Author responses to reviewers of *Atmospheric Chemistry and Physics* manuscript

Title: "Fates of secondary organic aerosols in the atmosphere identified from compound-specific dual-carbon isotope analysis of oxalic acid (Manuscript ID:acp-2022-707)"

Dear editor:

We gratefully thank the reviewers for constructive comments that have clearly contributed to improve the manuscript during revision.

All reviewer comments and our responses are listed below, organized such that each reviewer comment is shown first in *italics black font*, followed by our detailed response in upright black font. Our response refers to line numbers in the revised manuscript version. The English of this manuscript has been edited for proper English language, grammar, punctuation, spelling, and overall style by one or more of the highly qualified native English-speaking editors.

We thank you very much for kindly handling and reviewing our manuscript.

Best regards on behalf of all authors,

Gan Zhang

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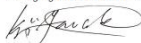
Edited provisional title
Fates of secondary organic aerosols in the atmosphere identified
from compound-specific dual-carbon isotope analysis of oxalic acid

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While this certificate confirms the authors have used Edanz's editing services, we cannot guarantee that additional changes have not been made after our edits.

General Comments:

This manuscript presents the spatial and seasonal (winter and summer) variations of diacids and related compounds and their stable carbon (^{13}C) isotope composition, and the radiocarbon (^{14}C) isotope ratios of oxalic acid (C_2) and water-soluble organic carbon (WSOC) in five cities of China. The data, particularly ^{14}C of C_2 diacid and WSOC, presented here is very interesting. Overall the paper has written well, except part of interpretations in section 3.4, and can be published in ACP, after addressing the comments given below.

Responses: Thank for your nice summary of our paper and positive assessment of the importance of this work. We have carefully revised the manuscript following your comments and suggestions. Our responses to your comments are given below, and the revised parts are shown after the responses (in blue font). Please refer to the revised manuscript, in which changes are highlighted in yellow.

Specific Comments:

RC1: *Abstract, Lines 6-7: Needs to be specified that the ^{14}C measurement was carried out only for C_2 diacid and WSOC (not for other species).*

AC1: Thanks for your comment. We have revised the relevant sentences in the "Abstract" and have clarified that ^{14}C measurement was only carried for oxalic acid and WSOC in this study:

The revised sentence:

Here, we use novel compound-specific dual-carbon isotope fingerprints (Δ^{14}C and δ^{13}C) for individual SOA tracer molecule (i.e., oxalic acid) to investigate the fates of SOAs in the atmosphere at five emission hotspots in China. (Line 5-8)

The dual-carbon isotope signatures of oxalic acid and bulk organic carbon pools (e.g., water-soluble organic carbon) were compared to investigate the fates of SOAs in the atmosphere. (Line

RC2: *Lines 14-15: The conclusion: "--- SOA formation from ----- in winter.", was drawn from the discussion in Section 3.4 on delta^{13}C of C$_2$ diacid and WSOC may not be appropriate. See the comment(s) on section 3.4 below. I wonder whether the authors meant that the SOA, including C$_2$ diacid, are formed from VOCs in gas phase in winter! In fact, as discussed in sub-section 3.3 (Lines 330-332), the aqueous phase formation of SOA is more prominent in winter.*

AC2: Thanks for your comments. In this sentence, we would like to express that the oxalic acid was predominantly formed through aqueous-phase secondary formation in winter. We have revised this sentence to express our point clearly.

The revised sentence:

Photochemical aging and aqueous-phase chemical processes dominant the formation of oxalic acid in summer and in winter, respectively. (Line 14-15)

For your concern about the discussion in **Section 3.4**, please refer to our response and the revised **Section 3.4** in author-response 4 (**AC4**).

