Dear ACP Editor,

We would like to thank the editor and the reviewers for the constructive suggestions, which are very helpful for improving our manuscript quality. We have carefully read the comments and revised the manuscript. Our responses to the two referees' comments are itemized below. All of the revisions and changes we made in the revised version are highlighted in red color.

Anything about our manuscript, please feel free to contact us via wanggh@ieecas.cn or ghwang@geo.ecnu.edu.cn .

Best regards,

Gehui Wang
08/31, 2018

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, O_3, RH, pH, etc); (3) the $\delta^{13}C$ 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. <u>Comments</u>: 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.

<u>Response</u>: (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. <u>Comments</u>: 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 O_3 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 NH_4NO_3 concentration in Line 184). The authors are encouraged to look in depth into the day vs. night comparison.

<u>Response</u>: 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 O_3 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 SO_2, 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 NO_2 with OH radical and subsequent partitioning into aerosol phase with ammonia to form NH_4NO_3. NH_4NO_3 is volatile and thus lower temperature at night is favorable for NH_4NO_3 enriching in aerosol phase, resulting in NH_4NO_3 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 (21.7±11.5 $\mu g\ m^{-3}$) of SO_4^{2-}, NO_3^- and NH_4^+ during the daytime was almost equivalent to that (20.4±8.2 $\mu g\ m^{-3}$) 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 C_2/C_4 and C_3/C_4 can be regarded as indicators of photochemical aging. Also, the measured C_2/C_3 and C_2/C_4 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 C_2/C_4 and C_3/C_4 from vehicle exhausts. Kawamura and Kaplan (1987) have reported that the ratios of C_2/C_4 and C_3/C_4 from vehicle exhausts were 4.1 and 0.35, respectively (see Page 12, Line 334- 335). The C_2/C_4 and C_3/C_4 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 C_2/C_4 and temperature at night" suggest "local photochemical oxidation"?

Response: Decomposition of C_4 and/or C_3 into C_2 is one of the major formation pathways of oxalic acid, which is favored by temperature. Thus, a linear correlation of C_2/C_4 or C_2/C_3

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 C_2/C_4 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 O_3 at night could be attributed to that most of BSOA tracers at night are carried over from later afternoon product and the O_3 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 C_9/C_6 (14±9.0) and C_9/Ph (7.2±2.2) at the mountaintop of Mt. Tai are higher than those in urban regions such as Xi’an, China (C_9/C_6: 3.1; C_9/Ph: 5.6) (Cheng et al., 2013) and also higher than those in other mountainous during summer such as Mt. Himalayan, India (C_9/C_6: 2.1; C_9/Ph: 0.2) (Hedge and Kawamura, 2012) and Mt. Fuji, Japan (C_9/C_6: 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 O_3 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.

References:

Carlton, A. G., Turpin, B. J., Lim, H.-J., Altieri, K. E., and Seitzinger, S.: Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, Geophysical Research Letters, 33, L06822, 10.1029/2005gl025374, 2006.

Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H.-J., and Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmospheric Environment, 41, 7588-7602, http://dx.doi.org/10.1016/j.atmosenv.2007.05.035, 2007.

Carlton, A. G., Wiedinmyer, C., and Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987-5005, 10.5194/acp-9-4987-2009, 2009.

Cheng, C., Wang, G., Zhou, B., Meng, J., Li, J., Cao, J., and Xiao, S.: Comparison of dicarboxylic acids and related compounds in aerosol samples collected in Xi'an, China during haze and clean periods, Atmospheric Environment, 81, 443-449, http://dx.doi.org/10.1016/j.atmosenv.2013.09.013, 2013.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System H+−NH4+−SO42-−NO3-−H2O at Tropospheric Temperatures, The Journal of Physical Chemistry A, 102, 2137-2154, 10.1021/jp973042r, 1998.

Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K+–Ca2+–Mg2+–NH4+–Na+–SO24−–NO3−–Cl−–H2O aerosols, Atmos. Chem. Phys., 7, 4639-4659, 10.5194/acp-7-4639-2007, 2007.

Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J.

Geophys. Res., 113, D15303, 10.1029/2007jd009505, 2008.

Kawamura, K., and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, Environmental Science & Technology, 27, 2227-2235, 10.1021/es00047a033, 1993.

Kawamura, K., Okuzawa, K., Aggarwal, S. G., Irie, H., Kanaya, Y., and Wang, Z.: Determination of gaseous and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai, Atmos. Chem. Phys., 13, 5369-5380, 10.5194/acp-13-5369-2013, 2013a.

Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S. G., Kanaya, Y., and Wang, Z. F.: High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the mountain aerosols over the North China Plain during wheat burning season, Atmos. Chem. Phys. , 13, 3695-3734, 10.5194/acpd-13-3695-2013, 2013b.

Li, J. J., Wang, G. H., Cao, J. J., Wang, X. M., and Zhang, R. J.: Observation of biogenic secondary organic aerosols in the atmosphere of a mountain site in central China: temperature and relative humidity effects, Atmos. Chem. Phys., 13, 11535-11549, 10.5194/acp-13-11535-2013, 2013.

Meng, J., Wang, G., Li, J., Cheng, C., Ren, Y., Huang, Y., Cheng, Y., Cao, J., and Zhang, T.: Seasonal characteristics of oxalic acid and related SOA in the free troposphere of Mt. Hua, central China: Implications for sources and formation mechanisms, Science of The Total Environment, 493, 1088-1097, http://dx.doi.org/10.1016/j.scitotenv.2014.04.086, 2014.

Pavuluri, C. M., Kawamura, K., and Swaminathan, T.: Water-soluble organic carbon, dicarboxylic acids, ketoacids, and α-dicarbonyls in the tropical Indian aerosols, Journal of Geophysical Research: Atmospheres, 115, D11302, 10.1029/2009jd012661, 2010.

Zhu, Y., Yang, L., Chen, J., Kawamura, K., Sato, M., Tilgner, A., van Pinxteren, D., Chen, Y., Xue, L., Wang, X., Herrmann, H., and Wang, W.: Molecular distributions of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in PM2.5 collected at Mt. Tai, in North China in 2014, Atmos. Chem. Phys. Discuss., 2018, 1-31, 10.5194/acp-2017-1240, 2018.

Anonymous Referee #4

General comments:

1. Comments:

This manuscript summarizes results from a summertime study at Mt. Tai in China where aerosol samples, ozone, and environmental parameters were measured. The authors determine daytime/nighttime concentrations and δ^{13}C of various carboxylic acids in an effort to characterize the role of bVOCs on SOA formation and aging. The paper is overall well-written although some parts need improvements. My major concern is about interpretation of the daytime/nighttime data. First of all, the standard deviations of the average values presented throughout the paper are rather large which mean that although the average values may be slightly different during day and night, statistically there’s not a significant difference between the observations. These need to be addressed/corrected throughout the paper. Secondly, as indicated in L171-172, nighttime data represent free tropospheric measurements, meaning whatever was left in the residual layer from daytime, so nighttime observations aren't truly representing nighttime emissions/oxidations. The most unique aspect of the paper is the δ13C analysis and interpretation of the results. I therefore support publishing the manuscript with major revisions after the authors have addressed my comments above as well as the other scientific comments and editorial suggestions listed below.

Response: We thank the reviewer for the helpful comments above. In the revised version, we have performed a statistic test (i.e., Student's t-test) to verify if the day and night aerosol chemistry is of significant difference. As shown in the Table S1, the concentrations and compositions of major species in $PM_{2.5}$ between day and night show a P value less than 0.005, which clearly demonstrates that the abundances and compositions of the major species during the day and night are statistically different. Figure S1 also shows that during the nighttime sulfate decreased while nitrate and ammonium increases. Such a diurnal change in inorganic ion compositions further suggests the significant difference in aerosol chemistry between day and night. Related statements have been added into the text.

