
Responses to the Comments of Referee #3

ACP review by Anonymous referee 3:

MS title: Molecular distribution and compound-specific stable carbon isotopic composition of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in PM2.5 from Beijing, China

Organic aerosols (OAs) account for major fraction of atmospheric particulate matter and also ubiquitous in nature. Among the OAs, the dicarboxylic acid and related polar compounds are one such widely studied chemical species that provide useful information about the relative significance of anthropogenic versus natural source contributions as well as primary emissions vs. secondary formation processes. In this context, combining the molecular distributions, concentrations, diagnostic mass ratios, air mass back trajectories and their stable carbon isotopic composition from this kind of studies are helpful in improving our current understanding of the complex nature of OAs. Therefore, the study is most relevant and publishable in ACP after a major revision.

I feel that conclusions are more clear and focused than the most of the text part of this MS. The comparison of mass ratios among seasons are too vague. This should be supported by the statistical analysis such as ANOVA. To me, comparison of mean and sd of mass ratios of dicarboxylic acids among seasons appear to be insignificant for this study. In order to truly appreciate the relative significance of various source emissions (biogenic vs. anthropogenic) based on mass ratios of dicarboxylic acids and other related polar compounds, I strongly recommend the authors to evaluate their seasonal datasets using a statistical test (e.g, ANOVA). I see that there is a missing link in terms of attributing the stable carbon isotopic composition of dicarboxylic acids' with source contributions. For example, how the lowest δ13C value of terephthalic acid (~-33.5‰) in winter indicates that it is emitted from plastic waste burning. Why not in other seasons? Is the plastic waste burning over Beijing is common only winter?

Response: Terephthalic acid was found to account for more than 77% of total diacids determined in aerosols from open-waste burnings (Kumar et al., 2015), and was a good tracer for fresh smoke waste burning particles (Kumar et al., 2015;Simoneit et al., 2005).

China has large rural population living in the village and straws are not a high-demand fuel. Hence during and after the harvest season, farmers often burn crop straws in the field as a convenient and inexpensive way to dispose agricultural waste to advance crop rotation (Fu et al., 2012;Wang et al., 2009;Ji et al., 2016). In most of the reports, open-waste burning are clubbed with biomass and fuel burning aerosols (Akagi et al., 2011;Lei et al., 2012). Substantial combustions activities, including fossil fuel burnings for domestic heating, open-waste and biomass burnings, occurred in autumn and winter. Furthermore, the inversion layer and low wind caused the accumulation of pollutants in winter, while low temperature reduced the photochemical processing of aerosols in Beijing. Thus, combining the conclusion found in previous studies, the comparison with other papers (figure 5), concentrations and $\delta^{13}C$ values of terephthalic acid (~-33.5‰), we think that abundant tPh is directly emitted by plastic waste burning in Beijing, especially for winter.

We have used principal component analysis (PCA) to discriminate the source apportionment of atmospheric aerosols. Please see section 3.5.

Another important issue is Section 3.6, 3.7 and 3.8: comparison of δ13C of diacids and other compounds measured here makes this study unique due to year round sampling and comparing seasons. However, all these sections are bit complicated to follow/read. Since the East Asian outflow influences the chemical composition of organic aerosols during winter and spring, it is relevant to compare the diacid δ13C values from this study with other sites/studies during this period only. No need to include autumn and summer. Therefore, I suggest authors to combine the winter and spring data sets and use the median values to compare with the other sites in E. Asia (e.g. Sapporo, Gosan & cruises).

Response: Thanks for your careful reading. Only combining the winter and spring data sets and using the median values to compare with the other sites may not show the year-round variation trend of $\delta^{13}C$ values and seasonal photochemical aging level of water-soluble organic acids in Beijing.

My other comments are as follows:

Line 35-37: The sentence is difficult to follow. Please rewrite.

Response: Rephrased. Thanks.

Line 38-40: Correlations of some oxocarboxylic acids and a-dicarbonyls with nss-K+, how significant these are? Mention clearly what is correlated with what? Some oxocarboxylic acids are not specific!

Response: Please see Page11, Line 297–300 and Page12, Line 315–321 in the revised MS, as well as figure S2&S3 in the supporting material. Major oxocarboxylic acids are glyoxylic and pyruvic acids, because glyoxylic acid is measured as the most abundant oxoacid, followed by pyruvic acid.

