

## ***Interactive comment on “Molecular distributions and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during and after the 2014 APEC” by Jiayuan Wang et al.***

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Referee No. 1

General comments: The study compared the PM before, during and after APEC in 2014. The study focused on organic compounds in fine particles and they understand how these organic compounds change during the emission control. Recently, many previous studies prove the organics in fine particles were dominant in North China plain which could be important policy to control VOCs in the future. However, details about organic compounds is scare. Obviously, the study is important to provide more details about organics. Moreover, during the APEC period, the Chinese central government made strick emission control in North China Plain in winter. After the APEC period, one

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severe haze-fog event occurred. The phenonmon provides one change to understand what kind of chemical mechanism to promote the haze formation following the source emission change. I think the study provide some insights to improve the air quality in Beijing and well understand details about organics. After the reading, the current ms need to be revised after one publication.

Response: We thank the reviewer' comments above and revised our manuscript. Following is our detailed response to the comments.

Comments (1) Abstract: The abstract is so long and two paragraph. I may suggest to take some details away and make major findings in the abstract.

Response: Suggestion taken. We have shortened the abstract by removing some details. See page 2, line 42-60.

Comments (2) Title: “Molecular distributions” what does this mean? I think the authors only provide the concentration changes of oxalic acid and related SOA. Seemly, the word is not correct here.

Response: We changed the title as “Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during and after the 2014 APEC event”.

Comments (3) L253-254, the statement is unexpected. Could you show the result in anywhere? Also, the data only containing  $\text{NH}_4^+$  as the basic ion is bias. What about  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ ? I think the bisulfate depending on the particle size. More smaller particle size is more acidic. Therefore, the conclusion should be revised. Also, I noticed several pervious papers in ACP. They found the Beijing air is  $\text{NH}_3$ -rich not  $\text{NH}_3$ -limited. Please find them and carefully made the conclusion.

Response: We are sorry that we did not give the related information in the ACPD version. The fact is that we have measured all cations and anions in the samples and input these data into ISORRPIA-II mode, which has treated the

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Na<sup>+</sup>–NH<sub>4</sub><sup>+</sup>–K<sup>+</sup>–Ca<sup>2+</sup>–Mg<sup>2+</sup>–Cl<sup>-</sup>–NO<sub>3</sub><sup>-</sup>–SO<sub>4</sub><sup>2-</sup> system, to estimate the aerosols liquid water content (ALWC) and acidity ([H<sup>+</sup>aero]). We agree with the reviewer that Beijing air is not NH<sub>3</sub>-limited, because we found that the molar ratio of NH<sub>4</sub><sup>+</sup> to SO<sub>4</sub><sup>2-</sup> plus NO<sub>3</sub><sup>-</sup> is 1.1 for the current work, which means that sulfate and nitrate in Beijing during the APEC campaign were completely neutralized. Such a conclusion is consistent with our work about Beijing haze published in PNAS recently (Wang et al., 2016). Weber et al (2016) reported that under the typical rural conditions over southeastern USA for ammonium sulfate aqueous particles the equilibrium NH<sub>3</sub> vapor concentration is approximately 160 μg m<sup>-3</sup> (220 ppbv), which is far beyond the real concentration of NH<sub>3</sub> in the atmosphere and means that ammonium bisulfate is the major form of sulfate existing in the atmosphere under a typical ambient level of NH<sub>3</sub> conditions. In the revised version, one paragraph and related data about the model calculation has been added into the text, see page 6, line 131-135 and page 22, Table 1. We also polished the statements related to aerosol acidity, see page 11, line 241-245.

Comments: (4) Section 3.3.2 Figure 6 shows three classes of air masses. I am confused the name of the type. I think the regional type is same to long-range transport type. Also, Local type is not local from the Figure 6. Obviously, the name should be modified. I suggest that long-range transport type should be clean air mass. Regional type should be polluted air mass. Local type should be mixed type of clean and polluted.

Response: Suggestion taken. In the current version, we re-named the three types of air masses as polluted, clean and mixed, as recommended by the reviewer, and revised all the related discussions. See Section 3.3.2 and Figure 6.

Comments: (5) L269-271 and L339-341 the result is not stable for temperature. The PM<sub>2.5</sub> decrease is associated with air masses or wind direction. If the air mass was from northwest, the PM<sub>2.5</sub> concentration decreased because it bring the clean air into Beijing. Also the temperature is decrease. As it is, you can make conclusion about the PM<sub>2.5</sub> concentration and oxalic formation? If the authors want to make such conclu-

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sion, you need to compare the PM<sub>2.5</sub> and oxalic concentration at similar air masses such both from south.