Please see Line 211-217 in Page 8 and Line 223-233 in Page 8-9, respectively.

Scientific Comments:

2. Comments: L40: define C6, Ph, Gly, and mGly (also in L249). Also how are the ratios mentioned here expected to behave for anthropogenic precursors?

Response: Suggestion taken. We have defined C_6, Ph, Gly, and mGly in the revised manuscript. Please see Line 42-43 in Page 2 and Line 310-311 in Page 12, respectively. C_6 and Ph are believed to be formed via secondary oxidations of anthropogenic cyclic olefins (e.g., cyclohexene) (Hatakeyama et al., 1987) and aromatic hydrocarbons, respectively. C_9 is mainly produced from photochemical oxidation of oleic acid, which is a biogenic unsaturated fatty acid containing a double bond at the C-9 position (Wang et al., 2010). Therefore, both ratios of C_9/C_6 and C_9/Ph are indicative of the source strengths of biogenic versus anthropogenic emissions. Please see Line 362–370 in Page 13-14 of the revised manuscript. Model simulation (Fu et al., 2008) and field observations (Meng et al., 2014) have suggested that the concentration ratio of particulate Gly/mGly is about 1:5 when biogenic sources are predominant and is about 1:1 when anthropogenic sources are predominant. Therefore, the mass ratio of particulate Gly/mGly is also indicative of the source strengths of biogenic versus anthropogenic emissions. Please see Page 14, Line 377-380.

3. Comments: L41: how is ‘related SOA with biogenic precursor’ defined/ determined?

Response: Thanks for your suggestion. “related SOA” is defined as “major dicarboxylic acids and related SOA”, which consists of major dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls (i.e., C_2, C_3, C_4, ωC_2, Pyr, Gly and mGly), while “biogenic precursor” is defined as “SOA tracers derived from isoprene-, α-/β-pinene- and β-caryophyllene”. We have added these definitions into the revised manuscript. Please see Page 2, Line 42-46.

As for the analysis method of biogenic precursors, we have added the related information as follows:

The analysis method of biogenic precursors has been reported elsewhere (Li et al., 2013). Briefly, one fourth of the filter was cut and extracted with a mixture of dichloromethane and methanol (2:1, *v/v*) under ultrasonication. The extracts were concentrated using a rotary evaporator under vacuum conditions and then blow down to dryness using pure nitrogen. After reaction with a mixture of N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine (5:1, *v/v*) at 70°C for 3 h. Biogenic secondary organic aerosol (BSOA) tracers in the derivatized samples were determined by GC-MS. These data were used in this study to explore the biogenic sources of dicarboxylic acids and related SOA.

Please see Page 6-7, Line 165-173.

4. Comments: L164: What’s the influence of organic acids on pH? Since the AIM model incorporates only the major inorganic ions, how do you think your pH results are affected by the presence of organic acids?

Response: The Extended AIM Thermodynamic Model (E-AIM, Model II, http:// www.aim.

env.uea.ac.uk/aim/) was employed to calculate aerosol liquid water content (LWC) and in-situ particle pH (pH_{IS}). E-AIM II is an equilibrium thermodynamic model that can simulate liquid and solid phase of ionic compositions accurately in the SO_4^{2-}-NO_3^-- NH_4^+-H^+ system under certain temperature and relative humidity (Clegg et al., 1998a; Li et al., 2013). Compared with SO_4^{2-}, NO_3^- and NH_4^+, organic acid has little influence on estimation of aerosol acidity due to their low abundance in aerosols (Zhou et al., 2018). Organic acids may contribute free H^+ in aerosol aqueous phase and affect partitioning/dissociation of inorganic species in acidic particles. However, Huang et al. (2010) found that oxalic acid, the single most abundant organic acid, contributed little to the free acidity of rain water. This implied that the contribution of organic acids to aerosol free H^+ in the Mt. Tai aerosols was most likely minor. Moreover, quantity of free H^+ released from organosulfates was proved to be small compared with that estimated from inorganic anion and cation balance. Hygroscopicity of organic compounds are significantly weaker than inorganic species such as NH_4NO_3 and $(NH_4)_2SO_4$ (Ansari and Pandis, 2000). Therefore, organic species generally have minor influence on pH_{IS}. So, we did not take into account the organic species, neither did previous studies about the in-situ acidity of aerosol (Li et al., 2013; Meng et al., 2014; Xue et al., 2011). Both field observation and laboratory simulation suggest that oxalic acid is largely derived from the acid-catalyzed heterogeneous oxidation of glyoxal and related precursors in the aqueous phase. As shown in Fig. 6f in the revised manuscript, oxalic acid exhibits a significant negative correlation with pH_{IS} for the daytime (R^2=0.68) and nighttime (R^2=0.75) samples, respectively，suggesting that acidic conditions are favorable for the formation of organic acids in the aerosol aqueous phase.

5. Comments: L177: Looking at the observed variability in the values presented in Table 1, there isn’t a significant change between daytime and nighttime concentrations although the average for some species is higher during daytime. I think this point needs to be clarified here and throughout the paper.

Response: The variability of the data presented in Table 1 and throughout the paper is large, but our statistic t-test analysis results (Table S1) show that both concentrations and mass ratios between day and night are significantly different. Therefore, our statements, such as "the higher SOA concentrations and mass ratios in daytime are due to the strong photochemical oxidation" and other related discussions, are reasonable. We have also modified the related discussions as follows:

OC and WSOC in the $PM_{2.5}$ samples in daytime are similar to those in nighttime (Table 1), but OC/EC and WSOC/OC ratios are around 1.4 times higher in daytime than in nighttime (Fig. 4), indicating an enhancing SOA production due to the stronger photochemical oxidation in daytime rather than the changes in the boundary layer heights (Hegde and Kawamura, 2012).

Please see Page 8, Line 218-222.

6. Comments: L217: is the vegetation (tree types) also similar at this location and Mt. Fuji? I think that's more important rather than latitude and altitude of the sites.

Response: We have checked the vegetation compositions at Mt. Tai and Mt. Fuji, and found both are dominated by broad-leaved forest. We have modified the related statement.
Please see Page 10, Line 269-270.

7. Comments: L243-245: Based on the average values in the table, total α-dicarbonyls were actually higher in daytime, so I don't think the data support the statement mentioned here. Do you mean only glyoxal and methylglyoxal? Also based on the graph, it seems on most days the difference between daytime and nighttime total conc. of α-dicarbonyls was minor, so the pattern you're highlighting is not consistent. Please clarify.

Response: In the current work, total α-dicarbonyls means only glyoxal and methylglyoxal. As seen in Table 2, concentrations of α-dicarbonyls were 19 ± 11 ng/m^3 in daytime, which were lower than that (27 ± 17 ng/m^3) in nighttime. As we mentioned before, we have done a t-test analysis to check if the diurnal difference is of a statistic meaning (Table S1). The t-test results show that concentrations and mass ratios of major species between day and night are of a P-value less than 0.005, which clearly suggests that the diurnal differences are statistically significant.

8. Comments: L265-267: I'm not understanding the difference between the beginning statement and the second part of the sentence. C4 is still a longer-chain diacid compared to C3. Please clarify and be more precise in what constitutes a longer-chain diacid.

Response: Suggestion taken. The longer-chain diacids are defined as the number of carbons contained in the diacids is larger than four such as C_5-C_{11}. To clarify this, we have revised the sentence as follows:

Previous studies have proposed that the hydroxylation of C_4 can be further oxidized into C_2 and C_3, and C_3 can also be oxidized into C_2 through intermediate compounds such as hydroxymalonic acid or ketomalonic acid.