Line 188-190: What is the reason that oxalic acid concentration is found to be highest in autumn and lowest in winter? Similarly, What causes the difference in the seasonality for the relative abundances of oxalic acid? Why is it maximum in summer? Explain/suggest.

Response: Most organic compounds showed the highest concentrations in autumn and lowest values in winter, which are associated with the sampling time. Different sampling time is related with various atmospheric conditions and strength of primary emissions.

We conducted air mass back trajectories at the sampling location, which indicates most of the wind came from the southern industrialized areas and mixed with regional wind in autumn, spring and summer. From the figure 1 in the revised MS, we can see intensive biomass burnings in surroundings areas, especially for autumn and spring. Please see figure 3 in the revised MS. A big pollution process was observed from 10.3 to 10.8 in autumn, followed by secondary oxidation ways, which leaded to the increased concentrations of oxalic acid in fall. In contrast, the less polluted air parcels came from the northern areas during wintertime in Beijing. Although fossil fuel burning as a major source contributed to the abundance of diacids and related compounds like Ph, tPh, ωC_2 and Pyr, the photodegradation of these organic acids to form oxalic acid was weak. Therefore, oxalic acid showed the lowest concentrations in winter.

Strong solar radiation and high temperature can accelerate the photochemical processing of aerosols. Typically, the prolonged photochemical oxidation of organics in the atmosphere leads to enhanced relative abundance of oxalic acid in total diacids in summer.

Line 192: Update the references with a recent review.

Response: Updated. Please see Page 8, Line 197.

Line 195 to 197. Authors need to provide, why there exist differences in the molecular distribution of measured water-soluble organic compounds among seasons and why do they show different patterns for e.g., why the third most abundant compound is glyoxylic acid in cold period and malonic acid in warmer period?.

Response: Different molecular distributions of diacids and related compounds are attributed to strength of primary emissions and photochemical aging level, as well as atmospheric conditions. Please see the review published in 2016, which gave detailed information in various sampling seasons and areas (Kawamura and Bikkina, 2016).

Primary emissions, such as biomass burning, fossil fuel burning and motor vehicles, accounted for a large contribution of glyoxylic acid and related precursors. We conducted air mass back trajectories at the sampling location, which indicates most of the wind came from the southern industrialized areas and mixed with regional wind in autumn, spring and summer. From the figure 1 in the revised MS, we can see intensive biomass burnings in surroundings areas, especially for autumn and spring. Please see figure 3 in the revised MS. A big pollution process was observed from 10.3 to 10.8 in autumn, followed by secondary oxidation ways, which leaded to the increased concentrations of glyoxylic acid.

Meanwhile, the photochemical aging level of organic aerosols is weak in comparison with the strength of primary emissions in Beijing, although it enhanced in summer. These conclusions illustrate that the supplement of ωC_2 is faster than its photodegradation to form other diacids in air. Low wind speed and inversion layer in autumn and winter can make species accumulate quickly, which makes ωC_2 as the third most abundant compound in cold seasons.

Breakdown of relatively long carbon-chain diacids and other related precursors is one of the key sources of low carbon-numbered diacids in the atmosphere. The photochemical contribution of related precursors to diacids, like the transformation of succinic acid to malonic acid, enhanced in warmer seasons due to increased relative humidity and temperature as well as stronger solar radiation. Thus malonic acid is the third most abundant compound malonic acid in warmer period.

Line 199-202: The sentence is not clear. What is single dicarboxylic acid?

Response: We have changed "single" to "individual". Please see Page 8, Line 204 in the revised MS.

Line 203: I am confused with subheading seasonal variability. Authors have already mentioned about differences in the molecular distributions of dicarboxylic acid among seasons already in the previous section. This section has to combine with the section 3.1.

Response: Thanks for your suggestion. We think it is better to divide this part into two sections. The section 3.1 is just to elaborate the seasonal molecular distributions, while the section 3.2 is to show the seasonal concentrations of water-soluble organic acids to discuss the possible sources in detail.

Line 209: abbreviate C9

Response: Corrected. Please see Page 9, Line 214 in the revised MS.

Line 204-213: The seasonal trends were attributed to different emissions. This is not enough. Explain what source emissions might contribute for each type and also justify why you think this is the only possibility?

Response: Please see following sentences in section 3.2–3.4 in the revised MS.
We have discussed in detail.

Line 214: Why the total diacid concentrations are the highest in autumn and why it is lowest in winter? Explain.

