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Interactive comment on "Molecular distribution and stable carbon isotopic compositions of dicarboxylic acids and related SOA from biogenic sources in the summertime atmosphere of Mt. Tai in the North China Plain" *by* Jingjing Meng et al.

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Anonymous Referee #3 General comments: 1. Comments: This manuscript reported the concentrations and isotopic compositions of dicarboxylic acids in the summertime of Mt. Tai. The bulk of the results presented focuses on the following aspects: (1) comparing the concentrations of species and the ratios of different dicarboxylic acids between day and night; (2) correlating the species concentrations with other parameters (T, O3, RH, pH, etc); (3) the δ13C of the dicarboxylic acids. The authors concluded that the dicarboxylic acids in Mt. Tai, a forested area with high elevation, mainly originate from local photochemical oxidation of biogenic emissions. Given the surrounding in Mt. Tai and sampling time, this conclusion is not surprising. Overall, the data analysis is routine and the conclusion is generally supported by experimental evidence. I recommend publication after major revisions.

Response: We thank the reviewer for the helpful comments above and below.

Major Comments: 2. Comments: My major concern is the lack of innovation of this study. As noted in the abstract, a few studies have performed similar measurements and analysis in the same site. The novelty of this manuscript as claimed by the authors is that the measurements were performed in summertime for the first time. It is not well justified that why it is important to conduct the measurements in summer. Also, considering the surroundings of measurement site and sampling time (i.e., summer), isn't the conclusion largely expected? It is not clear what are the scientific questions that authors aimed to address.

Response: (1) The innovation of this study is described as follows: Firstly, several field measurements had been conducted to investigate the molecular compositions, sources and formation mechanisms of SOA including dicarboxylic acids at Mt. Tai, but most of them were performed in May and June and mainly focused on the impact of anthropogenic activities such as field burning of wheat straw, while no information on dicarboxylic acids and related SOA in Mt. Tai during the typical summertime season (i.e., July and August) is available when the emission of biogenic volatile organic compounds (BVOCs) is dominant. A 3-D model simulation shows that about 79% of oxalic acid in the global atmosphere is originated from the oxidation of natural vegetation emissions (Myriokefalitakis et al., 2011), suggesting the dominant contribution of BVOCs to the global SOA loading. Therefore, it is necessary to investigate the abundances, compositions and formation mechanisms of oxalic acid and related SOA when vegetation emission is dominant, especially in the forested highland region where aerosols are more accessible to clouds due to higher elevation (See Page 4, Line 91-105). Secondly, compound-specific stable carbon isotope analysis is a powerful tool to provide important information of the sources and atmospheric processing of organic aerosols. Analyses of stable carbon isotope ratios of dicarboxylic acids and related SOA can be effectively applied to assessing the photochemical aging level and relative contributions of primary emissions to aerosols in the atmosphere. To our best knowledge, characteristics of the stable carbon isotopic compositions of dicarboxylic acids and related SOA in mountainous regions have not been investigated before. The current work is for the first time to report the stable carbon isotopic compositions of dicarboxylic acids and related compounds in a mountainous area, which are very helpful for improving our understanding on the sources, formation mechanisms and atmospheric behavior of SOA (Please see Page 4-5, Line 106-118). (2) The scientific questions that we aimed to address were listed as follows: The scientific questions that we aimed to address are sources and formation mechanisms of oxalic acid and related SOA in the free troposphere over Mt. Tai (Please see Page 5, Line 118-123).