Please see Page 12, Line 328-330.

9. Comments: L269-275: Again it seems that given the variability of the observed diacid ratios in this study and those of previous studies, there's no significant difference between observations at different photochemical ages. I'm not convinced the conclusions regarding age are strongly supported by the data.

Response: As seen in our previous response, we did a statistic analysis, which shows that the diurnal variation is statistically significant.

10. Comments: L275-277: Photochemical oxidation is stronger compared to what? Nighttime or aqueous oxidation? Please clarify.

Response: Thanks for your suggestion. Photochemical oxidation is stronger in the daytime than that in the nighttime. We have revised the old sentence as follows:

Compared with those in the nighttime, the higher ratios of C_2/C_4 and C_3/C_4 (Fig. 4) in the daytime again indicated that the photochemical modification of aerosols is stronger.

Please see Page 13, Line 339-341.

11. Comments: L298-299: again given the variability observed in the daytime/nighttime data, the difference in the average values isn't significant.

Response: Here we agree with the comments above. The t-test analysis shows that differences in ratios of C_9/C_6 and C_9/Ph between day and night are not significant. Thus, we have revised the related discussions as follows:

As shown in Fig. 4, both ratios of C_9/C_6 and C_9/Ph are similar in the daytime to those in the nighttime.

Please see Page 14, Line 370-371.

12. Comments: L328: what are the SOA tracers from these compounds? It will be useful to add to the legend in Table 4 what parent hydrocarbon is associated with each tracer.

Response: Suggestion taken. The SOA tracers from these compounds consist of the secondary organic aerosols (SOA) derived from isoprene, α-/β-pinene and β-caryophyllene. We have added this explanation to the legend in Table 4.

Please see the red words in Page 31, Table 4.

13. Comments: L339: some of the acids related to α-pinene and β-caryophyllene oxidation also correlate well with the diacids, so why only highlight isoprene contribution to SOA? In fact, the following sentence indicates that bSOA in general control production of the diacids, so perhaps it's better to combine these few sentences together.

Response: Suggestion taken, we have combined these sentences together.

Please see Page 15, Line 412-419.

14. Comments: L360: I disagree with the statement that daytime ozone oxidation of isoprene and α-pinene was more important than OH oxidation of these compounds. Lifetime of these bVOCs even at background OH levels is a lot shorter than with respect to ozone oxidation. The observed correlation is just a correlation and not a causality. Related to this, I think the conclusion in the sentence starting in L454-455 needs to be removed.

Response: We agree with the reviewer on the comments above. We have revised the discussions about the reason why the lack of correlation was observed between BSOA tracers and O_3 at night as follows:

These results suggest that the daytime oxalic acid and related SOA in the mountaintop of Mt. Tai are largely derived from O_3 and OH radical oxidation of BVOCs such as isoprene and α-pinene, while the nighttime oxalic acid and related SOA might be mostly produced by NO_3 radical and other oxidizing agents such as H2O2 (Claeys et al., 2004; Herrmann et al., 1999). In addition, the titration of O_3 by the residual NO in the nighttime atmosphere could also be responsible for the lack of the correlation between BSOA tracers and O_3.

Please see Page 16, Line 434-441.

We have deleted the conclusion in the sentence starting in L454-455 in the old version manuscript.

15. Comments: L366-368: SOA formation potential under different oxidants are also different, and so can contribute to the higher observed tracers during daytime.

Response: We agree with the comments above that SOA formation potential under different oxidants are different, which could contribute to the higher observed tracers during daytime. As seen in Table 1, O_3 concentration during the sampling period is 50% higher in daytime than in nighttime, clearly indicating that oxidation potential in daytime at the Mt. Tai site is stronger. Moreover, isoprene is only emitted by trees during daytime. Thus, we think the higher loadings of BSOA tracers in daytime are caused not only by stronger photochemical oxidation but also by enhanced emissions of BVOCs.

We have revised the statement. Please see Page 16-17, Line 446-452.

16. Comments: L381-382: In addition to the similar formation pathways (aqueous oxidation) for sulfate and oxalic acid, since oxalic acid formation is acid-catalyzed, one expects to have a good correlation with sulfate and oxalic acid (since the site is far from agricultural sources, I’m assuming most of the sulfate is acidic). Please add this discussion as a contributor to the good correlation as well.

Response: Suggestion taken. Please see Page 17, Line See 462-463.

17. Comments: L393: aerosol composition is also very important for determining LWC of aerosols at a given RH.

<u>Response</u>: We agree with the comments above. Aerosol LWC in this study was calculated by using AIM-II model, which considered a SO_4^{2-}-NO_3^-- NH_4^+-H^+ system and allowed variable temperature and relative humidity (Clegg et al., 1998b; Li et al., 2013), therefore aerosol LWC is controlled by the ambient relative humidity (Clegg et al., 1998b) and the concentrations of inorganic salt (Fountoukis and Nenes, 2007). As shown in Table 1 of the revised manuscript, the total concentration (21.7±11.5 µg m^{-3}) of SO_4^{2-}, NO_3^- and NH_4^+ during the daytime was almost equivalent to that (20.4±8.2 µg m^{-3}) during the nighttime. However, the relative humidity (92±5.0%) in daytime was higher than that in nighttime (77±8.2%). Therefore, we only discussed the effect of RH on aerosol LWC.

We have changed old sentence as follows:

Both RH and aerosol composition are key factors controlling the aerosol LWC.

Please see Page 18, Line 480-481.

18. <u>Comments</u>: L428-429: Please indicate here specifically what trends in the ratios would suggest aging.

<u>Response</u>: Suggestion taken. The higher the mass ratios of $C_2/\omega C_2$, C_2/Gly and C_2/mGly, the more aged the organic aerosol. To express clearly, we have revised the old sentence as follows:

Thus, the higher mass ratios of $C_2/\omega C_2$, C_2/Gly and C_2/mGly indicate that organic aerosols are more aged (Wang et al., 2017).

Please see Page 19, Line 518-519.

19. <u>Comments</u>: L440-442: I'm a bit confused about this sentence. Higher values of glyoxal and methyl glyoxal relative to what? Please clarify. Also, from sentence above, I was under the impression that freshly emitted BVOCs are depleted in ^{13}C, so why do the authors indicate that Gly and mGly are formed from oxidation of bVOCs enriched in ^{13}C?

<u>Response</u>: Suggestion taken. The $\delta^{13}C$ values of Gly (−17.4±1.9) and mGly (−18.8±2.1) were relatively higher than fresh BVOCs such as isoprene (–32‰ − –27‰) emitted directly from vegetation. To express this point clearly, we have revised the related sentence as follows:

Therefore, the δ^{13}C values of Gly and mGly are relatively higher than fresh BVOCs such as isoprene, largely attributed to the secondary formation from the oxidation of isoprene and other biogenic precursors.

Please see Page 19-20, Line 531-533.

20. Comments: L448 (also in the abstract): Indicate that ‘average’ concentration of some species are higher in the day compared to night since as mentioned above, the variability in the measured data was too high to conclude beyond the average.

Response: As mentioned above, our t-test analysis showed that the diurnal difference is significant, although the variability in the measured data was very high.

Minor Comments:

21. Comments: L56: consider changing to “…, of which up to 80% are water soluble”.

Response: Suggestion taken. Please see Page 3, Line 59.

22. Comments: L73: “… C2 is largely produced…”.

Response: Suggestion taken. Please see Page 3, Line 75.

23. Comments: L80: change “liquid water content-enriched aerosol” to “aqueous aerosol”.

Response: Suggestion taken. Please see Page 3, Line 81-82.

