

Responses to the Comments of Referee #1

Interactive comment on “Molecular distribution and compound-specific stable carbon isotopic composition of dicarboxylic acids, oxocarboxylic acids, and α -dicarbonyls in PM_{2.5} from Beijing, China” by Wanyu Zhao et al.

Anonymous Referee #1

Received and published: 23 August 2017

The manuscript presented the chemical characterization of a set of organics in PM_{2.5} from Beijing with information on compound-specific stable carbon isotopic ratios. The source identification or apportionment for particulate matters is a challenge task especially in highly polluted areas with complex primary and secondary sources. This study provided a year-round molecular distribution of organics with $\delta^{13}\text{C}$ information. Detailed discussion was presented on the concentrations, ratios, and correlations among the individual compounds and total WSOC. The authors concluded that primary emissions such as biomass burning, fossil fuel combustion, and plastic burning, are the major contributors to the organic acids and carbonyls. It is also concluded that the photochemical formation of these species in Beijing is insignificant. This study provides a set of valuable data on the particle phase organics, especially the compound-specific $\delta^{13}\text{C}$. The compound-specific $\delta^{13}\text{C}$ data are useful for the source identification and may have other implications atmospheric chemistry. This is valuable for publication. However, the discussion and the statements in the current form can be further improved. Please see the following comments which the authors may need to consider in the revision.

[Response: We thank the reviewer’s careful reading and important comments, which improve the quality of our manuscript.](#)

Comments:

1, P4, L89, It is suggested the authors to provide a bit more background on the implication of stable carbon isotope ratios in atmospheric chemistry. The discussion and analysis of the compound-specific $\delta^{13}\text{C}$ data can be further elaborated and compared

to those at different geological locations if there is any.

Response: As suggested by the reviewer, the following words have been added in the revised manuscript. Furthermore, the analyses of stable carbon isotope ratios of water-soluble organic acids can be effectively applied to assessing the photochemical aging level and relative contributions of primary emissions to aerosol samples in atmosphere using the estimated kinetic isotope effect of target compound with OH radical (Kawamura and Watanabe, 2004; Wang and Kawamura, 2006; Kawamura and Bikkina, 2016). Please see line 88–92 in page 4.

The discussion and analysis of the compound-specific $\delta^{13}\text{C}$ data is further elaborated in section 3.6–3.8.

The $\delta^{13}\text{C}$ values of diacids and related compounds in Beijing is compared with other areas in sections 3.7 in the revised MS.

2, P5, L129, What was the sampling time for each sample? How the sample was handled before analysis, this is critical for $\delta^{13}\text{C}$ measurements?

Response: Thanks for your suggestion. Each sample was collected onto pre-heated (450°C, 6 hours) quartz-fiber filters (Pallflex) by using a high-volume air sampler (TISCH, USA) at an airflow rate of 1.0 m³/min for 23 h from September 2013 to July 2014 (n=65). We have rephrased and added some sentences in the revised MS. Please see line 131–133 in page 5.

3, P6, L146, The manuscript should provide more details on the method of compound-specific $\delta^{13}\text{C}$, at least should be included in the supplementary. Current description on the method and quality control is over simplified.

Response: Thanks for your suggestion. We have added some sentences. “In short, some internal standard (n-alkane C13) was added into derivatized fraction of each sample at a proper proportion. $\delta^{13}\text{C}$ values of the derivatized dibutyl esters or dibutoxy acetals, measured using GC (HP6890)/isotope ratio mass spectrometer (irMS), were then calculated for diacids, ketoacids and α -dicarbonyls based on the isotopic mass balance equation.” Please see Page 6, Line 151–155 in the revised MS.

4, P7, L173, The manuscript provided the backward trajectories, but there is only one sentence really discussed these information on P21, L578. Please also indicate in the caption of Fig. 1 the meanings of the numbers and colored backward trajectories.

Response: Thanks for your suggestion. We have rephrased and added some sentences. “Burning activities in East Asia were illustrated by fire spots, and the datasets were downloaded from MODIS website (<https://firms.modaps.eosdis.nasa.gov/download/request.php>). The backward trajectories were assorted into several major classifications on the basis of prevalent winds direction. And the numbers in each panel imply the percentages of hourly trajectories in the sampling season to better illustrate the air mass origins, as given below in this study (Fig. 1).”