3. Comments: Another major comment is regarding the comparison between daytime and nighttime. Due to the high elevation, the sampling site is in the residual layer at night. At night, the residual layer is isolated from surface emissions. The dicarboxylic acids and other species at night are mainly carried over from late afternoon formation. Also, the late afternoon mixing ratios of BVOCs, NOx and O3 govern overnight chemistry within the residual layer. Please refer to Edwards et al. (2017). Assuming no further oxidation at night, the species concentrations are expected to be similar to that in the late afternoon. Thus, the day (8am-8pm) vs night (8pm-night day 8am) comparison may merely reflect the difference in species concentration between noon and 6pm (when sampling site is above the boundary layer). This study is an excellent opportunity to study the residual layer chemistry. However, in current most of discussions (Line 184, Line 223, Line 298, etc), the format is like “something is higher in daytime than nighttime, suggesting stronger photochemistry or stronger biogenic activity in the day”. The authors should clearly state the physical model behind the day vs. night comparison and better explain the observations (including the NH4NO3 concentration in Line 184). The authors are encouraged to look in depth into the day vs. night comparison.

Response: We agree the comments above that the current work is an excellent opportunity to study the residual layer chemistry. Oxalic acid in the mountain atmosphere showed a strong linear correlation with temperature (Figure 6b) during the day and night, suggesting a dependent relationship of oxalic acid production with temperature. As the temperature was constantly variable and O3 level (22±12 ppb, Table 1) was high throughout the night at Mt. Tai, thus we assume that both gas-phase and aerosol-phase oxidations should continuously proceed throughout the whole night. As suggested by the reviewer, we did more analysis to discuss the potential factors causing the day and night differences in sulfate, nitrate and ammonium (see Figure S1 and Page 8-9, Line 223-233). Sulfate is mainly produced from aqueous phase oxidation of SO2, which is favored by higher temperature and humid conditions. Thus, concentration and relative abundance of sulfate are higher in daytime than in nighttime (Table 1 and Fig. S1). Particulate nitrate is mainly formed via gas phase oxidation of NO2 with OH radical and subsequent partitioning into aerosol phase with ammonia to form NH4NO3. NH4NO3 is volatile and thus lower temperature at night is favorable for NH4NO3 enriching in aerosol phase, resulting in NH4NO3 more abundant at night during the Mt. Tai observation period. These discussions were added into the revised manuscript.

4. Comments: Line 193-194. Why is LWC higher in daytime than nighttime?

Response: Aerosol LWC is controlled by the ambient relative humidity (Clegg et al., 1998) and the concentrations of inorganic salt (Fountoukis and Nenes, 2007). As shown in Table 1, the total concentration (21.7ïĆś11.5 μg m-3) of SO42-, NO3- and NH4+ during the daytime was almost equivalent to that (20.4ïĆś8.2 μg m-3) during the nighttime, but the relative humidity (92±5.0%) in daytime was higher than that in nighttime (77±8.2%). Therefore, the concentration of LWC in daytime was higher than that in nighttime. We have added these discussions into the revised manuscript. Please see Page 9, Line 239-245.

5. Comments: Line 243-248. The discussions on the higher concentration of dicarbonyls at night is confusing. Firstly, dicarbonyls are produced from photooxidation of

isoprene and other VOCs, not aqueous phase reaction. Secondly, how does the "opposite pattern" suggest "aerosol aqueous phase oxidation"? Thirdly, I believe "impressed" is a typo. In light of my previous comments, the authors should explore more reasons in terms of this day vs night comparison.

Response: Suggestion taken. Dicarbonyls in the aerosol phase are produced by the gas-phase photooxidation of isoprene and other VOCs and the subsequent partitioning into the aerosol aqueous phase. The higher concentrations of dicarbonyls at night can in part be attributed to the nighttime lower temperatures, which are favorable for the partitioning of gaseous glyoxal and methylglyoxal into the aerosol phase. We are sorry that the "impressed" word here is a typo. We have revised the statements, please see Page 11-12, Line 302-310.

6. Comments: Line 268-269. Please provide evidence that C2/C4 and C3/C4 can be regarded as indicators of photochemical aging. Also, the measured C2/C3 and C2/C4 ratios are actually very close to that from vehicle exhausts. This is contradictory to the conclusion that dicarboxylic acids are mainly from biogenic emissions.