Response: We agree with the reviewer that the much less abundant PM<sub>2.5</sub> and oxalic acid during-APEC is related to the air masses, which originated from Siberia and Mongolia and brought clean air into Beijing. We looked at the correlation of C<sub>2</sub>/TDOC with temperature for each type of air masses, and found the correlation still exists and event more significant, for example, the R<sup>2</sup> is 0.56 and 0.67 for the polluted type of air masses and the clean type of air masses, respectively, which indicates that higher temperature conditions are favorable for oxidation of precursors to produce oxalic acid. We have revised the related discussions. See page 10, line 251-258. For the conclusion in previous version, i.e., L339-341, we have deleted these sentences in the current revised paper, because we believe the original version of statement overemphasized the importance of temperature in for PM<sub>2.5</sub> reduction and thus is not accurate enough. The lower PM<sub>2.5</sub> and SOA concentrations during-APEC period are not only due to the efficient emission controls but also due to the favorable meteorological conditions. During the APEC period air masses arriving in Beijing mostly originated from Siberia and Mongolia, which are clean, cold, and relatively drier compared with those before-APEC. Thus, PM<sub>2.5</sub> and oxalic acid concentrations are much lower. See the revised sentences in page 15, line 328-335, and line 351-357.

Comments: In the context, the authors miss comma before and. Such L50 before-, during-, and after-APEC. L216 L319, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>. L293 North L294 is – was L341 not only, but also changed to by both the emission controls and the lower tem.;

Response: Suggestion taken. We have corrected these. See page 12, line 281-282 and page 14, line 308.

Referee 2

General comments This manuscript investigates aerosol chemical compositions before, during and after the APEC event. The authors also provide some valuable mea-

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surement data, e.g., particulate organic matters on molecular level and isotope compositions, to testify the effect of emission reduction, temperature and RH on secondary aerosol formation. Overall, this paper is definitely of interest for the scientific community and the findings are relevant to a better understanding the influence of pollution control on atmospheric aerosols. However, some revision work as listed below should be done before publication could be considered.

Response: We thank the reviewer' comments above and revised our manuscript. Following is our detailed response to the comments.

General comment: The authors try to ascribe the low concentration of and relative abundances of SIA, WSOC, TDOC and C2 during and after APEC to the low temperature condition. However, as shown in figure 6 in the manuscript, the backward trajectory cluster analysis demonstrates that there are more stagnant air masses before APEC than those during APEC, and "...the resident time of the air masses within Hebei province is very short, thus aerosols...is of local characteristics and relatively fresh". This is self-contradictory. If the backward trajectory cluster analysis is right, all the secondary features before APEC can be ascribed to the more time for the formation of secondary aerosols, instead of high temperature which favor the secondary formation. The authors need to clarify this contradiction.

Response: Suggestion taken. We agree with the reviewer that reaction time, in addition to temperature, is also important for secondary aerosol formation, i.e., the stagnant condition before-APEC is favorable for secondary aerosol formation. However, we do not think all the secondary features before APEC should be ascribed to the more time for the formation of secondary aerosols, because temperature and relative humidity are also important factors for photochemical oxidation especially for aerosol aqueous phase oxidation. Higher temperatures and humid conditions are favorable for SOA aqueous-phase production, which could result in abundant oxalic acid enriched with heavier <sup>13</sup>C (Aggarwal and Kawamura, 2008; Wang et al., 2012). In the current revised version, we have modified all the related explanations about the lower concentra-

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tions and relative abundances of SIA, WSOC, TDOC and C2 during- and after-APEC throughout the paper including abstract.

Comments: 1. Line 232, "In comparison with those before-APEC the decreased ratio C2/TDOC and increased ratios of Gly/TDOC and mGly/TDOC during and after-APEC, together with a decreased ratio of WSOC/OC discussed previously, further suggest a reducing production of SOA during the whole campaign." This sentence is very obscure.

Response: We have modified this statement. See page 10, line 218-223.

Comments: 2. Line 254, "As seen in Fig. 5d, H<sup>+</sup>aer correlated well with SO<sub>4</sub><sup>2-</sup> (R<sup>2</sup> = 0.58), probably suggesting SO<sub>4</sub><sup>2-</sup> is the key factor controlling the aerosol acidity." The logic of this sentence is questionable. The acidity of aerosols is decided by the anion-cation balance, not a single ion.

Response: We agree with the reviewer that the acidity of aerosols is decided by the anion-cation balance, not a single ion. The fact is that we determined all cations and anions in the samples not a single ion, and put these data into ISORROPIA-II model, which treated the Na<sup>+</sup>-NH<sub>4</sub><sup>+</sup>-K<sup>+</sup>-Ca<sup>2+</sup>-Mg<sup>2+</sup>-Cl<sup>-</sup>-NO<sub>3</sub><sup>-</sup>-SO<sub>4</sub><sup>2-</sup> system, to estimate the aerosol aqueous H<sup>+</sup> concentration (Hennigan et al, 2015; Weber et al., 2016). We revised this sentence to make the explanation more reasonable. See page 11, line 241-245.

Comments: 3. Line 262, as discussed above, good correlation between the temperature and C2/TDOC may because the different origin of air mass.

