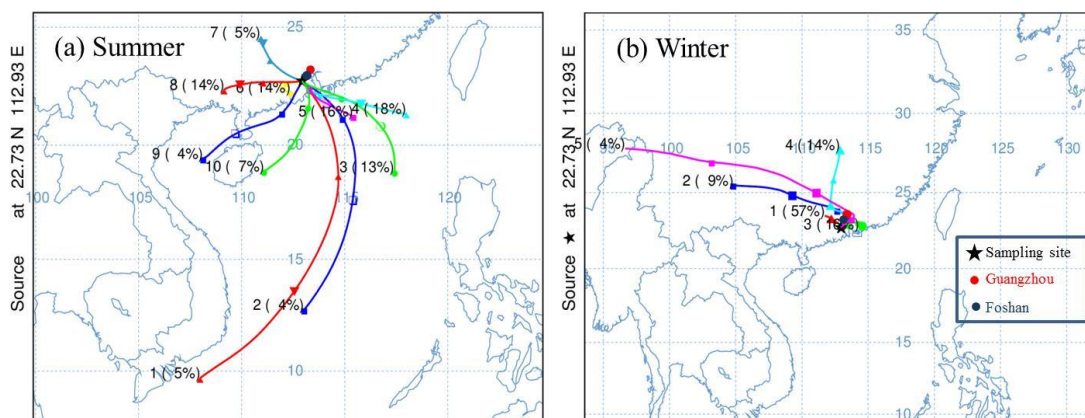
3. Page 7, line 201-209, as for the ISORROPIA model, which mode you used? stable mode or metastable mode? What is the basis of the mode you choose? Since this work claimed that there are at least eight types of oxalic acid-containing particles, which means that aerosols measured here can not be taken as a single phase. In other words, the ISORROPIA mode should be run as a stable mode. Did the authors run this mode for the acidity and ALWC calculation? Please clarify.

Response: We have used stable mode and reverse type in the ISORROPIA model to calculate the concentration of H^+ and ALWC. Then we calculated the in-situ pH based on the below equation:

$$pH_{is} = -\log \alpha_{\text{H}^+} = -\log(\gamma_{\text{H}^+} \times n_{\text{H}^+} \times 1000/V_a) \quad , \text{ where } n_{\text{H}^+} \text{ is the concentration of } \text{H}^+ \text{ (mol m}^{-3}\text{) and } V_a \text{ is the volume concentration of the } \text{H}_2\text{O (cm}^3 \text{ m}^{-3}\text{). In order to classify this point, we add the description of the running mode and type in the ISORROPIA mode. “We choose stable mode and reverse type in the ISORROPIA model to calculate the concentration of } \text{H}^+ \text{ and the liquid water content in this work.” has been added in lines 231-233.}$$

4. Page 7, line 211-216, please give the locations of Guangzhou and Foshan in Figure S4.

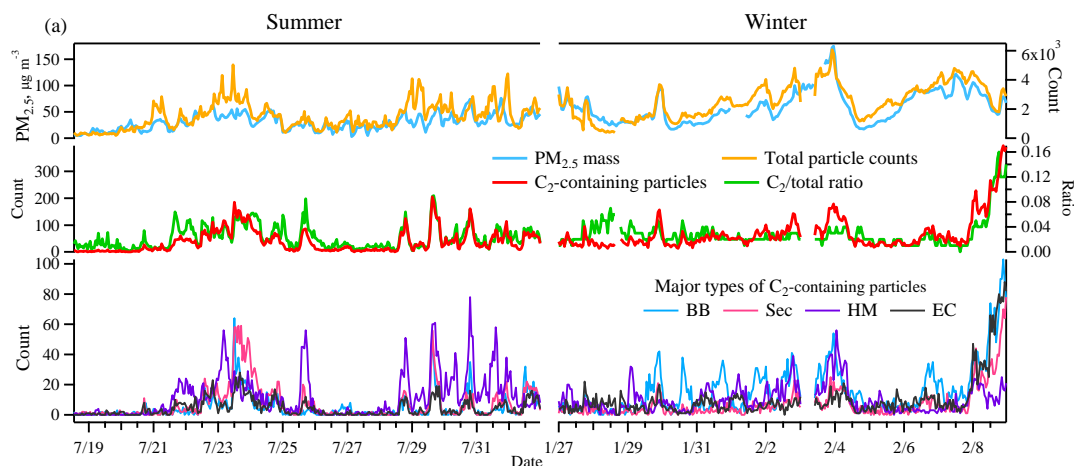
Response: We have added the locations of Guangzhou and Foshan in Figure S4 as follows:



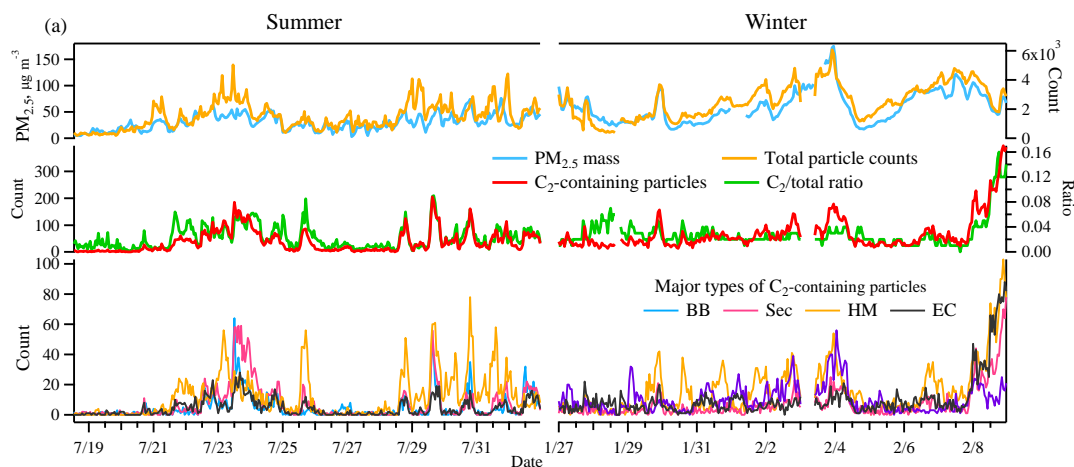
5. Page 8, line 239, in Figure 1a, the color of HM type particles is blue not purple?

