Responses to the Comments of Referee #2

Review of "Molecular distribution and compound-specific stable carbon isotopic composition of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in PM2.5 from Beijing, China" by Zhao et al.

In this study, the authors measured the concentrations and stable carbon isotopic composition of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in Beijing, China. The annual variation of species, mass ratios between species, and δ13C are used to infer the sources and formation processes of measured species. The authors found that (1) anthropogenic primary emissions are the major contribution to the measured species and (2) the photooxidation is weak and contributes insignificant amount of measured species. However, I find the conclusions are not well justified. Particularly, many discussions suffer flaws in its logical flow and it is unclear how the conclusions are drawn from the analysis/evidence. also, some discussions contradict with each other. Therefore, I would not recommend this manuscript for publication in its current state.

Response: We thank the referee's careful reading and helpful comments, based on which we tried to improve the quality of our manuscript as follows.

Major Comments

1. Many discussions contradict with each other. This causes severe confusion and leaves the conclusions ambiguous. One major conclusion in this study is that "the degree of photochemical formation of diacids in Beijing is insignificant". However, there are many discussions in the manuscript which contradict with this conclusion. For example, Line 337-339. The authors state that "C2/Tot showed strong correlations with C2/C4 in all four seasons, indicating the significance of photooxidation pathways of biogenic unsaturated fatty acids". This sentence directly contradicts the main conclusion of this study.

Response: Thanks for your suggestion. We have rephrased the sentence in the revised MS. "Typically, concentrations of C2, C4 and C9 diacids showed similar seasonal variation trends (Fig. 1), implying that they were derived from common 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 secondary formation ways." Please see line 344–348 in page 13.

In Line 419-421, it is stated that "the high ratios of M/F throughout the whole year imply that aerosols in Beijing are not seriously subjected to secondary oxidation process". While the photooxidation may be weak in winter, it is strong in summer. The statement in Line 419-421 directly contradicts to many studies (for example, those cited in the introduction section). How do authors reconcile the discrepancies?

Response: We have added the sentence as "Though M/F obtained the lowest ratio values in summer, dicarboxylic acids and related compounds in Beijing are not seriously subjected to secondary oxidation process in the whole year with comparison to the strength of primary emissions." Please see line 432–435 in the revised MS.

Many studies cited in the introduction prefer to study the formation mechanisms and source apportionments of aerosols in haze days, while we focused more on the characterization of water-soluble organic acids 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 for PM2.5 in Beijing. Each of these sources has an annual mean contribution of 16, 14, 13, 3, 28, and 26 %, respectively, to PM2.5. Similarly, the relative contributions of these sources to PM2.5 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.

Some other contradictions are listed below. This is by no means an exclusive list. The authors must check carefully about inconsistency throughout the manuscript.

In Line 381, “these findings imply that Ph is largely emitted by anthropogenic sources in winter”. In line 385, “Ph are mostly formed via secondary oxidations of anthropogenic aromatic hydrocarbons.”

Response: We have rephrased these sentences in in the revised MS. “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 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.

C6 and Ph can be formed via secondary oxidations of anthropogenic cyclic olefins (e.g., cyclohexene) and aromatic hydrocarbons, respectively, whereas C9 is mainly produced by photochemical oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987;Kawamura and Ikushima, 1993).” Anthropogenic sources include biomass burning, fossil fuel burning and plastic waste burning, motor vehicles. Please see line 391–401.

In Line 239-242 and Line 257, “...indicating that substantial amounts of C9 may be stemmed from the local and surrounding combustion activities in Beijing.” Line 386, “C9 is a photochemical product of biogenic unsaturated fatty acids.” Then, C6/C9 is used to evaluate the source strength of anthropogenic vs biogenic emissions.

Response: Biomass burning may be technically defined as anthropogenic combustion activity (at least this is the case for 90% of all fires on a global basis), but the materials are mostly of biogenic origin. Hence, azelaic acid could be produced by the biomass burning because the biomass should contain its precursors (unsaturated fatty acids)(Kawamura et al., 2013).

Similarly, during the biomass burning, cyclic olefins may also be produced in a similar manner as in fossil fuel combustion processes and further oxidized to C6 in the atmosphere during the transport. Although these possible pathways may cause a slightly complicated situations of C6/C9 ratios as a tracer, previous study reported that contributions of C6 and Ph from biomass burning are minimal (Kawamura et al., 2013). Therefore, C6/C9 is used to evaluate the source strength of anthropogenic vs biogenic emissions.

2. Many discussions suffer flaws in logical flow and the link between evidence and conclusion is not clear. To name a few,

(1) Line 43-46. Why could "lower δ13C of major species in Beijing than western North Pacific" indicate "weak photooxidation in Beijng"? What is the rationale to compare Beijing with western North Pacific?