Response: Different sampling time is related with various strength of primary emissions and atmospheric conditions. Please see figure 3 in the revised MS. A big pollution process was observed from 10.3 to 10.8 in autumn, followed by secondary oxidation ways, which leaded to the increased concentrations of organic acids, especially for C2–C4 diacids. These three diacids account for a large proportion of total diacids, thus total diacids had the highest concentrations in autumn.

In contrast, although there was a big pollution process from 12.20 to 12.26 in winter, it contributed much to the enhancement of Ph and tPh. Only small growth of concentrations was observed for C_2, C_3 and C_4 diacids due to insignificant secondary formation during wintertime, so concentrations of total diacids showed the lowest values in autumn.

Line 216: Why Beijing dataset has to be compared with Tanzania, Africa? Both are different settings? Compare with polluted atmosphere with another city in S. Asia or E. Asia. Given the diverse geographical locations, comparison with only one or two sites cannot be acceptable. Please compare or provide a table and discuss how different or similar this study site with those documented from other cities in China and India.

Response: We have also compared Beijing dataset with those in Tokyo, Japan and Gosan, Jeju island in Korea. Please see Page 9, Line 222–225 in the revised MS.

Please see table 2 in the revised MS. We discussed the differences and similarities of datasets between Beijing and other areas in all sections.

Line 223-230: After discussing the sources of oxalic acid, why there is a sudden jump to malonic acid data from this study. What about oxalic acid? If it is not important why authors are describing so much about its sources here. Connect here with their formation in different seasons. What are the different sources of oxalic acid, causing this variability through sampling period?

Response: Oxalic acid has been recognized as the end product that is associated with atmospheric chain reactions of organic species with oxidants. Malonic and succinic acids are important precursors of C_2. These diacids always have similar primary emissions or secondary formation ways. Please see Page 9, Line 240–242. In order to avoid repetition and link up with other parts, we have discussed its sources in detail in section 3.3.

Line 231: Why malonic acid is highest in autumn?

Response: Please see figure 3 in the revised MS. A big pollution process was observed from 10.3 to 10.8 in autumn, followed by secondary oxidation ways, which leaded to the increased concentrations of malonic acid.

Line 231-234: The connectivity between lines or sentences is missing. Why suddenly succinic acid to malonic acid ratio after mentioning the seasonal variability of malonic acid? What about the seasonal variability of succinic acid? Instead of picking up each compound measured and discussing its seasonality, I suggest authors to briefly summarize or infer logically the possible formation pathways of observed abundant compounds.

Response: Please see Page 9, Line 236–242 in the revised MS.

Line 231-235: Authors attributed the relative dominance of succinic acid over malonic acid as the major contribution from primary emissions to dicarboxylic acids measured here. Although this could be possible, however, one cannot rule about the transport during each season. So if you see the air mass back trajectories at the receptor site, then this inference based on C4/C3 has certain uncertainty or bias. So you need to mention this in the MS.

Response: We conducted air mass back trajectories at the sampling location, which indicates most of the wind came from the southern industrialized areas and mixed with regional wind in autumn, spring and summer. Please see figure 1 in the revised MS. Anthropogenic and biogenic organic compounds could have been mixed in some samples, followed by photochemical oxidation pathways. In contrast, clean north wind dominated in winter, but local inversion layer often occurred in Beijing, which caused the accumulation of organic aerosols. Because of the low temperature and weak solar radiation, the secondary oxidation level of aerosols may be not as strong as those in other seasons. Thus C3/C4 ratio showed the lowest mean value in winter.

C3 diacid can be produced as a result of hydrogen abstracted by OH radicals, followed by decarboxylation processing of C4 diacid (Kawamura and Sakaguchi, 1999). The mass concentration ratio of C3/C4 is a good indicator for evaluating the contributions of dicarboxylic acids from primary emissions or secondary oxidation production in the atmosphere. The value of C3/C4 ratio is greater than unity for photochemically aged aerosols whereas it reaches 0.5 for vehicular emissions (Kawamura and Kaplan, 1987).

Line 235: The diurnal variation tendency of C2?? Is it diurnal or daily variability?

Response: Corrected. It's daily variability.

Line 255-257: Why the correlation of azelaic acid (C9) with K+ and Cl- solely attributed to coal burning? Why not biomass burning?