Please see Page 7, Line 181–186 and Page 42, Line 1000–1001 in the revised MS.

5. Please be consistent with terminologies and abbreviations. The abbreviations are switched back and forth, such as C2/Oxalic acid, C4/Malonic acid. The terminologies sometimes are confusing including the vehicular/vehicle emissions, biomass burning activities/biogenic burning emissions, automobile emission, motor exhaust. If there is a difference between two similar ones, please define first to avoid the confusion.

Response:

Reponse: We are sorry for this mistake. Biogenic burning emissions may be not same as biomass burning activities. We have corrected in the revised MS.

There is no difference between vehicular emissions, vehicular exhaust and motor vehicles.

6, Some statements or conclusions are not well justified. Here is a list of statements that the authors may need to elaborate or use different wording.

(1) P10, L267-268, the Ph concentration was higher in winter as compared to summer, but the contribution to the PM_{2.5} may be low. Also, how about the contribution of Ph from the photochemical oxidation and other fossil fuel burning other than vehicle emissions?

Response: Phthalic acid is either formed via photochemical pathways of naphthalene or directly released into air by fossil fuel burning and the incomplete combustion of aromatic hydrocarbons in motor vehicles. Moreover, the abundant presence of Ph may also be caused by enhanced emission of phthalates from plastics used in heavily populated and industrialized regions in China.

The relative abundance of Ph in total diacids was lower than the value of C2/Tot ratio. But concentrations of Ph and Ph/Tot both showed the highest values in winter. Combining the ratios of C2/Tot and C3/C4, the photochemical aging tracer of organic aerosol, which obtained the lowest values in winter and further indicated the substantial anthropogenic primary emissions, we found that photochemical oxidation pathways of Ph is insignificant compared to strength of primary emissions in wintertime. The highest concentration of Ph is attributable to the enhanced fossil fuel burning for house heating and stagnant atmospheric conditions during wintertime in Beijing. But Ph/Tot ratio was also relatively high in summer. Previous study reported that a great amount of naphthalene obtained in Beijing is an important raw material for the substantial formation of phthalic acid (Liu et al., 2007). Therefore increased ambient temperatures and stronger solar radiation in summertime facilitate the transformation of gaseous PAHs (e.g., naphthalene) to produce relative high levels of Ph in Beijing.

We have corrected the mistake and rephrased “Phthalic acid is either formed via photochemical pathways of naphthalene, or directly released into air by fossil fuel burning and the incomplete combustion of aromatic hydrocarbons in motor vehicles. Moreover, the abundance of Ph may also be caused by increased phthalates emissions from plastic waste burnings in heavily polluted areas in China (Deshmukh et al., 2015). Phthalic acid esters are used as plasticizers in resins and polymers (Simoneit et al., 2005). Therefore, anthropogenic activities contributed to relatively high concentrations of Ph in PM2.5 in Beijing.” Please see line 268–274 in the revised MS.

“The Ph/Tot ratios in winter were nearly 2–3 times greater than those in spring and autumn. These findings imply that phthalic acid is largely emitted by anthropogenic sources in winter, mainly as a result of intensive fossil fuel combustion. It is worth noting that Ph/Tot ratio was also relatively high in summer. Previous study reported that a great

amount of naphthalene obtained in Beijing is an important raw material for the substantial formation of phthalic acid (Liu et al., 2007). Therefore increased ambient temperatures and stronger solar radiation in summertime facilitate the transformation of gaseous PAHs (e.g., naphthalene) to produce relative high levels of Ph in Beijing.” Please see line 390–397 in the revised MS.

(2) P12, L330-331, The value of C2/Tot is compared to the case of Central Himalayas, why this particular location is chosen, how about the other locations? How do you evaluate the oxidation capability between these two locations which will certainly affect the C2/Tot ratios?