RC3: *"During aqueous-phase --- react faster than ---". I wonder whether this statement is right! In fact, the reactivity of ^{12}C is higher compared to that of ^{13}C, irrespective of the phases (gas / liquid), and hence the first generation product(s) are depleted in ^{13}C and the remained reactant(s) are enriched with the ^{13}C, but not depend on the ^{13}C content of the precursor.*

AC3: Thanks for your comment. Per your great suggestion, we aware the confusing expression of this sentence. We have revised the text to express our point more clearly:

The revised sentence:

During aqueous-phase reactions, the reactivity of isotopically lighter carbon (^{12}C) is higher compared to that of isotopically heavier carbon (^{13}C), and this will cause the δ^{13}C values to be lower for the particulate products than the gaseous reactants. (Line 320-322)

RC4: *Lines 380~: The interpretation of the comparison of delta^{13}C of C$_2$ diacid and WSOC and the conclusions drawn from it in this sub-section need to be reconsidered. In fact, the delta^{13}C of a molecule, e.g., C$_2$ diacid, is significantly vary with the photochemical secondary formation and/or transformations (aging). Whereas the delta^{13}C of bulk content, e.g., WSOC, remains almost stable, corresponding to the isotopic signature of the origin(s), because the WSOC consist both the reactants and products of the photochemical reactions, until unless the physical aging (gas-liquid and/or gas-particle partitioning) is significant. Therefore, it is not appropriate to compare the delta^{13}C of C$_2$ diacid and WSOC in absolute terms and implicate them to trace the sources of SOA. Rather, it is better to confine to discuss their delta^{13}C individually to identify the origins and the extent of the aging of aerosols.*

AC4: Thank you very much for your very pertinent comment! This is exactly what we think. Actually, in the **Section 3.4**, we would like to express that the δ^{13}C of WSOC bear with it much more information about the isotopic signature of sources because the isotopic fractionation effects during atmospheric processes would introduce only minor changes in it. In fact, we found that the mean δ^{13}C values for WSOC in summer (-24.8‰ $\pm$ 0.9‰) and winter (-24.1‰ $\pm$ 0.4‰) were very similar. As you mentioned, the δ^{13}C of WSOC remain almost stable because WSOC consist both the reactants and products of the photochemical reactions. Therefore, the δ^{13}C values of WSOC pool would refer to both the reactants (enriched in ^{13}C) and products (depleted in ^{13}C) of the atmospheric processes. Oxalic acid is probably the most abundant compound in WSOC aerosol. The δ^{13}C signatures in oxalic acid relative to WSOC would indicate that the oxalic acid is a freshly formed product (δ^{13}C depleted) or a remining reactant (δ^{13}C enriched) in the WSOC, and a comparison between oxalic acid and WSOC will provide added-value in depicting the larger variation range in δ^{13}C of oxalic acid than WSOC.

As you suggested, we have discussed the δ^{13}C of oxalic acid (**Section 3.3**, Line 281-349) and WSOC (Line 380-397) individually to identify their origins and atmospheric processes. Based on these discussions, we further compare the δ^{13}C of

oxalic acid and WSOC in different seasons to gain deeper insights. Per your good suggestion, we aware our confusing expression of the relationship between diacids and WSOC aerosol pool. Therefore, we have rewritten the **Section 3.4** and have revised the interpretations in **Section 3.4**. Please refer to the revised manuscript, in which changes are highlighted in yellow.

The revised text:

As mentioned above, the average $\delta^{13}C$ and $\Delta^{14}C$ values for WSOC remain almost stable between winter and summer (Fig. 5a), mainly because the source patterns of WSOC were similar in different seasons. Bulk aerosol pool such as WSOC consist both the reactants and products of the photochemical reactions. Therefore, the isotopic fractionation effects during atmospheric processes would introduce only minor changes in the $\delta^{13}C$ values of WSOC. Oxalic acid contributed a mean of 5.5% (range 1.4%–10.7%) of the WSOC concentration and was probably the most abundant compound (Myriokefalitakis et al., 2011). However, the carbon isotope compositions of oxalic acid were significantly different between winter and summer (Fig. 6). This suggested that oxalic acid could have different carbon sources and be affected by different atmospheric processes between winter and summer.

The $\delta^{13}C$ values of oxalic acid were higher and the $\Delta^{14}C$ values indicated more oxalic acid than WSOC was formed from non-fossil carbon in summer (Fig. 5a and Fig. 6a). The $\delta^{13}C$ value has been found to increase as the number of carbon atoms in diacids decreases (Aggarwal and Kawamura, 2008; Pavuluri et al., 2011), suggesting that shorter-chain diacids, which can form through photochemical aging of longer-chain diacids, will become enriched in ^{13}C during aging. The $\delta^{13}C$ values of WSOC pool would refer to both the reactants and products of the atmospheric processes. Enrichment of ^{13}C in oxalic acid relative to WSOC (Fig. 6a) therefore probably reflected that oxalic acid was photochemical aging product (remaining reactant) in WSOC aerosols in summer. The $\Delta^{14}C$ values indicated more oxalic acid than WSOC was formed from non-fossil carbon in summer (Fig. 6a). This could have been because fossil-carbon components are more recalcitrant than biomass and biogenic components of organic aerosols to oxidative aging (Elmquist et al., 2006; Kirillova et al., 2014b; Kirillova et al., 2014a), meaning aged oxalic acid (with a higher $\delta^{13}C$ value) will preferentially form from non-fossil carbon (with a higher $\Delta^{14}C$ value). As discussed above,