Response: "Azelaic acid correlated well with K^+ ($0.3 \leq r2 \leq 0.4$) and $Cl^–$ ($0.4 \leq r2 \leq 0.5$) in cold seasons (Fig. S1), indicating that substantial amounts of C9 may be stemmed from the local and surrounding combustion activities in Beijing." Combustion activities include biomass/biofuel burnings and fossil fuel burnings.

Line 269-271: According to authors "The predominance of terephthalic acid over phthalic acid observed in this study is in contrast with those reported by Ho et al., ". Is it due to variability in the sources or increase plastic waste burning is increasing. Comment on this.

Response: It is due to the increase of plastic waste burning. Terephthalic acid is the tracer of plastic waste incineration. Please see Page 11, Line 277–279 in the revised MS.

Line 277-278: Provide a reference for the argument that monocarboxylic acids are photochemically oxidized & form dicarboxylic acid. Why authors think it is relevant here rather than direct emissions or other sources.

Response: We have added two references. Please see Page 11, Line 284 in the revised MS. All diacids, oxoacids and α-dicarbonyls can be emitted from primary emissions or formed via photochemical oxidation of related precursors in atmosphere. We have discussed their direct emissions and secondary photodegradations in line 294–305 and

355–367.

Line 281: the sentence is not clear.

Response: Corrected. Please see line 287–289 in the revised MS.

Line 290-292: These sentences are not clear. You can combine into one as “wC2 and Pyr is more abundant in cold seasons (Table 1) and correlated with K+ and Cl-”. What is the common combustion source, mention it?

Response: Potassium ion (K+) is a good tracer of biomass burnings (Andreae, 1983). And a great deal of chloride in wintertime Beijing is linked to increased emissions of coal incineration, particularly under stagnant meteorological conditions that facilitate the formation of particle-phase ammonium chloride (Sun et al., 2013). ωC2 and Pyr show similar seasonal patterns (Fig. 3g–h) and correlated well with K+ (Fig. S2) and Cl– (Fig. S3) in cold seasons, which demonstrate that ωC2 and Pyr originated from common combustion emissions like biomass burnings, fossil fuel burnings. We have rephrased. Please see line 297–300 in the revised MS.

Line 326-328: I don’t follow the comparison with the Central Himalayan aerosols as well as the logic of the statement. rewrite.

Response: 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 (~0.8±0.04) than summer (~0.5±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).

The C2/Tot ratios were the lowest in winter (0.39±0.05), while C2/Tot ratios are similar in the other three seasons (0.54–0.58). 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.

We have rephrased the sentences. Please see line 333–338 in the revised MS.

Line 333-339: In urban Beijing, how can authors assume that succinic acid formation forms the photooxidation of unsaturated fatty acids? What about the photochemical oxidation of adipic acid, which is a product of cyclic olefins with oxidants in and around the city? Why not is C4 derived from anthropogenic emissions such as fossil fuel combustion, vehicular emissions in Beijing? The linear relationship between C2/Tot (or relative abundance of oxalic acid in total diacid mass) and the C2/C4 just indicate that oxalic acid has a significant contribution from or formed from the photochemical oxidation of succinic acid, not more than that. So authors need to dilute their emphasis on source attribution directly based on a linear relationship. If still, authors think that succinic acid might have produced from the photochemical breakdown of higher homologues of dicarboxylic acids from the biogenic unsaturated fatty acids, they should the linear relationships with oleic acid and azelaic acid first and then lower homologues of dicarboxylic acids with azelaic acid. I suggest authors think and rewrite along these lines.

Response: In figure 3, a big pollution process was observed from 10.3 to 10.8 in autumn, followed by secondary oxidation ways, which leaded to the increased concentrations of organic acids in fall. C2, C4, C9, ωC2 and Pyr showed similar concentration variations, indicating they may have common primary sources or photochemical pathways. In section 3.2, C9, ωC2, Pyr, Gly and MeGly correlated well with nss-K+, further implying that these organic acids were emitted from biomass burnings.

We have rephrased. “Typically, concentrations of C2, C4 and C9 diacids, as well as ωC2 and Pyr showed similar varational trends in autumn, implying that they were derived from similar primary emissions or photochemical processing. Furthermore, C2/Tot (C2%) showed strong correlations with C2/C4 in all four seasons (Fig. S4), indicating the importance of biogenic unsaturated fatty acids, followed by photochemical processing.” Please see line 344–348 in the revised MS.