24. Comments: L87: change “independent” to “isolated”.

Response: Suggestion taken. Please see Page 4, Line 89.

25. Comments: L88: change “One of the severest air-polluted regions” to “one of the regions with worst air pollution in the world”.

Response: Suggestion taken. Please see Page 4, Line 90.

26. Comments: L90: change “few information” to “little information”.

Response: Suggestion taken. Please see Page 4, Line 95-96

27. Comments: L109: indicate also the altitude of the sampling site in the main text.

Response: Thanks for your suggestion. We have added the altitude of the sampling site in the revised manuscript. Please see Page 5, Line 128-130.

28. Comments: L121: “site”.

Response: Suggestion taken. We corrected the typo, see Page 4, Line 142.

29. Comments: L152 ad L163: “in-situ particle pH”.

Response: Suggestion taken. Please see Page 7, Line 186-187.

30. Comments: L159: add “… to remove insoluble particles…”.

Response: Suggestion taken. Please see Page 7, Line 193-194.

31. Comments: L222: replace “difference” with “pattern”.

Response: Suggestion taken. Please see Page 10, Line 276.

32. Comments: L238: The sentence is too long. Consider starting a new sentence after the references.

Response: Thanks for your suggestion. We have changed the old sentences as follows:

Ketocarboxylic acids are the major intermediates of aqueous phase photochemical oxidation producing dicarboxylic acids in the atmosphere (Kawamura and Ikushima, 1993;Pavuluri and Kawamura, 2016). The concentrations of ketocarboxylic acids are 43 ± 28 ng m^{-3} in the daytime and 37 ± 19 ng m^{-3} in the nighttime, respectively, with glyoxylic acid (ωC_2) being the dominant ω-oxoacid, followed by pyruvic acid (Pyr) and 3-oxobutanoic acid (ωC_3) (Table 2 and Fig. 2).

Please see Page 11, Line 291-296.

33. Comments: L246: consider replacing “precursors” to “compounds”.

Response: Suggestion taken. We have rephrased the sentences, please see Page 11, Line 302-303.

34. Comments: L248: consider replacing “impressed” with “more significant”.

Response: Suggestion taken. Please see Page11-12, Line 308-310.

35. Comments: L258: “by wet deposition”.

Response: Suggestion taken. Please see Page 12, Line 320-321

36. Comments: L265: “by photochemical degradation”.(?)

Response: We have rephrased the expressions as follows:

Previous studies have proposed that the hydroxylation of C_4 can be further oxidized into C_2 and C_3, and C_3 can also be oxidized into C_2 through intermediate compounds such as hydroxymalonic acid or ketomalonic acid

Please see Page 12, Line 328-330.

37. Comments: L278: delete ‘would’.

Response: Suggestion taken. Please see Page 13, Line 345.

38. Comments: L282: “at Mt. Tai”.

Response: Suggestion taken. Please see Page 13, Line 353.

39. Comments: L289: consider changing “troposphere” to “atmosphere”.

Response: Suggestion taken. Please see Page 13, Line 361.

40. Comments: L377: “linear”.

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

41. <u>Comments</u>: L447: either “ground” or “surface”; probably don’t need to have both words.

<u>Response</u>: Thanks for your suggestion. We have deleted “surface”. Please see Page 20, Line 538-539.

42. <u>Comments</u>: Table1: is the upper end of RH at night 93% rather than 193%?

<u>Response</u>: Sorry for the mistake, we had corrected it. Please see Table 1 in Page 29.

43. <u>Comments</u>: Change the order of Fig. 6 and Fig. 5 as Fig. 6 is referred to before Fig. 5. Also it seems the next Figure that authors refer to is Fig. 8. Please use the figures in the same order they appear in the text.

<u>Response</u>: We disagree on the comments above. Fig. 5 was used to elucidate the dicarboxylic acids and related SOA are mostly derived from the local sources rather than long-range transport, which was discussed in Part 3.3. Fig. 6 was used to investigate the effects of temperature, relative humidity, and O_3 concentrations on the formation of oxalic acid and related SOA, which was discussed in Part 3.5. Thus, Fig. 5 should be shown before Fig. 6.

Reference:

Ansari, A. S., and Pandis, S. N.: Water Absorption by Secondary Organic Aerosol and Its Effect on Inorganic Aerosol Behavior, Environmental Science & Technology, 34, 71-77, 10.1021/es990717q, 2000.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System H+−NH4+−Na+−SO42-−NO3-−Cl-−H2O at 298.15 K, The Journal of Physical Chemistry A, 102, 2155-2171, 10.1021/jp973043j, 1998a.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System H+−NH4+−SO42-−NO3-−H2O at Tropospheric Temperatures, The Journal of Physical Chemistry A, 102, 2137-2154, 10.1021/jp973042r, 1998.

Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K+–Ca2+–Mg2+–NH4+–Na+–SO24−–NO3−–Cl−–H2O aerosols, Atmos. Chem. Phys., 7, 4639-4659, 10.5194/acp-7-4639-2007, 2007.

Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J. Geophys. Res., 113, D15303, 10.1029/2007jd009505, 2008.

Hatakeyama, S., Ohno, M., Weng, J., Takagi, H., and Akimoto, H.: Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air, Environmental Science & Technology, 21, 52-57, 10.1021/es00155a005, 1987.

Hegde, P., and Kawamura, K.: Seasonal variations of water-soluble organic carbon, dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls in Central Himalayan aerosols, Atmos. Chem. Phys., 12, 6645-6665, 10.5194/acp-12-6645-2012, 2012.

Kawamura, K., and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, Environmental Science & Technology, 27, 2227-2235, 10.1021/es00047a033, 1993.

Li, J. J., Wang, G. H., Cao, J. J., Wang, X. M., and Zhang, R. J.: Observation of biogenic secondary organic aerosols in the atmosphere of a mountain site in central China: temperature and relative humidity effects, Atmos. Chem. Phys., 13, 11535-11549, 10.5194/acp-13-11535-2013, 2013.

Meng, J., Wang, G., Li, J., Cheng, C., Ren, Y., Huang, Y., Cheng, Y., Cao, J., and Zhang, T.: Seasonal characteristics of oxalic acid and related SOA in the free troposphere of Mt. Hua, central China: Implications for sources and formation mechanisms, Science of The Total Environment, 493, 1088-1097, http://dx.doi.org/10.1016/j.scitotenv.2014.04.086, 2014.

Pavuluri, C. M., and Kawamura, K.: Enrichment of (13)C in diacids and related compounds during photochemical processing of aqueous aerosols: New proxy for organic aerosols aging, Scientific Reports, 6, 36467, 10.1038/srep36467, 2016.

Wang, G., Xie, M., Hu, S., Gao, S., Tachibana, E., and Kawamura, K.: Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation, Atmos. Chem. Phys., 10, 6087-6096, 10.5194/acp-10-6087-2010, 2010.

Wang, J., Wang, G., Gao, J., Wang, H., Ren, Y., Li, J., Zhou, B., Wu, C., Zhang, L., Wang, S., and Chai, F.: Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during, and after the 2014 APEC, Atmos. Chem. Phys., 17, 981-992, 10.5194/acp-17-981-2017, 2017.

Xue, J., Lau, A. K. H., and Yu, J. Z.: A study of acidity on PM2.5 in Hong Kong using online ionic chemical composition measurements, Atmospheric Environment, 45, 7081-7088, http://dx.doi.org/10.1016/j.atmosenv.2011.09.040, 2011.

Zhou, M., Zhang, Y., Han, Y., Wu, J., Du, X., Xu, H., Feng, Y., and Han, S.: Spatial and temporal characteristics of PM2.5 acidity during autumn in marine and coastal area of Bohai Sea, China, based on two-site contrast, Atmospheric Research, 202, 196-204, https://doi.org/10.1016/j.atmosres.2017.11.014, 2018.