biogenic emissions made larger contributions of oxalic acid than WSOC in summer, which gave the same results.

In contrast, the $\delta^{13}C$ values were lower and the $\Delta^{14}C$ values indicated more oxalic acid than WSOC was formed from fossil carbon in winter (Fig. 5a and Fig. 6b). The lower $\delta^{13}C$ values for oxalic acid found in winter suggested that oxalic acid indicates freshly formed SOA product in WSOC aerosols, as opposite to remaining reactant in summer. WSOC aerosols are mixtures of primary organic aerosols (e.g., sugars) and SOAs. Only a small fraction of water-soluble primary organic aerosols would have had fossil fuel sources (Liu et al., 2014; Mo et al., 2021). Therefore, a higher fossil-carbon contribution to water-soluble SOA than WSOC aerosol was expected, and this was indicated by the $\Delta^{14}C$ values for oxalic acid indicating important fossil-carbon sources. It has been suggested that substantial fossil-carbon-derived precursors are probably oxidized to give water-soluble SOAs through aqueous-phase chemical processes, giving products such as oxalic acid with lower $\delta^{13}C$ values and higher fossil-carbon contributions (Xu et al., 2022). Aqueous-phase processes are facilitated by a high ALWC, which is higher in winter than summer because the hygroscopic particle (e.g., ammonia and nitrate) mass is higher in winter than summer (Lv et al., 2022; Xu et al., 2022) and meteorological conditions (e.g., the boundary layer height, temperature, and wind speed) are unfavorable in winter (Gkatzelis et al., 2021). Photochemical aging is suppressed in winter because of lower temperatures and weaker solar radiation than in summer. This means that more aqueous-phase production of fresh SOA than aerosol photochemical aging will occur in urban areas in China in winter. (Line 398-445)

RC5: Technical Comments:

Fine editing is needed for language errors. For example, Line 17: "--- variations need including in ---". It should be corrected as "--- variations need to be included in ---". Line 148: "--- acid, ----". It should be plural. Lines 260-261: "--- in summer than winter ---" should be "--- in summer than in winter ---".

AC5: Thank you very much! We have revised these language errors. Please refer to the revised manuscript, in which changes are highlighted in yellow.

General Comments:

This study determined dual-carbon isotope fingerprints (Δ14C and δ13C) of oxalic acid to investigate the sources and chemical processes of SOAs in the atmosphere at five typical regions in China. As described by the authors, the compound-specific dual-carbon isotope method used in this study is a novel and useful way to study SOAs fates. The study was well organized, and the paper was also well written. A major concern is that the sample numbers analyzed in this study may be not enough to represent the general properties of SOA fates in each urban and suburban areas, which should be clarified in related sections of the manuscript. Anyway, this is a good study in my opinion, and worthy to be published in ACP after a minor revision.

Responses: Thank for your nice summary of our paper and positive assessment of the importance of this work. We have carefully revised the manuscript following your comments and suggestions. Our responses to your comments are given below, and the revised parts are shown after the responses (in blue font). Please refer to the revised manuscript, in which changes are highlighted in yellow.

Specific Comments:

RC1:*As described above, the authors should clarified the major conclusions in this study were based on the limited samples, especially for Beijing. For example, in Abstract, I suggest to add "during the sampling period" at the end of the sentence in Line 9-11.*

AC1: Many thanks for your comments. Per your suggestion, we have added "during the sampling period" at the end of the sentence in Line 9-11. We have also discussed the "limitations of the work" in the last paragraph of the manuscript, including the limited sample numbers in each city.