Response: We did use purple color to represent the HM type particles in the manuscript but agreed that the purple color is not clearly distinguishable from red and light blue color. We have replaced purple color by orange color.

The original Figure 1(a) is as follows:



The revised Figure 1(a) with color change for HM type is as follows:



“In summer HM type particles (purple) and total oxalic acid particles exhibited similar diurnal patterns” is changed to “In summer HM type particles (orange color) and total oxalic acid particles exhibited similar diurnal patterns” in lines 269-270.

6. Page 10, section 3.2. Zn and Pb are typical tracers for vehicle emissions. The strong associations between heavy metals and oxalic acid in summer can be ascribed to the dominant emissions from vehicle exhausts. Oxalic acid can be produced via lots of formation pathways. Do you have direct evidence on the Fenton-like reaction? In the abstract section, authors stated that during summer ozone and oxalic acid-containing particles presented a similar temporal variation pattern, which indicates that photochemical reaction is important for oxalic acid production. Thus, as

for the above two formation mechanisms, which is more important for oxalic acid?

Response: Abundant secondary ions including m/z -46[NO₂]⁻, -62[NO₃]⁻, -80[SO₃]⁻ and -97[HSO₄]⁻ as well as 64[Zn]⁺ and 208[Pb]⁺ were found in HM type particles, suggesting that the HM type particles generally undergo an aging process after emitted from vehicle exhaust. This is supported by road-way tunnel measurements show a small contribution of direct emission from vehicle exhaust to the concentration of DCAs (Huang and Yu, 2007). In this work the sampling site is surrounded by farm land and villages, with no local industrial or traffic emissions. We suggest that HM type particles are mainly the result of regional transport after mixing and aging in the atmosphere.

In summer, oxalic acid-containing particles and ozone concentration followed a similar photochemical trend, and in-situ pH (2-4) was favorable for the Fenton-like reactions on HM type particles. We propose a photochemical formation pathway of oxalic acid in summer. Although the direct Fenton-like reactions were not observed in this work, the diurnal variation of ozone, HM particles and in-situ pH supported the possibility of oxalic acid production from the Fenton-like reactions. Based on above discussion we believe that photochemical reaction may be more important for oxalic acid production in this work.

We have also added the discussion about the contribution of traffic emission to oxalic acid formation in summer as follows:

“The influence from traffic emission was investigated through the diurnal variations of total EC type particles and NO₂ (Figure S7). The EC type particles increased from 12:00 to 21:00, which had same variation as total oxalic acid, but NO₂ 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 421-426.

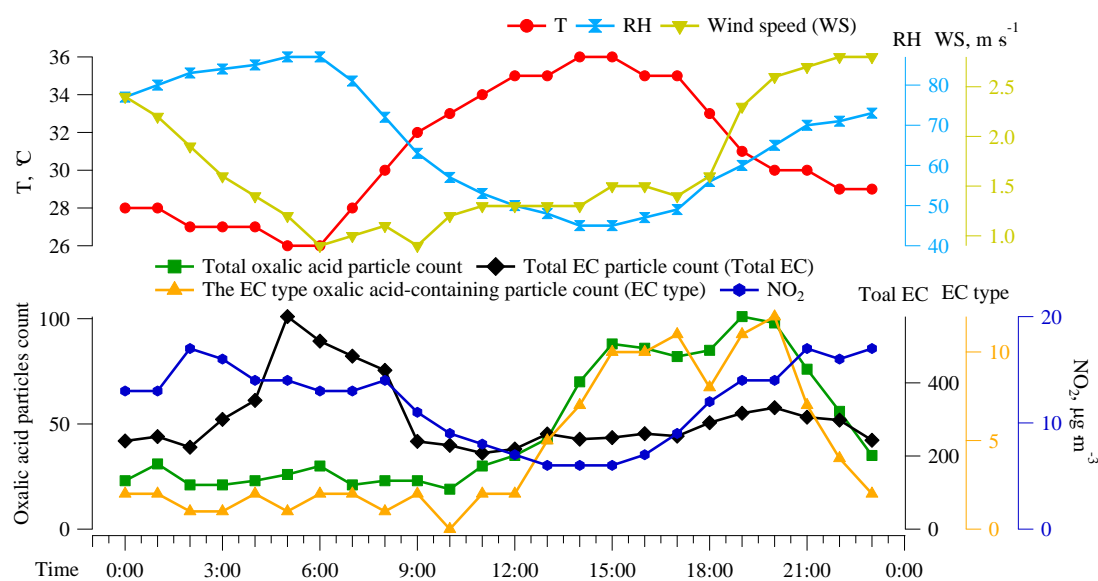


Figure S7. The diurnal variations of temperature (T), RH, wind speed (WS), oxalic acid particles, total EC particles, the EC type oxalic acid-containing particles and ambient NO₂ concentrations from July 28 to August 1 in 2014.

References:

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