The ratio of C2/total dicarboxylic acids can be used to assess the aging process of organic aerosols, because oxalic acid has been recognized as the end product that is associated with atmospheric chain reactions of organic species with oxidants. Typically, higher ratios are observed with the progress of aerosol aging (Kawamura and Sakaguchi, 1999). Over south Asia, Indo-Gangetic plain is considered as a densely populated region, and thus as a potentially strong source region of anthropogenic aerosols. Northern part of these highly populated and industrialized areas is one of chains of Himalaya Mountains. Due to its high elevation, the Himalayan range acts as a boundary limiting the northern extent of the Indian summer monsoon, and therefore, observations at a high altitude location, Nainital (29.4° N; 79.5° E, 1958 m a.s.l.) would provide information about emissions over the Indian subcontinent. Their observation site is located at the highest mountain top (over Kumaon region) and about 2 km far from Nainital city (population ~0.5 million). The site is devoid of any major local pollution sources nearby and is generally free from the snow coverage during most of the time. North and northeast side of the study area are characterized by sharply peaking topography of Himalayan mountain ranges, whereas south-western side plains with very low elevation (<500 m a.s.l.) are densely populated with land merging into the Ganga basin (Hegde and Kawamura, 2012).

The C2/total diacid ratios show higher values in winter ($\sim 0.8 \pm 0.04$) than summer ($\sim 0.5 \pm 0.01$), suggesting that the winter aerosols may be more aged in Central Himalayas. As the anthropogenic aerosols that are emitted from the industrial regions of Indo

Gangetic Plain areas can travel to the north and reach the sampling site by the northerly wind (comparatively lower temperature and weaker wind speed) during the winter period, aging of these aerosols might occur during the transport and thereby significantly contribute to the higher C₂/total diacid ratios. In contrast, this trend is reversed during summer. Because the temperature over the region increase and high wind favors quick transport of pollutants, fresher aerosols are transported over the sampling site (Hegde and Kawamura, 2012).

Please see line 333–338 in the revised MS. So it's rational to compare the values of C₂/total diacid ratio in Beijing with those in Central Himalayas to find out that the photochemical formation of dicarboxylic acids is insignificant in urban Beijing.

(3) P13, L345-354, the discussion in this paragraph is hard to follow. Simply base on the relationships among these species and drawing this conclusion (Line 353-354) is not convincing.

Response: “ ω C₂ and Pyr are more abundant in cold seasons (Table 1) with similar seasonal patterns (Fig. 3g–h). Both correlated well with K⁺ (Fig. S2) and Cl⁻ (Fig. S3) in sampling seasons. These connections demonstrate that ω C₂ and Pyr originated from common combustion emissions or similar secondary formation pathways.”

“Glyoxal (Gly) and methylglyoxal (MeGly) correlated well with nss-K⁺ (Gly: $0.3 \leq r_2 \leq 0.9$, MeGly: $0.3 \leq r_2 \leq 0.9$) throughout the whole year (Fig. S2), whereas Gly and MeGly showed good relations with Cl⁻ (Gly: $0.3 \leq r_2 \leq 0.8$, $0.4 \leq r_2 \leq 0.8$) in autumn, winter and summer (Fig. S3). Concentrations of these two carbonyls are largely affected by biogenic precursors (e.g., isoprene and monoterpenes) emitted from vegetation and biomass burning activities during entire sampling periods in addition to coal burning and motor exhaust (aromatic hydrocarbons).” Please see line 297–300 and 315–321 in the revised MS.

Please see line 348–356 in the revised MS, where elaborated the meaning of correlation between C₂/Pyr, C₂/ ω C₂, C₂/Gly and C₂/Tot.

No strong positive correlation was observed between C₂/Pyr, C₂/ ω C₂, C₂/Gly and C₂/Tot suggests that supplement of Pyr, ω C₂ and Gly were faster than their secondary

transformations to C2 in Beijing. The aging level was not strong enough for intermediate diacids contributing to the production of C2.

(4) P15, L405, The Ph/C6 ratio was lower than 2.5 in other seasons and it is only 4.1 in winter, but why it is concluded that more emissions from diesel burning (ratio of 6.58) than gasoline fuel vehicles (2.05)?

Response: We have rephrased the sentence. “This phenomenon shows abundances of diacids attributable to more emissions from gasoline fuel vehicles than diesel burning.”

Please see line 418–420 in the revised MS.

7, P20, L454, It is not clear what is connection between the information in L545-547 and the statement in L547-549.

Response: A previous study noted that increasing concentrations of oxalic and malonic acids inhibit the growth of total fungi number due to the lower pH, which in turn changes the efficiency of fungi to degrade the malonic acid (Côté et al., 2008).