The revised text-1:

Coal combustion and vehicle exhausts accounted for ~55% of the sources of carbon in oxalic

acid in Beijing and Shanghai, but biomass-burning and biogenic emissions accounted for ~70% of the sources of carbon in oxalic acid in Chengdu, Guangzhou, and Wuhan during the sampling period. (Line 8-11)

The revised text-2:

In this study, one pooled sample was used to represent the winter or summer at a sampling site. Future compound-specific dual-carbon isotope studies covering a wide range of the temporal and spatial scale are strongly warranted to gain deeper insight into the fates of SOAs in China. (Line 509-512)

RC2: *I noted that the samples in each site were combined to 1 bulk samples to analyze Δ14C value, meaning that there were at most 2 samples in each regions (urban and suburban). Thus I think the SD of Δ14C value listed in Section 3.2 was not appropriate.*

AC2: Thanks for your kind reminding. We have revised the corresponding content in **Section 3.2**. In the revised manuscript, we did not report the SD of $\Delta^{14}C$ value in single city. Please refer to the revised manuscript, in which changes are highlighted in yellow.

The revised text:

However, a large proportion (56%) of the oxalic acid in Beijing (in North China) was derived from fossil carbon. (Line 220)

The revised figure:
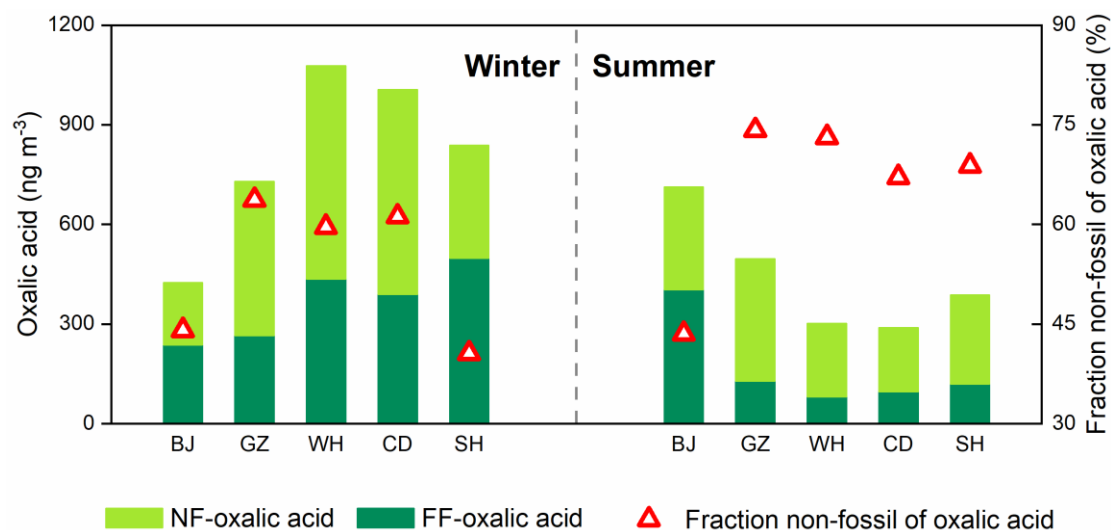
Figure 2. Mass concentrations of oxalic acid derived from non-fossil sources (NF) and fossil fuel (FF) and the mean proportions of non-fossil oxalic acid found for Beijing (BJ), Guangzhou (GZ), Wuhan (WH), Chengdu (CD), and Shanghai (SH) in winter and summer.

RC3: *Line 467-470, this conclusion was not reasonable. At first, "...fossil carbon made larger contributions to the oxalic acid than the WSOC aerosol ..." could not support "...water-soluble SOA was predominantly produced from fossil-fuel-derived carbon...". Secondly, "...water-soluble SOA was predominantly produced from fossil-fuel-derived carbon..." was in contradiction with the results showed in Figure 7 (fossil in winter: 46%).*

AC3: Many thanks. We agree that the conclusion in the Line 467-470 overinterpret what can be inferred from the data. Therefore, we have deleted this sentence.

The revised text:

The $\delta^{13}C$ values were lower for the oxalic acid than the WSOC and the $\Delta^{14}C$ values indicated that fossil carbon made larger contributions to the oxalic acid than the WSOC aerosol in winter (Fig. 5b). The marked differences between the different organic aerosol components indicated that dual-carbon-isotope studies of more aerosol molecules and components should be performed to improve our understanding of the origins and evolution of organic aerosols in the atmosphere. (Line 469-474)