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

Jingjing Meng[1,3], Gehui Wang[2,3,4*], Zhanfang Hou[1,3], Xiaodi Liu[1], Benjie Wei[1], Can Wu[3], Cong Cao[3], Jiayuan Wang[3], Jianjun Li[3], Junji Cao[3], Erxun Zhang[1], Jie Dong[1], Jiazhen Liu[1], Shuangshuang Ge[2], Yuning Xie[2]

[1] School of Environment and Planning, Liaocheng University, Liaocheng 252000, China

[2] Key Laboratory of Geographic Information Science of the Ministry of Education, School of Geographic Sciences, East China Normal University, Shanghai 200062, China

[3] State Key Laboratory of Loess and Quaternary Geology, Key Lab of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

[4] School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an 710049, China

*Corresponding author: Prof. Gehui Wang

E-mail address: wanggh@ieecas.cn, or ghwang@geo.ecnu.edu.cn

Abstract: Molecular distributions and stable carbon isotopic ($\delta^{13}C$ values) compositions of dicarboxylic acids and related SOA in $PM_{2.5}$ aerosols collected on a day/night basis at the summit of Mt. Tai (1534 m a.s.l) in the summer of 2016 were analyzed to investigate the sources and photochemical aging process of organic aerosols in the forested highland region of North China Plain. The molecular distributions of dicarboxylic acids and related SOA are characterized by the dominance of oxalic acid (C_2), followed by malonic (C_3), succinic (C_4) and azelaic (C_9) acids. The concentration ratios of C_2/C_4, diacid-C/OC and C_2/total diacids are larger in daytime than in nighttime, suggesting that the daytime aerosols are more photochemically aged than those in the nighttime due to the higher temperature and stronger solar radiation. Both ratios of C_2/C_4 ($R^2>0.5$) and C_3/C_4 ($R^2>0.5$) correlated strongly with the ambient temperatures, indicating that SOA in the mountaintop atmosphere are mainly derived from the photochemical oxidation of local emissions rather than long-range transport. The mass ratios of azelaic acid to adipic acid (C_9/C_6), azelaic acid to phthalic aid (C_9/Ph), and glyoxal to methylglyoxal (Gly/mGly) and the strong linear correlations of major dicarboxylic acids and related SOA (i.e., C_2, C_3, C_4, ωC_2, Pyr, Gly and mGly) with biogenic precursors (SOA tracers derived from isoprene, *α*-/*β*-pinene and *β*-caryophyllene) further suggest that aerosols in this region are mainly originated from biogenic sources (i.e., tree emissions).

C_2 concentrations correlated well with aerosol pH, indicating that particle acidity favors the organic acid formation. The stable carbon isotopic compositions ($\delta^{13}C$) of the dicarboxylic acids are higher in daytime than in nighttime with the highest value (−16.5±1.9‰) found for C_2 and the lowest value (−25.2±2.7‰) found for C_9. An increase in $\delta^{13}C$ values of C_2 along with increases in C_2/Gly and C_2/mGly ratios was observed, largely due to the isotopic fractionation effect during the precursor oxidation process.

Keywords: Dicarboxylic acids; Glyoxal and methylglyoxal; Secondary organic aerosols (SOA); Biogenic sources; Formation mechanisms

1. Introduction

Secondary organic aerosols (SOA) accounts for a substantial fraction (20-90%) of the total $PM_{2.5}$ mass in the troposphere, of which up to 80% are water-soluble (Hallquist et al., 2009; Kroll and Seinfeld, 2008). Due to the low vapor pressures and high hygroscopicity (approximately less than 10^{-7} Pa) (Bilde et al., 2015; Ehn et al., 2014), dicarboxylic acids and related compounds are ubiquitously found in atmospheric water and particles (Kawamura and Bikkina, 2016; Sorooshian et al., 2007a). Because of the water-soluble and hygroscopic properties, dicarboxylic acids and related compounds play important roles in atmospheric aqueous chemistry and influence radiative forcing of aerosols via acting as cloud condensation nuclei (CCN) (Hoque et al., 2017; Wang et al., 2012, 2016; Zhang et al., 2016;).

Although they can be emitted directly from sources such as incomplete combustion of fossil fuels (Kawamura and Kaplan, 1987) and biomass burning (Kawamura et al., 2013a,b; Narukawa et al., 1999), atmospheric dicarboxylic acids and related compounds are largely produced by photochemical oxidation of unsaturated fatty acids, PAHs (Kawamura et al., 1996), cyclic alkanes and other compounds (Kawamura and Usukura, 1993). Oxalic acid (C_2) is the smallest and the most abundant dicarboxylic acid (Wang et al., 2009, 2015). Modeling studies and cloud measurements have suggested that C_2 is largely produced from aqueous-phase oxidation of less oxygenated organic precursors such as glyoxal (Gly), methyglyoxal (mGly) and pyruvic acid (Pyr) in clouds or wet aerosols and the photochemical breakdown of longer-chain dicarboxylic acids (Wang et al., 2012, 2015).

There is a growing consensus on highlighting the significance of oxalic acid and related SOA formation from the photochemical oxidation of anthropogenic/biogenic volatile organic compounds (VOCs) via the aqueous phase in clouds or aqueous aerosol from many field observations and laboratory experiments as well as modeling studies (Bikkina et al., 2017; Cheng et al., 2017; Ervens et al., 2014; Fu et al., 2008; Lim et al., 2005; Miyazaki et al., 2009; Mochizuki et al., 2017). A ubiquitous layer of dicarboxylic acids was found above the clouds by aircraft measurements in US, indicating that organic acids are important CCN in the free troposphere (Sorooshian et al., 2007a, b). Compared to the aerosols in lowland areas, alpine aerosols have more sinificant influence on cloud formation, because they are more accessible to clouds due to higher elevation. Mt. Tai is an isolated peak located in the center of the North China Plain (NCP), one of the regions with worst air pollution in the world (Wang et al., 2009; Yang et al., 2017). A few studies have 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 (Kawamura et al., 2013a, b; Zhu et al., 2018), while very little 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.

Compound-specific stable carbon isotope analysis is a powerful tool to provide important information of the sources and atmospheric processing of organic aerosols, because the isotopic fractionation of carbon occurs upon chemical reactions or phase transfer (Pavuluri and Kawamura, 2016; Zhang et al., 2016). Analyses of stable carbon isotope ratios ($\delta^{13}C$) 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 (Zhao et al., 2018). 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. In this study, we first investigated the diurnal variations in molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds. Then we discussed the impact of temperature (T), relative humidity (RH), particle acidity (pH_{IS}), liquid water content (LWC) and O_3 concentration on oxalic acid and related SOA to explore their sources and formation mechanism in the forested highland of the North China Plain.

2. Experimental section

2.1 Aerosol sampling

$PM_{2.5}$ samples were collected at the Meteorological Observation Station of Mt. Tai, which is located at the summit of Mt. Tai (36.25° N, 117.10°E; 1534 m a.s.l.) in the North China Plain (Fig. 1). The sampling site was located about 1 km to the north of the peak, with an altitude of 1465 m a.s.l., and there is little anthropogenic emission nearby. About 80% of the mountainous land is covered by vegetation known to comprise 989 species, which is densely wooded in summer (Fu et al., 2010). $PM_{2.5}$ samples were collected from July 20 to August 20, 2016 each lasting for 12h on a day/night basis using a mid-volume air sampler (KC-120H, Qingdao Laoshan Company, China) equipped with prebaked (450°C, 8 h) quartz fiber filters (Whatman, USA) at an airflow rate of 100 L min^{-1}. The daytime samples were collected from 8:00 to 20:00, while nighttime samples were collected from 20:00 to 8:00 of the next day. Field blank samples were also collected by mounting the blank filter onto the sampler for 15 min without sucking any air before and after the campaign. A total of 57 samples (daytime: 28; nighttime: 29) were collected during the campaign. After sampling, each filter was sealed in an aluminum foil bag and stored at −20°C prior to laboratory analyses. Moreover, the concentration of ozone was simultaneously monitored at the site by an UV absorption analyzer (Model 49C, Thermo Electron Corporation).

