Review of "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 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 $\delta^{13}C$ 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.

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 insiginificant". 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.

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?

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.”

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.

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 $\delta^{13}C$ 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?

(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).

(3) Line 321 – 325. The first sentence discussed that C_2/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 “$PM_{2.5}$ particles in winter are mainly primary”, as many studies suggest that a large fraction of $PM_{2.5}$ is secondary in winter (Huang et al., 2014).

(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.

(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.

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

(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.

(8) Line 519-524. In the evidence, the authors compare the $\delta^{13}C$ 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.

(9) Line 534-535. Please provide evidence that tPh is related to plastic waste burning. For example, what is the $\delta^{13}C$ 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.

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)?

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?

Minor Comments

1. Line 36. It seems like that a word is missing after “relatively”.
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.
3. Line 281-282. The sentence is not clear. Please rephrase.
4. Line 291-292. Please show the R2 value when discussing the correlations.
5. Line 311-316. These sentences just repeat Line 302-302 and don’t offer any insights regarding the sources of Pyr and wC2.
6. Line 337-339. It is not clear to me how this conclusion can be drawn.
7. Line 520. What is the reason to compare C9 with C2-C4?

Reference

Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E., and Prevot, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222, 10.1038/nature13774
http://www.nature.com/nature/journal/v514/n7521/abs/nature13774.html#supplementary-information, 2014.