Response: "The systematic differences in stable carbon isotope ratios of diacids and other polar acids were attributable to kinetic isotope fractionation processes in the atmosphere (Hoefs and Hoefs, 1997), while secondary oxidation of these water-soluble organic acids is more influential for diacid carbons to enrich in 13C (Wang and Kawamura, 2006). For example, the relatively short carbon-chain diacids enriched in 13C were ascribed to the kinetic isotopic effect (KIE) for the photochemical breakdown of longer-chain diacids (Anderson et al., 2004;Irei et al., 2006). And lower dicarboxylic acids with enrichment of 13C may be less active to oxidants (e.g., OH radicals). Therefore, the determinations of δ13C values of dicarboxylic acids and related compounds show vital information about the atmospheric aging processes of aerosols derived from local emissions or long-range transport ways in air." Please see line 518–527 in the revised MS.

Particulate organic matters in remote marine areas are intensively aged during long-range transport and are affected by both the sea-to-air emissions and the terrestrial outflows (Wang and Kawamura, 2006). In general, δ13C values of diacids from marine aerosols are larger than those obtained in Beijing aerosols. This enrichment in 13C can be explained by the isotopic fractionation for more aged aerosols. Please see line 591–595 in the revised MS.

(2) Line 258-268. Firstly, the authors mentioned that phthalic acids (Ph) can be formed

vis photooxidation of naphthalene or directly emitted by fossil fuel burning and incomplete combustion. Secondly, the authors stated that the great amount of naphthalene is the precursor of Ph. However, the conclusion the authors draw is that "vehicle emissions are one of the major pollution sources in Beijing". My confusions regarding this paragraph are listed below. (a) Since Ph can be from both fossil fuel burning and vehicle emissions, what's the evidence to suggest that vehicles emissions contribute more to Ph than fossil fuel burning? (b) Do the authors suggest that Ph is mainly primary or secondary? Please be clear about vehicle emissions (i.e., primary) vs. the oxidation of vehicle emissions (i.e., secondary).

Response: We have rephrased these sentences in in the revised MS. "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 emissions contributed to relatively high concentrations of Ph in PM2.5 in Beijing." Please see line 268–274 in the revised MS. No matter whether phthalic acid is formed via the secondary oxidation ways of precursors, the emission sources are defined as anthropogenic activities, such as plastic waste burning, biomass burning, fossil fuel burning as well as motor vehicles.

(3) Line 321–325. The first sentence discussed that C2/Tot is the lowest in winter, indicating that organic aerosol in winter is less aged. This makes sense. However, the next sentence is "Because PM2.5 particles mainly originate from motor vehicles, fossil fuel and biomass combustion activities from local regions in winter, the aging process might occur during atmospheric transport." I can't see the link between these two sentences. What is the reason to mention "the aging process might occur during atmospheric transport?" Also, the authors need to support the statement that "PM2.5 particles in winter are mainly primary", as many studies suggest that a large fraction of PM2.5 is secondary in winter (Huang et al., 2014).

Response: We have rephrased these sentences in in the revised MS. "As for water-soluble organic acids in this paper, the ratios of C_2/Tot were the lowest in winter (0.39±0.05) (Table 3), indicating that wintertime organic aerosols may be less aged (Fig. 4a). After the main emission of $PM_{2.5}$ particles from motor vehicles, fossil fuel and biomass burning activities from local regions in winter, the aging process might occur during atmospheric transport." Please see line 328–332 in the revised MS. Huang et al. (2014) concluded that in comparison with secondary sources, primary emissions contributed slightly less to fine particles in haze events at urban locations in China. Their study focused on the fine aerosol and used both molecular markers and radiocarbon (14C) measurements. Different sampling time and locations are related with various strength of primary emissions and atmospheric conditions. Many scholars like to study the formation mechanisms and source apportionments of aerosols in haze days, while we focused more on the characterization of water-soluble organic acids in common days containing polluted and clean days in Beijing at a molecular level. Different sampling time and study target may get different conclusions.

(4) Still in this paragraph. Line 326-330. The authors firstly compared the C2/Tot between Beijing and Central Himalayas. Then, the next sentence is the conclusion that "the photochemical formation of dicarboxylic acids is insignificant in urban Beijing". How would this comparison justify the conclusion? What's the rationale to compare Beijing to Central Himalayas? The conclusion is over-stated to me. The only major evidence that authors provide in this paragraph is that C2/Tot is the lowest in winter than other seasons. This evidence can only suggest that OA is less aged and primary emissions contribute more to C2/Tot in winter than other seasons. It can't suggest whether dicarboxylic acids are mainly from primary or secondary. Also, it is inappropriate to use the C2/Tot ratio (i.e., only one dicarboxylic acids) to represent all dicarboxylic acids.

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. Please see line 328–332 in the revised MS.

(5) Line 350-355. What's the rationale to correlate C2/wC2 to C2/Tot? What does the correlation mean? Please elaborate on what the negative correlation between C2/wC2 and C2/Tot suggest? It is not clear why these phenomena suggest these species are from biogenic burning emissions.

Response: 1. Please see line 348–357 in the revised MS, where elaborated the meaning of correlation between C2/ωC_2 and C2/Tot.

2. The negative correlation between C2/ωC2 and C2/Tot suggests that supplement of ωC2 was 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.