Response: We have looked at the correlation for the different air masses, and found the linear correlation still exists and is even more significant. For example, the linear correlation coefficients are R<sup>2</sup>=0.56 for the polluted type of air masses and R<sup>2</sup>=0.67 for the clean type of air masses, further demonstrating that temperature is an important factor for organic aerosol oxidation, i.e., higher temperature is favorable for organic

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aerosol oxidation. We have modified these discussions. See page 10-11, line 251-258.

Comments: 4. Line 279, is it possible that the change of  $\delta^{13}\text{C}$  in C2 is due to the different source of C2 precursors?

Response: We do not think so. Oxalic acid (C2) in the atmosphere mostly exists in aerosol phase and is produced via aerosol-phase oxidation of organic compounds with two or more carbon atoms. Changes in  $\delta^{13}\text{C}$  of atmospheric C2 is caused by stable carbon isotope fractionation process, which occurs during the C2 precursor oxidation process and called as kinetic isotope effects (KIE), rather than by the different source of C2 precursors (Kawamura et al., 2016, Hoefs 2009). Many studies have found that oxalic acid is enriched with heavier  $^{13}\text{C}$  during aerosol ageing process, thus  $\delta^{13}\text{C}$  of C2 often displays a positive correlation with its relative abundance. Because during aerosol ageing process organic aerosols release  $\text{CO}_2/\text{CO}$  by reaction with OH radical and other oxidants, resulting in the evolved species enriched with lighter isotope ( $^{12}\text{C}$ ) and the remaining substrate enriched in  $^{13}\text{C}$  due to KIE effects (Hoefs, 1997; Rudolph et al., 2002).

Comments 5. Line 288, I am a little confused about the definition of the pollution type. Do the authors find higher relative concentration of primary pollutant, e.g., BC, CO, in the local type? Also, the air masses from Siberia should be very clean. Is there any evidence of the pollutant transport during the periods of this type? Otherwise, the use of "transport" in the definition will be misleading.

Response: In the revised paper we have re-named the three types of air masses, as recommended by the reviewer 1. Yes, we found higher relative concentration of primary pollutant (e.g., BC and CO) in the local type (now is re-named as the mixed type). Higher relative abundances of primary species were observed for the PM<sub>2.5</sub> samples collected after-APEC, for example, EC/PM<sub>2.5</sub> is 3. Long-range transport is a commonly used term by aerosol researchers when they talk about aerosol origins. There is a cer-

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tain amount of natural organic aerosols in the atmosphere over Siberia and Mongolia, although their concentrations are much lower compared to the anthropogenic aerosols in the downwind regions such as Beijing. During the moving of air masses from Siberia and Mongolia to east China, these particles can be transported. However, as recommended by the reviewer 1, we re-defined the three types of air masses and revised related statements to avoid any possible misleading. See page 12-13, line 273-303.

Comments: 6. Line 308, still, is it possible that the difference of  $\delta^{13}\text{C}$  in each type is due the different source of C2 precursors?

Response: We don't think so. See our response above.

Comments: 7. Line 315, the authors compared two pollutant episodes before and after APEC, and conclude that the difference is mainly due to the temperature. However, as it is also discussed in Part 3.3.2, the two episodes are in different pollution types with totally different air mass origin. The authors need to exclude the influence of air mass before making such conclusions.

Response: We think in the ACPD version we overemphasized the role of temperature and neglected other factors such as stagnant condition that caused a longer reaction time before-APEC for SOA formation. Thus our conclusion that the difference before-and after-APEC is mainly due to the temperature is not accurate enough. We have revised our explanation about the aerosol composition difference. See page 14, line 309-313; page 14-15, line 324-335.

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Hoefs, J. (1997), *Stable Isotope Geochemistry*, Springer, New York. Kawamura, K., and Bikkina, S.: A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation, *Atmospheric Research*, 170, 140-160, 2016. Rudolph, J., Czuba, E., Norman, A., Huang, L., and Ernst, D.: Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related sources and atmospheric observations in an urban atmosphere, *Atmos. Environ.*, 36, 1173-1181, 2002. Wang, G., Kawamura, K., Cao, J., Zhang, R., Cheng, C., Li, J., Zhang, T., Liu, S., and Zhao, 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, *Environ. Sci. Technol.*, 46, 4783-4791, 2012. Wang, G., Zhang, R., Zamora, M. L., Gomez, M. E., Yang, L., Hu, M., Lin, Y., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Jiayuan Wang, Marrero-Ortiz, W., Tian, P., Secrest, J., Peng, J., Du, Z., Jing Zheng, Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent Sulfate Formation from London Fog to Chinese Haze, *Proceedings of National Academy of Science of United States of America*, doi/10.1073/pnas.1616540113., 2016. Weber, R. J., Guo, H., Russell, A. G., and Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, *Nature Geoscience*, doi:10.1038/NGEO2665, 2016.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2016-662/acp-2016-662-AC1-supplement.pdf>

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-662, 2016.