Line 335: Authors need to provide a proper reference for invoking contribution of emissions from the phytoplankton in remote oceans (update the reference with diacid review, doi: 10.1016/j.atmosres.2015.11.018 and others cited in).

Response: We have updated the reference with the diacid review published in 2016. Please see Page 13, Line 343 in the revised MS.

Line 340-344 and 345-346 is missing. Connect these two as “We, therefore, would like to investigate the significance of these formation pathways by examining the interrelationships between...”

Response: Thanks for your suggestions. Please see line 355–357 in the revised MS.

Line 347: correct the sentence as "in all seasons except winter"

Response: Corrected. Please see Page 14, Line 358.

Line 352-353: how the negative correlation between oxalic to glyoxylic acid mass ratio and the relative abundance of oxalic acid in summer demonstrate that C2, wC2, Pyr and Gly are from biomass burning emissions? Elaborate further.

Response: 1. Pyr, ωC_2, Gly and MeGly correlated well with K+ in the sampling time, indicating that biomass burning contributed a large part of these organic acids.

2.Please see line 348–357 in the revised MS, where elaborated the meaning of correlation between C2/Pyr, C2/ωC2, C2/Gly and C2/Tot.

3. No strong positive correlation was observed between C_2/Pyr, C_2/ωC2, C_2/Gly and C2/Tot suggests that supplement of Pyr, ωC2 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. Combining the results obtained in section 3.2 and relationships between C2/Tot and C2/Pyr, C2/ωC2, C2/Gly, we found that C2, Pyr, ωC2 and Gly are from biomass burning emissions.

Line 361: provide a reference that C3/C4 is a good indicator for dicarboxylic acid contribution from primary emissions vs. secondary formation process.

Response: Provided. Please see Page 14, Line 372.

Line 366: correct the sentence as "throughout the sampling year"

Response: Corrected. Please see Page 14, Line 377.

Line 367-368. I couldn't find any difference between the two statements.

Response: Thanks for your careful reading. We have rephrased. Please see Page 14, Line 377–379.

Line 376-377: Confusing!. State clearly that the direct emissions from localized sources in Beijing contributed to atmospheric dicarboxylic acids.

Response: "These results demonstrated that in addition to slightly enhanced atmospheric photochemical reactions in summer, incomplete combustions, like motor vehicles and biomass burnings, overwhelmingly contributed to dicarboxylic acids in Beijing." We have rephrased. Please see line 385–387 in the revised MS.

Line 380-384: I understand for the summer season that Ph might have a contribution from photochemical oxidation of PAHs. What is the reason for its higher abundance in winter season?

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 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). The Ph/Tot ratios in winter were nearly 2–3 times greater than those in spring and autumn, which was caused by substantial coal burning for house heating in Beijing. Therefore, these findings imply that phthalic acid is largely emitted by anthropogenic sources in winter, mainly as a result of intensive fossil fuel combustion.

Line 396-398: As stated in Line 385, if both adipic acid (C6) and phthalic acid (Ph) are produced from the photochemical oxidation of cyclic olefins, why C6/C9 is lowest in winter and whereas Ph/C9 is highest in winter. Perhaps both could have been produced by different sources. That is the reason why comparing seasonal means directly can yield erroneous interpretations. May be the seasonal averages are not significantly different.

Response: C6 is formed via secondary oxidations of cyclic olefins (e.g., cyclohexene), and Ph is a photochemical product of aromatic hydrocarbons. The precursor sources of C6 and Ph are technically defined as anthropogenic emissions. In contrast, C9 is mainly produced by photochemical oxidation of biogenic unsaturated fatty acids. Thus, the mass concentration ratios of C6/C9 and Ph/C9 may effectively indicate the source strength of anthropogenic and biogenic emissions to these organic acids.

Due to large emission of fossil fuel burning, Ph showed the highest concentrations in winter. 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. Phthalic acid esters are used as plasticizers in resins and polymers. Thus Ph/C9 is highest in winter.

Previous study reported that contributions of C6 and Ph from biomass burning are minimal (Kawamura et al., 2013). Biomass burning is a substantial polluted factor in Beijing. Compared to the emission strength of biomass burning, the source of cyclic olefins may be not strong. Therefore, mean values of C6/Tot are constantly low in all four seasons, whereas the seasonal ratios of C9/Tot are the highest (0.09) in winter due to stagnant atmospheric conditions, which result in the lowest value of C6/C9 ratios in winter (0.34±0.13).