Response: We are sorry for the mistake about the mass ratios of C2/C4 and C3/C4 from vehicle exhausts. Kawamura and Kaplan (1987) have reported that the ratios of C2/C4 and C3/C4 from vehicle exhausts were 4.1 and 0.35, respectively (see Page 12, Line 334- 335). The C2/C4 and C3/C4 ratios in this study are 8.0 ± 2.7 and 1.6 ± 0.6, respectively, higher than those in aerosols freshly emitted from vehicle exhausts. In addition, elemental carbon (EC) concentrations were very low and similar between day and night during the observation period (Table 1), suggesting that the impact of pollutants derived from anthropogenic sources including vehicle exhausts during the campaign was negligible. Therefore, traffic emission is not expected to have a large contribution to dicarboxylic acids in this study. It's consistent with the conclusion that dicarboxylic acids in Mt. Tai during summer are mainly from biogenic emissions rather than anthropogenic emissions.

7. Comments: Line 279-282. This is one of many cases that the authors need to better explain the link between evidence and conclusion. Why would the "correlation between C2/C4 and temperature at night" suggest "local photochemical oxidation"?

Response: Decomposition of C4 and/or C3 into C2 is one of the major formation pathways of oxalic acid, which is favored by temperature. Thus, a linear correlation of C2/C4 or C2/C3 with temperature has been frequently observed (Kawamura and Ikushima, 1993; Meng et al., 2013; Pavuluri et al., 2010). Temperature measured at the sampling site is a meteorological parameter, which only reflects the local meteorological conditions rather than the upwind conditions. Therefore, a significant correlation between C2/C4 and temperature can only be observed when SOA is largely derived from local precursor oxidation rather than from long-range transport. We have added related discussions into the text, please see Page 13, Line 341-350.

8. Comments: Line 360-362. The role of nighttime chemistry is not justified at all. The lack of correlation between BSOA tracers and O3 at night could be attributed to that most of BSOA tracers at night are carried over from later afternoon product and the O3 at night may be quickly titrated by residual NO. Again, this comment falls in the scope of day vs. night comparison.

Response: Thanks for your suggestion. We have revised the related contents in the revised manuscript. Please see Page 16, Line 432-441.

Minor Comments:

9. Comments: Line 61. "water" is uncountable noun. Replace "waters" with "water".

Response: Suggestion taken. Please see Page 3, Line 63.

10. Comments: Line 132. What type is the GC column?

Response: The type of the GC column is fused silica capillary column (HP-5, 0.2 mm × 25 m, film thickness 0.5 μm). We have added the details about the type of the GC column into the revised manuscript. Please see Lage 6, Line 153-156.

11. Comments: Line 304. The change in topic is too quick. Rephrase the sentence to improve the transition.

Response: Suggestion taken. We have rephrased the sentence as follows: However, the average values of C9/C6 (14±9.0) and C9/Ph (7.2±2.2) at the mountaintop of Mt. Tai are higher than those in urban regions such as Xi'an, China (C9/C6: 3.1; C9/Ph: 5.6) (Cheng et al., 2013) and also higher than those in other mountainous during summer such as Mt. Himalayan, India (C9/C6: 2.1; C9/Ph: 0.2) (Hedge and Kawamura, 2012) and Mt. Fuji, Japan (C9/C6: 3.1) (Mochizuki et al., 2017), indicating the important contribution of biogenic sources to SOA in the Mt. Tai region. Model simulation (Fu et al., 2008) and field observations (Meng et al., 2014) have suggested that……. Please see Page 14, Line 371-377.

12. Comments: Line 360. As mentioned above in the text, it is not only from O3 oxidation, also OH oxidation.

Response: Thanks for your suggestion. We have added “and OH radicals” in the old sentences. Please see Page 16, Line 436.

13. Comments: Line 377. Replace “linger” with “linear”.

Response: Suggestion taken. Please see Page 17, Line 463.

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