Response to Referees

We thank the two anonymous referees for their helpful comments. We respond to each specific comment below. The referee comments are shown in red bold italics. Our replies are shown in black and the corresponding text shown in blue.

Anonymous Referee #1

1. ***The evidence supporting aqueous production of oxalic acid was also weak as it relied simply on correlations without any consideration of meteorological data. Thus, Section 3.3 needs to be improved to increase the strength of this manuscript.***

   Thank you for the comment. We agree that meteorological evidence of the aerosols undergoing aqueous processing would have made the case stronger. However, as these aerosol samples were collected on bulk 24-h filters, detailed information about the history of the sampled air is not available. However, the fact that oxalic acid is highly correlated to many of its known aqueous precursors, in addition to sulfate, corroborates the idea that the oxalic acid in Chinese urban aerosols were mainly produced secondarily in the aqueous phase in summer. We modified the text to make this point and added references to previous studies.

   > Section 3.3 "High correlations between oxalic acid (or oxalate) and sulfate in ambient aerosols have been reported in many previous studies (e.g., Yu et al., 2005; Sorooshian et al., 2006, 2007). These studies attributed such high correlations to aqueous production being the dominant source of oxalic acid, supported by time-resolved measurements and box model simulations (e.g., Sorooshian et al., 2006). In our case, because the $PM_{2.5}$ samples were collected on 24-h bulk filters; detailed analyses of the history of the sampled air were not possible. However, the fact that oxalic acid is highly correlated to many of its known aqueous precursors, in addition to sulfate, corroborates the idea that the oxalic acid in Chinese urban aerosols were most likely mainly produced secondarily in the aqueous phase in summer."

2. ***In light of the title, I would urge the authors to consider whether the Furukawa and Takahashi paper already implied a relationship between zinc and oxalate.***

   Thank you for the suggestion. We have changed the title of the paper to "Seasonal and spatial variability of the OM/OC mass ratios and region-wide high correlation between oxalic acid and zinc in Chinese urban organic aerosols". We also modified the text throughout to stress that the uniqueness of this report was that the high correlation between oxalic acid and zinc was present on a regional scale.

3. ***Section 2: I was confused as to whether the purpose of this section was to***

strictly report data collection methods or to combine this also with some results. It would be ideal to keep this strictly as an introduction of methods and avoiding introducing results such as those in Figure 1 until the subsequent sections. In my opinion, it is distracting to mix methods with results in a section.

Thank you for pointing this out. Figure 1 shows the distribution of OC levels as reported by Cao et al. (2007), and our analyses were based on that dataset. We showed this figure to provide context for the pollution levels in Chinese cities. We modified the text to make clear that Figure 1 was from Cao et al. (2007).

> Section 2: "Figure 1 shows the mean summertime and wintertime OC concentrations for the 14 Chinese cities as reported in Cao et al. (2007)."

4. ***Pg 1249: Line 15: "matter"***

Fixed as suggested. Thank you.

5. ***Pg 1249, Line 23: "properties"***

Fixed as suggested. Thank you.

6. ***Pg 1258, Line 12: here and other places: how is outlier defined?***

All but one of the statistics reported in this paper were based on the full data without excluding any outliers. The only exception was the correlation between oxalic acid and levoglucosan in winter, where we excluded two cities with levoglucosan concentrations more than three times the concentrations of any other cities. We added text to clarify this point.

> Section 3.3: "Table 3 shows the 21 species with highest correlation against oxalic acid in Chinese urban aerosols in summer (all correlations have one-tail p-values<0.025 and are not driven by outliers). (Here and throughout, all statistics were calculated from the full dataset without filtering for outliers unless otherwise noted)."

> Section 3.3: "In winter, levoglucosan and oxalic acid concentrations were both high in all 14 Chinese cities, and the two species were highly correlated (r=0.72, excluding Chongqing and Xi'an, where levoglucosan concentrations exceeded 2700 ng m-3 and were more than three times the levoglucosan concentrations of any of the other cities)."

7. ***Section 3.3: The authors use correlations to suggest aqueous processing generated SOA in the summer. But this is based on only correlations without much other support. To help improve their case, the authors should more deeply investigate meteorological parameters across the study region to relate moisture/clouds to their high OM/OC ratios and the production of oxalic acid. More discussion of meteorology is needed in connection with the chemical data***

to make a more convincing link.

Please see (1).

8. ***Table 3: the second column appears to be incorrectly labeled with Zn instead of oxalic acid.***

   Fixed as suggested. Thank you.

9. ***Table 3: While Section 3.4 and Table 4 do a good job of this, results in Section 3.3 and Table 3 should be compared to data in other regions to put these measurements into greater context. Examples include: Yu et al. (2005), Environ. Sci. Technol., 39, 128–133. Sorooshian et al.(2007), J. Geophys. Res., 112, D13201.***

   We added reference to Yu et al. (2005) and Sorooshian et al. (2007) reporting correlation between oxalic acid and sulfate. We also referred the readers to Ho et al. (2007) and Wang et al. (2006b) which compared the concentrations of organic compounds in Chinese urban aerosols against the reported range of concentrations in urban aerosols in other parts of the world.