2.2 Chemical analyses

2.2.1 Sample extraction, derivatization, GC/MS and GC/FID quantification

Dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in $PM_{2.5}$ were determined using the method described by previous studies (Kawamura et al., 1996; Meng et al., 2013, 2014;). Briefly, one half of the filter was cut into pieces and extracted with pure Milli-Q water under ultrasonication for three times each for 15 min. The water extracts were concentrated to near dryness and then reacted with 14% BF_3/*n*-butanol at 100°C for 1 hr to form butyl esters/dibutoxy acetals. After derivatization, *n*-hexane was added and washed with pure water for three times. Finally, the hexane layer was concentrated to 200 µL and determined using a capillary gas chromatography (Agilent GC 7890A) coupled with a split/splitless injector. The GC was equipped with a flame ionization detector (FID) and a fused silica capillary column (HP-5, 0.2 mm × 25 m, film thickness 0.5 µm). The GC oven temperature was programmed from 50 (2 min) to 120°C at 15°C min^{-1}, and then to 300 at 5°C min^{-1} with a final isothermal hold at 300°C for 16 min. Peak identification was performed by comparing the GC retention time with that of authentic standards and confirmed by mass spectrum of the sample using a GC-mass spectrometer (GC-MS). Recoveries of the target compounds were 80% for oxalic acid and 85% to 110% for other species. The target compounds in the field blank samples were lower than 4% of those in the ambient samples. Data presented here were corrected for both field blanks and recoveries.

The analysis method of biogenic precursors has been reported elsewhere (Li et al., 2013). Briefly, one fourth of the filter was cut and extracted with a mixture of dichloromethane and methanol (2:1, *v/v*) under ultrasonication. The extracts were concentrated using a rotary evaporator under vacuum conditions and then dried using pure nitrogen. After reaction with a mixture of N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine (5:1, *v/v*) at 70°C for 3 hr. Biogenic secondary organic aerosol (BSOA) tracers in the derivatized samples were determined by GC-MS. These data were used in this study to explore the biogenic sources of dicarboxylic acids and related SOA.

2.2.2 Stable carbon isotope composition of dicarboxylic acids and related SOA

The stable carbon isotopic compositions ($\delta^{13}C$) of shorter-chain dicarboxylic acids and related SOA were measured using the method developed by Kawamura and Watanabe (2004). Briefly, the $\delta^{13}C$ values of the derivatized samples above were determined by gas chromatography–isotope ratio mass spectrometry (GC-IR-MS; Thermo Fisher, Delta V Advantage). The $\delta^{13}C$ values were then calculated for free organic acids using an isotopic mass balance equation based on the measured $\delta^{13}C$ values of derivatives and the derivatizing agent (BF_3/n-butanol) (Kawamura and Watanabe, 2004). To ensure the analytical error of the $\delta^{13}C$ values less than 0.2 ‰, each sample was measured three times. The $\delta^{13}C$ data reported here are averaged values of the triplicate measurements.

2.2.3 Elemental carbon (EC), organic carbon (OC), inorganic ions, water-soluble organic carbon (WSOC), aerosol liquid water content (LWC), and in-situ particle pH (pH_{IS}).

Briefly, EC and OC in the $PM_{2.5}$ samples were determined by using DRI Model 2001 Carbon Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 2004). As for the measurement of inorganic ions and WSOC, an aliquot of the sample filters was extracted with 30 mL Milli-Q water using an ultrasonic bath for three times each for 15min, and filtered through PTFE filters to remove insoluble particles and filter debris. The water extract was then separated into two parts. One part was analyzed for inorganic ions using an ion chromatography (Dionex 600, Dionex, USA), and the other part of the water extract was used to determine WSOC using a Total

Carbon Analyzer (TOC-L CPH, Shimadzu, Japan). As for the calculation of aerosol liquid water content (LWC) and in-situ particle pH (pH_{IS}), the Aerosol Inorganic Model (AIM) using a SO_4^{2-}-NO_3^-- NH_4^+-H^+ system (AIM-II) were employed (Li et al., 2013).

3 Results and discussion

3.1 General description of chemical components in Mt. Tai

The concentrations of dicarboxylic acids and related SOA, EC, OC, WSOC and inorganic ions in $PM_{2.5}$ samples from Mt. Tai are summarized in Table 1. During the campaign the height of boundary layer at Mt. Tai was frequently reduced to ~600 m at night, which kept the sampling site in the free troposphere at night. In contrast, the boundary layer extended far above the mountaintop during the daytime (Zhu et al., 2018). However, as a tracer of combustion source, EC concentration is very low and shows a similar level in the day and night periods, suggesting that the impact of anthropogenic emissions from the lowland region on the mountaintop atmosphere is insignificant. As seen in Table 1 and Table 2, the day and night data presented a large variability. To verify if the day and night aerosol chemistry is of significant difference, a Student's t-test was performed for the day and night samples. As shown in the Table S1, the concentrations and compositions of major species in $PM_{2.5}$ between day and night show a P value less than 0.005, which clearly demonstrates that the abundances and compositions of the major species during the day and night are statistically different.

OC and WSOC in the $PM_{2.5}$ samples in daytime are similar to those in nighttime (Table 1), but OC/EC and WSOC/OC ratios are around 1.4 times higher in daytime than in nighttime (Fig. 4), indicating an enhanced SOA production due to the stronger photochemical oxidation in daytime rather than the changes in the planetary boundary layer heights (Hegde and Kawamura, 2012).

SO_4^{2-} is mainly produced from aqueous phase oxidation of SO_2, which is favored by higher temperature and humid conditions (Kundu et al., 2010b, Zhang et al., 2015;

Wang et al., 2018). Thus, the concentration and relative abundance of SO_4^{2-} are higher in daytime than in nighttime (Table 1 and Fig. S1). On the contrary, the concentrations of NO_3^- and NH_4^+ present higher values in nighttime compared to those in daytime (Table 1). Particulate NO_3^- is mainly formed via gas phase oxidation of NO_2 with OH radical and subsequent partitioning into aerosol phase with ammonia to form NH_4NO_3 (Pathak et al., 2009; Zhang et al., 2015). NH_4NO_3 is volatile and thus lower temperature at night is favorable for NH_4NO_3 enriching in aerosol phase (Bian et al., 2014), resulting in NH_4NO_3 more abundant at night during the Mt. Tai observation period. As shown in Table 1, the remaining four kinds of cations (K^+, Na^+, Ca^{2+} and Mg^{2+}), which can be regarded as the key markers of primary sources, did not exhibit significant diurnal variations, again suggesting that the effect of planetary boundary layer heights is minor. In this work, LWC and pH_{IS} were calculated by using AIM-II model, because both species cannot be directly measured. LWC exhibits higher concentration (94± 100μg m^{-3}) in daytime than that (75 ± 69μg m^{-3}) in nighttime (Table 1). 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 (21.7±11.5 μg m^{-3}, Table 1) of SO_4^{2-}, NO_3^- and NH_4^+ during the daytime was almost equivalent to that (20.4±8.2 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. In contrast, pH_{IS} shows lower value (-0.04 ± 0.5) in daytime compared to that (0.4 ± 0.6) in nighttime (Table 1), indicating the daytime aerosols are more acidic.