3. Please see line 297–300 in the revised MS and figure S2 in supporting material, where stated these species are from biogenic burning emissions. 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). Please see line 256–260 in the revised MS, where stated the meanings of K^+ and Cl^-.

(6) Line 400. Missing connection between evidence and conclusion. "The outcomes above..." are merely some trends.

Response: The mass ratios of diacids in comparison with those in other sampling sites can better assess the emission strength of anthropogenic activities in Beijing.

Please see line 407–414 in the revised MS.

(7) Line 405-407. The Ph/C6 value is larger than unity for both diesel and gasoline. Thus, "Ph/C6 values larger than unity during the whole sampling year" can't justify that "diesel contributes more to diacids". The right evidence to imply the conclusion is that Ph/C6 values are closer to diesel than gasoline.

Response: The Ph/C6 ratio were comparable to or lower than 2.5 in other seasons and only showed the largest mean value (4.1) in winter. Following the reviewer' suggestion, we have revised the text as follows.

"Ph/C6 ratios reached to the highest values in winter (4.06±0.78) and the lowest in autumn (1.66±0.78). Kawamura and Kaplan (1987) demonstrated that the Ph/C6 ratio from gasoline fuel vehicle (2.05) is lower than that from diesel fuel vehicles (6.58). This phenomena shows abundances of diacids attributable to more emissions from gasoline fuel vehicles than diesel burning."

Please see line 416–420 in the revised MS.

(8) Line 519-524. In the evidence, the authors compare the δ13C value between continental higher plants and marine plankton activities. However, the conclusion is that "anthropogenic primary emissions are important". I can't find the link between evidence and conclusion.

Also, Is C9 from anthropogenic emissions or the oxidation of anthropogenic emissions? Be clear.

Response: Rephrased. Thanks for your suggestion. Please see line 536–541 in page 20.

(9) Line 534-535. Please provide evidence that tPh is related to plastic waste burning. For example, what is the δ13C value of tPh from plastic waster burning? I also want to point out that previous discussion in the manuscript (Line 269-271) does not provide evidence that tPh is related to plastic water burning. It is only mentioned that plastic water burning could be a source of tPh.

Response: In general, secondary oxidation of water-soluble organic acids is more influential for diacid carbons to enrich in 13C (Wang and Kawamura, 2006). tPh is a good tracer of open-waste burning (Kumar et al., 2015). Therefore, the low δ13C values of tPh in winter indicated that tPh is directly emitted plastic waste burning.

The result given by Ho et al. (2010) in line 276–277 reported Ph as the second most abundant compound in Beijing. The purpose of Ho's result exhibited in the revised MS is as a contrast with our conclusion to illustrate the abundance of tPh in Beijing. Simoneit et al. (2005) provided evidence that tPh is related to plastic waste burnings. It has been stated in line 277–278 in the revised MS.

3. Be consistent with terminology. For example, are “biomass combustion activities” (Line 324) the same as “biogenic burning” Line 354. what about “fossil fuel combustion” (Line 382) vs. “automobile emission” (Line 265) vs. “vehicle emission” (Line 268)?

Response: Corrected.

4. The PCA analysis does not provide further insights about the sources. The manuscript would benefit from more thorough evaluation of PCA results. For example, do the two factors represent different sources?

Response: The PCA analysis further showed solid evidence to prove the results found in previous sections.

Minor Comments

1. Line 36. It seems like that a word is missing after “relatively”.

Response: Corrected. Thanks for your suggestion.

2. Line 57-60. This sentence is confusing. The link between “WSOC/OC”, “fraction of total carbon mass in particles”, and “incomplete combustion activities” is unclear.

Response: A major fraction of organic aerosols is water-soluble, accounting for 20−60% of aerosol carbon mass in fossil fuel combustion-derived particles and 45−75% of that in biomass burning-derived particles (Pathak et al., 2011;Falkovich et al., 2005).

3. Line 281-282. The sentence is not clear. Please rephrase.

Response: We have rephrased the sentence. Please see line 287–289 in the revised MS.

4. Line 291-292. Please show the R2 value when discussing the correlations.

Response: Please see figure S2 and figure S3 in the supporting material.

5. Line 311-316. These sentences just repeat Line 302-302 and don’t offer any insights regarding the sources of Pyr and wC2.

Response: The line 309–313 is the conclusions reported in previous studies, while the line 315–323 is the demonstration of sources in our paper.

6. Line 337-339. It is not clear to me how this conclusion can be drawn.

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.

7. Line 520. What is the reason to compare C9 with C2-C4?

Response: "For example, the relatively short carbon-chain diacids enriched in 13C were ascribed to the kinetic isotopic effect (KIE) for the photochemical breakdown of longer-chain diacids (Anderson et al., 2004; Irei et al., 2006). And lower dicarboxylic acids with enrichment of 13C may be less active to oxidants (e.g., OH radicals). Therefore, the determinations of δ13C values of dicarboxylic acids and related compounds show vital information about the atmospheric aging processes of aerosols derived from local emissions or long-range transport ways in air." Please see line 521–527 in the revised MS.

The δ13C values of C9 in comparison with those of C2–C4 is to connect with the conclusions in previous studies.

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