   > Section 2: "The resulting concentrations measured for these species were either on the high end or exceeded the values reported for urban aerosols in other parts of the world (Wang et al., 2006b)."
   >
   > Section 2: "The concentrations of these species in Chinese urban aerosols were generally comparable to those measured in urban aerosols in other parts of the world (Ho et al., 2007)."
   >
   > Section 3.3: "High correlations between oxalic acid (or oxalate) and sulfate in ambient aerosols have been reported in many previous studies (e.g., Yu et al., 2005; Sorooshian et al., 2006, 2007)."

10. ***Table 5: Last column has typo for "concentration"***

    Fixed as suggested. Thank you.

11. ***Page 1260, Line 18: replace "acids" with "acid"***

    Fixed as suggested. Thank you.

12. ***Pg 1260, Line 20-22: The evidence was rather weak. I would prefer the authors not make such a confident claim here until they provide more substantial evidence. It is curious as to why a focus of the title and the discussion is on the oxalate acid-zinc correlation when that correlation is not much different than several other species in Table 5. Have correlations between the other species been documented already, and that is why the focus is mainly on zinc? Some clarification would be useful.***

Thank you for the comment. We modify the text to explain why oxalic acid in summertime Chinese urban aerosols was most likely produced in the aqueous phase. Please see (1) for our modifications.
We choose to focus on the high oxalic acid-Zn correlation because it could not be easily explained given our current understanding of the source of these species. All of the species with higher correlation against oxalic acid than zinc were either known aqueous precursors of oxalic acid or other dicarboxylic acids, which may have aqueous production pathways similar to those of oxalic acid (Table 3). We modified the text to clarify.

> Section 4: "Table 3 shows the 21 species with highest correlation against oxalic acid in Chinese urban aerosols in summer. All of the species with higher correlation against oxalic acid than zinc were either known aqueous precursors of oxalic acid or other dicarboxylic acids, which may have aqueous production pathways similar to those of oxalic acid (e.g., Ervens et al., 2004; Carlton et al., 2007; Altieri et al., 2008). To the best of our knowledge, such high correlation between aerosol oxalic acid and Zn on a regional scale has never been reported. We discuss the implications here."

Anonymous Referee #2

1. ***P1249, L10: Please explain OA before using the abbreviation.***
   Fixed as suggested. Thank you.

2. ***Table 1: "Northern Chinese cities" in the upper part of the table must be italic.***
   Fixed as suggested. Thank you.

3. ***P1262, L26: It was written that "The molar ratios of Zn relative to the sum of these dicarboxylic acids for eah city ranged from 0.22 to 6.06: : :" for the samples in winter. I would like to see the correlation diagram (similar to Fig. 2) for the winter samples, since it is possible that the correlation is seen within the region where the Zn ratio relative to dicarboxylic acids is low.***

   We added Figure S1 to the supplementary material and added reference in the main text.

> Section 4: "In winter, oxalic acid was not significantly correlated with Zn in the Chinese urban aerosol samples (Figure S1 in the supplementary material)."

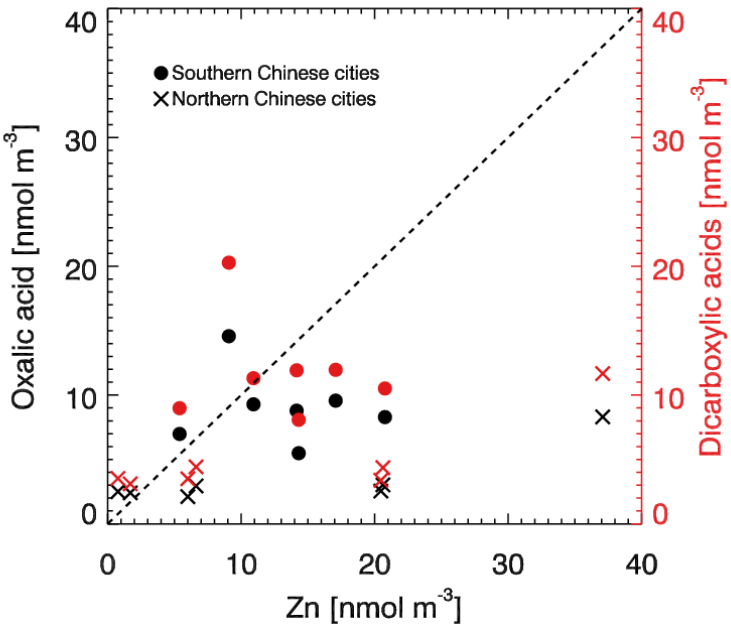

Figure S1. Zn versus oxalic acid molar concentrations (black) in aerosol samples collected from 14 Chinese cities in winter 2003. Also shown in red are the molar concentrations of Zn versus the the sum of the molar concentrations of the 12 dicarboxylic acids (terephthalic acid, 4-ketopimelic acid, oxalic acid, dodecanedioic acid, malonic acid, malic acid, phthalic acid, azelaic acid, glutaric acid, fumaric acid, adipic acid, and sebacic acid) that were highly correlated with Zn in the summertime Chinese urban aerosol samples. The dashed line indicates 1:1 molar concentrations.