3.2 Molecular distributions of dicarboxylic acids and related SOA

A homologous series of dicarboxylic acids (C_2–C_{11}), ketocarboxylic acids (ωC_2–ωC_9 and pyruvic acid), and α-dicarbonyls (glyoxal and methylglyoxal) in $PM_{2.5}$ samples of Mt. Tai were determined (Table 2). The molecular compositions of these compounds are illustrated in Fig. 2.

Total dicarboxylic acids are 430 ± 282ng m^{-3} (27–944 ng m^{-3}, Table 2) in daytime, around two times higher than those in nighttime (282 ± 161 ng m^{-3}, 73–671ng m^{-3}). The average concentration levels (354 ± 239 ng m^{-3}) are lower than those in Asian lowland (e.g. 14 Chinese cities (892 ± 457 ng m^{-3}) (Ho et al., 2007), Chennai in India (502.9 ± 117.9 ng m^{-3}) (Pavuluri et al., 2010)), the elevated regions (e.g. Mt. Hua in central China (744 ± 340 ng m^{-3}) (Meng et al., 2014) and the central Himalayan in Nainital, India (430 ng m^{-3}) (Hegde and Kawamura, 2012)), but higher than those in the continental background areas such as Qinghai Lake in Tibetan Plateau (231 ± 119 ng m^{-3}) (Meng et al., 2013) and marine regions such as North Pacific (68 ng m^{-3}) (Hoque et al., 2017) and the western North Pacific (99.2 ± 86.4 ng m^{-3}) (Boreddy et al., 2017).

Interestingly, we found that the levels of dicarboxylic acids are equivalent to those at Mt. Fuji in Japan in day and night (day: 424 ng m^{-3}; night: 266 ng m^{-3}) (Mochizuki et al., 2017), which are dominantly derived from the oxidation of biogenic VOCs such as isoprene and α-pinene in summer(Mochizuki et al., 2017). Both mountains are located at the similar latitude in East Asia, and the altitudes of the sampling sites at Mt. Tai and Mt. Fuji are almost the same. In addition, both Mt. Tai and Mt. Fuji are dominated by broad-leaved forest. Thus, one may expect that the emissions of biogenic VOCs at both sites during the same season are similar. Moreover, O_3 level during the observation period in Mt. Tai is also similar to that at Mt. Fuji, Japan ranging from a few ppb at night to about 60 ppb (Mochizuki et al., 2017) at the noontime, which means that photochemical activity at both sites during the campaigns are similar. Therefore, concentrations of dicarboxylic acids are comparable at both sites with a similar diurnal pattern.

At the Mt. Tai site, the concentrations of dicarboxylic acids in daytime were about two times higher than in nighttime, which can be ascribed to the stronger photochemical production of dicarboxylic acids and/or higher emissions of the precursors in daytime. As shown in Fig. 2, oxalic acid (C_2) is the dominant species in

Mt. Tai, followed by malonic acid (C_3), succinic acid (C_4), and azelaic acid (C_9) during the day and night, respectively. These four species account for 60, 12, 7.2, and 6.9% of the total dicarboxylic acids in the daytime and 53, 11, 8.5, and 7.6 % of the total in the nighttime, respectively. The molecular compositions in Mt. Tai is similar to that in other remote areas such as Mt. Fuji, Japan, Mt. Hua and Qinghai Lake, China in the summer (Meng et al., 2013, 2014; Mochizuki et al., 2017), but different from that in Asian urban regions where phthalic and/or tere-phthalic acids are more abundant than C_9 because of higher emissions of anthropogenic precursors (e.g., aromatics and plasticizers) (Cheng et al., 2015; He et al., 2014; Jung et al., 2010; Wang et al., 2002, 2017).

Ketocarboxylic acids in the atmosphere are the major intermediates of aqueous phase photochemical oxidation producing dicarboxylic acids (Kawamura and Ikushima, 1993; Pavuluri and Kawamura, 2016). The concentrations of ketocarboxylic acids are 43 ± 28 ng m^{-3} in the daytime and 37 ± 19 ng m^{-3} in the nighttime, respectively, with glyoxylic acid (ωC_2) being the dominant ω-oxoacid, followed by pyruvic acid (Pyr) and 3-oxobutanoic acid (ωC_3) (Table 2 and Fig. 2). Previous studies have proposed that ωC_2 can be initially formed from photochemical oxidation of glyoxal with OH radical and other oxidants in aqueous phase and then further oxidized into oxalic acid (Wang et al., 2012; Rapf et al., 2017). In contrast to the diurnal variations of dicarboxylic and ketocarboxylic acids, the concentrations of α-dicarbonyls exhibit higher concentrations in nighttime than in daytime (Fig. 2). Because α-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 (Carlton et al., 2006, 2007). The higher concentrations of α-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. Since α-dicarbonyls are the major precursors of oxalic acid (Fu et al., 2008; Wang et al., 2012; Warneck, 2003), the opposite pattern suggests that the aerosol aqueous phase oxidation in daytime is more significant in comparison with that in nighttime. The concentrations of glyoxal (Gly) are less than methylglyoxal (mGly), largely because of the stronger biogenic sources and the lower oxidation rate of mGly with OH radical in aerosol phase compared to Gly (Cheng et al., 2013; Meng et al., 2013) (see discussions in section 3.3).

Temporal variations in concentrations of total dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls are summarized in Fig. 3, along with the meteorological parameters. During the whole sampling periods, the concentrations of total dicarboxylic acids and related SOA fluctuated significantly with a maximum (1060 ng m^{-3}) on August 4 and a minimum (33 ng m^{-3}) on August 7. Our results showed that the levels of water-soluble organic compounds decrease by 30-80% when it was rainy, suggesting that dicarboxylic acids and related SOA can be removed efficiently by wet deposition, because these water-soluble compounds are not only easily washed out but also can be efficiently removed by serving as cloud condensation nuclei (CCN) during the wet deposition (Leaitch et al., 1996). Moreover, a reduced secondary formation due to weaker solar radiation and a reduced biogenic emission during the rainy days are also responsible for the lowest concentrations of dicarboxylic acid and related SOA.

3.3 Biogenic versus anthropogenic and local versus long-range transport sources

Previous studies have proposed that the hydroxylation of C_4 can be further oxidized into C_2 and C_3, and C_3 can also be oxidized into C_2 through intermediate compounds such as hydroxymalonic acid or ketomalonic acid (Hoque et al., 2017; Kawamura and Usukura, 1993; Kunwar et al., 2017). Therefore, both ratios of C_2/C_4 and C_3/C_4 can be regarded as indicators of photochemical aging of organic aerosols. The C_2/C_4 and C_3/C_4 ratios in the mountainous atmosphere are 8.0 ± 2.7 and 1.6 ± 0.6, respectively, higher than those in aerosols freshly emitted from sources such as vehicle exhausts (C_2/C_4: 4.1; C_3/C_4: 0.35) (Kawamura and Kaplan, 1987) and biomass burning plumes (C_2/C_4: 5.0; C_3/C_4: 0.7) (Kundu et al., 2010b), but lower than photochemically aged aerosols in remote regions such as a continental background site in Tibet Plateau (C_2/C_4: 11±7.2; C_3/C_4: 2.2±1.3) (Meng et al., 2013) and the North and South Pacific (C_2/C_4: 8.7; C_3/C_4: 3.0) (Hoque et al., 2017). Compared with those in the nighttime, the higher ratios of C_2/C_4 and C_3/C_4 (Fig. 4) in the daytime again indicated that the photochemical modification of aerosols is stronger. Decomposition of C_4 and/or C_3 into C_2 is one of the major formation pathways of oxalic acid, which is favored by temperature (Kawamura and Ikushima, 1993). A few studies have reported that when local sources are dominant over long-range transport, both ratios of C_2/C_4 and C_3/C_4 correlate strongly with the ambient temperatures (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 C_2/C_4 and temperature can only be observed when SOA is largely derived from local precursor oxidation rather than from long-range transport. In the current work, the ratios of C_2/C_4 ($R^2>0.5$) (Fig. 5a) and C_3/C_4 ($R^2\geq0.5$) (Fig. 5b) correlated well with the ambient temperatures in both the daytime and the nighttime, clearly suggesting that dicarboxylic acids and related SOA at Mt. Tai during the campaign are mostly derived from the local oxidation of BVOCs rather than long-range transport. Aggarwal et al., (2008) found that diacid-C/OC and C_2/total diacids should increase in daytime when local emission and photooxidation are more significant than long-range transport. In the summit of Mt. Tai, the daytime ratios of diacid-C/OC and C_2/total diacids are 5.5 ± 2.6% and 60 ± 7.7%, which are about 1.2 and 1.3 times higher than those in the nighttime, respectively (Fig. 4), further indicating the stronger photochemical oxidation in daytime and the dominance of local sources for the SOA production in the atmosphere of Mt. Tai.