Line 410-414: I am not able to follow the comparison of ratios. Authors need to evaluate the differences in the seasonal means using ANOVA.

Why not authors use PMF other than PCA for the source apportionment in this study, like their previous publications?

Response: Being similar to C3/C4 ratio, mass ratios of M/F provide some clues about aging of air masses because lower values are caused by photochemical isomerization from M (cis) to F (trans), representative of higher photochemical activities or viceversa (Kawamura and Bikkina, 2016).

Previous publications always use PCA for the source apportionment, because PMF need a large quantity of data to run in order to get a accurate source analysis. But the data of diacids and related compounds are not enough for PMF.

Section 3,4: I do not understand the title of this subheading. Already authors made a comparison in the previous section. Then why suddenly there is another section on this?

Response: The section 3.3 is correlation analysis and seasonal concentration ratios of diacids for sources' discussion in Beijing, while the section 3.4 shows the comparisons of the mean mass ratios of organic acids in our study with those in other polluted areas. The conclusions in section 3.4 further prove the results discussed in previous sections.

Line 519-523: I do not follow the logic here. How authors drew their conclusion that d13C of C9 indicate that azelaic acid is from biomass burning in surrounding areas?

Response: It is important to state that marine-derived particulate organic matter in the remote marine atmosphere (around −20‰) is somewhat more enriched with 13C than those reported for terrestrial vegetation (C3 plants; −27‰) (Turekian et al., 2003).

In contrast, the smaller δ13C values of C6 (−25.8‰) and C9 (−28.1‰) in the Sapporo aerosols suggest more contribution from anthropogenic sources and terrestrial higher plants (biomass burning) (Aggarwal and Kawamura, 2008).

We have rephrased. Please see line 536–541 in the revised MS.

Line 534-535: How the lowest δ13C value of terephthalic acid (~-33.5‰) indicates that it is emitted from plastic waste burning that too in winter. Why not in other seasons? Is the plastic waste burning over Beijing is common only winter. Line 534-535 and the next sentence are not connected. The reference cited is the work related to S. Asia. How about the conditions in E. Asia? Is the plastic waste burning is relevant for the study site? If so, please state it.

Response: Terephthalic acid was found to account for more than 77% of total diacids determined in aerosols from open-waste burnings (Kumar et al., 2015), and was a good tracer for fresh smoke waste burning particles (Kumar et al., 2015;Simoneit et al., 2005). China has large rural population living in the village and straws are not a high-demand fuel. Hence during and after the harvest season, farmers often burn crop straws in the field as a convenient and inexpensive way to dispose agricultural waste to advance crop rotation (Fu et al., 2012;Wang et al., 2009;Ji et al., 2016). In most of the reports, open-waste burning are clubbed with biomass and fuel burning aerosols (Akagi et al., 2011;Lei et al., 2012). Substantial combustions activities, including fossil fuel burnings for domestic heating, open-waste and biomass burnings, occurred in autumn and winter. Furthermore, the inversion layer and low wind caused the accumulation of pollutants in winter, while low temperature reduced the photochemical processing of aerosols in Beijing. Thus, combining the conclusion found in previous studies, the comparison with other papers (figure 5), concentration and δ^{13}C values of terephthalic acid (~-33.5‰), we think that abundant tPh is directly emitted by plastic waste burning in Beijing, especially for winter.

Line 538: What major compounds? Be specific (diacids, oxoacids or a-dicarbonyls or what you are referring to).

Response: Diacids includes oxalic, malonic, succinic, glutaric, adipic, azelaic, phthalic and terephthalic acids. The oxoacids includes glyoxylic and pyruvic acids.

Line 540: The decreasing trend in d13C of C5 to C9 is not obvious from the Figure 6 for all seasons (see for e.g., summer, panel d).

Response: Deleted.

Line 542-544: given the overlap of the box widths for oxalic, malonic and succinic acids, I wonder whether the 13C enrichment for these compounds is significantly different among seasons.

Response: The mean δ13C values of C2 and C3 were constant among seasons. In contrast, succinic acid showed the lowest values (–28.6‰) in summer. Please see table 5 in the revised MS.

The scale in Figure 6 is most difficult to compare between seasons. I suggest authors keep the same scale and then discuss the differences.

Response: Thanks for your suggestion. We have redrawn.

Figure 8: I do not follow the caption. What are the concentrations plotted on the x-axis.

Response: These are the seasonal concentrations of C2 plotted on the x-axis.

References:

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