Pavuluri and Kawamura (2012) found that $\delta^{13}\text{C}$ of LMW diacids (i.e., oxalic, malonic, succinic acids) in aged aerosols are less negative (i.e., enriched in ^{13}C with an increase in WSOC/OC ratios), perhaps due to kinetic isotopic fractionation caused by ambient photochemical degradation of oxalic acid and also malonic acid. The efficiency of fungi can result in the degradation level of oxalic and malonic acids.

8, It is suggested to use the words of “significant” or “insignificant” in the statements carefully unless statistical data or solid evidence are provided.

Response: Thanks for your suggestion. We have corrected in some parts.

9, As presented in the manuscript, if I understood it correctly, the authors concluded that primary emissions are the major contributors to the organic acids and carbonyls. It is also concluded that the photochemical formation of these species in Beijing is insignificant. Both of these two statements are very strong. Is there any source apportionment study in Beijing during the same period, are they consistent or controversial?

Sorry, no similar study on the source apportionment was found in Beijing during the same period. Our paper concluded that primary emissions are the major contributors to the organic acids in Beijing, although photochemical formation of these species slightly enhanced in summer. Ji et al. (2016) observed increasing photochemical activity of aerosol in autumn and winter due to stagnant atmospheric conditions and inversion layer, which are favorable for the absorption and condensation of semi-volatile organic compounds on existing particles. And he noted that biomass burning is a substantial pollution factor throughout the year in Beijing. Different sampling time is related with various atmospheric conditions and strength of primary emissions. The sampling time in our study is not very special. Many scholars like to study the formation mechanisms and source apportionments of aerosols in haze days, while we focused more on the characterization of organic acids in common days including polluted and clean days in Beijing at a molecular level. Different sampling time and study target may get different conclusions.

Zhang et al. (2013) found that soil dust, coal combustion, biomass burning, traffic and waste incineration emission, industrial pollution, and secondary inorganic aerosol (SIA) are six main sources of PM_{2.5} in Beijing. Each of these sources has an annual mean contribution of 16, 14, 13, 3, 28, and 26 %, respectively, to PM_{2.5}. Similarly, the relative contributions of these sources to PM_{2.5} in Beijing greatly varied with the changing seasons, which proves the “complex air pollution” in Beijing. The highest contributions occurred in spring for soil dust (23 %) and traffic and waste incineration emission (5 %), in winter for coal combustion (57 %), in autumn for industrial pollution (42 %), in summer for SIA (54 %), and in both spring and autumn for biomass burning (19 and 17 %, respectively). The conclusions in this article demonstrated that regional primary sources could be crucial contributors to PM pollution in Beijing, compared to the enhanced photochemical formations of SIA in summer.

10, Figure 6, please describe the meanings of different symbols and percentages for the box. It is suggested to use same scale for different seasons.

Response: The y-axis in figure 6 showed the $\delta^{13}\text{C}$ values of diacids, glyoxylic and

pyruvic acids, and the x-axis represented the abbreviations of species detected in this study. Please see table 1 in the revised MS.

And we have redrawn the figure 6 with same scale.

Hegde, P., and Kawamura, K.: Seasonal variations of water-soluble organic carbon, dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls in Central Himalayan aerosols, *Atmospheric Chemistry and Physics*, 12, 6645-6665, 2012.

Ji, D., Zhang, J., He, J., Wang, X., Pang, B., Liu, Z., Wang, L., and Wang, Y.: Characteristics of atmospheric organic and elemental carbon aerosols in urban Beijing, China, *Atmospheric Environment*, 125, 293-306, 10.1016/j.atmosenv.2015.11.020, 2016.

Kawamura, K., and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *Journal of Geophysical Research: Atmospheres*, 104, 3501-3509, 1999.

Liu, Y., Tao, S., Yang, Y., Dou, H., Yang, Y., and Coveney, R. M.: Inhalation exposure of traffic police officers to polycyclic aromatic hydrocarbons (PAHs) during the winter in Beijing, China, *Science of the total environment*, 383, 98-105, 2007.

Pavuluri, C. M., and Kawamura, K.: Evidence for 13-carbon enrichment in oxalic acid via iron catalyzed photolysis in aqueous phase, *Geophysical Research Letters*, 39, 3802, 2012.

Zhang, R., Jing, J., Tao, J., and Hsu, S. C.: Chemical characterization and source apportionment of PM_{2.5} in Beijing: seasonal perspective, *Atmospheric Chemistry & Physics*, 13, 7053-7074, 2013.