Both ratios of C_9/C_6 and C_9/Ph can be used as indicators to qualitatively evaluate the source strength of anthropogenic versus biogenic precursors for producing dicarboxylic acids and related SOA (Jung et al., 2010), because C_6 and Ph are largely produced by the oxidation of anthropogenic cyclohexene (Hatakeyama et al., 1987) and aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993), respectively. In contrast, C_9 is mainly produced by the oxidation of biogenic unsaturated oleic acid, which contains a double bond at the C-9 position (Wang et al., 2010). Therefore, both ratios of C_9/C_6 and C_9/Ph are indicative of the source strengths of biogenic versus anthropogenic emissions. As shown in Fig. 4, both ratios of C_9/C_6 and C_9/Ph are similar in the daytime to those in the nighttime. However, the average values of C_9/C_6 (14±9.0) and C_9/Ph (7.2±2.2) at the mountaintop of Mt. Tai are higher than those in urban regions such as Xi'an, China (C_9/C_6: 3.1; C_9/Ph: 5.6) (Cheng et al., 2013) and also higher than those in other mountainous during summer such as Mt. Himalayan, India (C_9/C_6: 2.1; C_9/Ph: 0.2) (Hedge and Kawamura, 2012) and Mt. Fuji, Japan (C_9/C_6: 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 the concentration ratio of particulate Gly/mGly is about 1:5 when biogenic sources are predominant and is about 1:1 when anthropogenic sources are predominant such as in urban areas. As shown in Table 3, the ratios of Gly/mGly in the Mt. Tai atmosphere are 1:5.1 in daytime and 1:4.8 in nighttime, further suggesting that Gly and mGly in the Mt. Tai samples are mostly derived from biogenic sources. This result is also in agreement with the high abundance of C_9 relative to the total dicarboxylic acids (7.2%), which is about two times higher than that (3.5%) in 14 Chinese megacities (Ho et al., 2007). Moreover, a trace amount of elemental carbon (EC) was found for most of the samples (Table 1), suggesting that the impact of pollutants derived from anthropogenic sources on the mountaintop atmosphere during the campaign are negligible. Consequently, it can be concluded that the summertime SOA of Mt. Tai are mainly derived from local photochemical oxidation of biogenic precursors rather than long-range transport of anthropogenic precursors during the sampling period.

3.4 Production of dicarboxylic acids and related SOA from biogenic sources

A three-dimensional modeling study has proposed that 79% of oxalic acid is originated from the photochemical oxidation of isoprene and other biogenic hydrocarbons in cloud (Myriokefalitakis et al., 2011). Laboratory experiments and model simulations have demonstrated that the photooxidation of isoprene (Carlton et al., 2006, 2007; Huang et al., 2011) and monoterpenes (Fick et al., 2003; Lee et al., 2006) can produce Gly and mGly via reactions with OH radical and/or O_3 in the aerosol aqueous phase or the gas phase and subsequently partition into cloud droplets, where both carbonyls are oxidized further by OH radical to form oxalic acid (Lim et al., 2005; Tan et al., 2010).

In order to further ascertain the contribution of BVOCs to dicarboxylic acids and related SOA during the high biological activity period in Mt. Tai, SOA tracers derived from isoprene-, *α*-/*β*-pinene- and *β*-caryophyllene in the $PM_{2.5}$ samples collected at the Mt. Tai site were determined. Their total concentrations (the sum of isoprene+ *α*-/*β*-pinene+ *β*-caryophyllene derived SOA tracers) are 1.3 times higher in the daytime (106 ± 56 ng m^{-3}) than those in the nighttime (79 ± 38 ng m^{-3}) (unpublished data), which is consistent with the diurnal variation patterns of dicarboxylic acids, ketocarboxylic acids and WSOC (Tables 1 and 2). Previous studies reported that 2-methylglyceric acid, which is an isoprene oxidation product, and 3-hydroxyglutaric acid, which is *α*-/*β*-pinene oxidation product, can serve as organic precursors for the production of dicarboxylic acids and ketocarboxylic acids (Fu et al., 2013). As shown in Table 4, major dicarboxylic acids and related SOA (e.g. C_2, ωC_2, Gly and mGly) correlated positively with the isoprene, *α*-/*β*-pinene and *β*-caryophyllene oxidation products during the day and night ($R>0.55$, $P<0.01$) (Table 4), respectively, indicating that BVOCs oxidation products can serve as precursors for the production of oxalic acid via α-dicaronyls oxidation (Myriokefalitakis et al., 2011). These strong correlations further highlight the important contribution of BSOA to dicarboxylic acids and related SOA in Mt. Tai in summer season.

3.5 Effects of temperature, relative humidity, and O_3 concentrations on the formation of oxalic acid and related SOA

Because oxidants such as OH radicals were not measured in Mt. Tai, O_3 is considered here as an indicator of the total oxidant concentrations in this study. A significant linear correlation of oxalic acid with O_3 concentrations was observed for the daytime samples (R^2=0.91), but no correlation (R^2=0.05) was found for the nighttime samples (Fig.6a). Such a phenomenon was also observed in Mt. Fuji, Japan (Mochizuki et al., 2017) and Beijing, China (He et al., 2014). Additionally, C_2/ Gly, C_2/mGly and C_2/total diacids ratios correlate positively with O_3 concentrations in the daytime, but such correlations were not found in the nighttime (Fig 8(a-c)). Mochizuki et al. (2017) have reported a robust correlation between concentration ratios of oxalic acid to isoprene plus α-pinene (oxalic acid/(isoprene+α-pinene)) and O_3 concentrations in a large forest region of Mt. Fuji, Japan in the daytime. In the current work, BSOA tracers correlate strongly with O_3 concentrations in the daytime (R>0.6, P<0.01), but no correlation was found at night (Table 4). These results suggest that the daytime oxalic acid and related SOA in the mountaintop of Mt. Tai are largely derived from O_3 and OH radical oxidation of BVOCs such as isoprene and α-pinene, while the nighttime oxalic acid and related SOA might be mostly produced by NO_3 radical and other oxidizing agents such as H_2O_2 (Claeys et al., 2004; Herrmann et al., 1999). In addition, the titration of O_3 by the residual NO in the nighttime atmosphere could also be responsible for the lack of the correlation between BSOA tracers and O_3 (Edwards et al., 2017).

As shown in Table 4, nearly all of the detected BSOA tracers including 2-methylglyceric acid, 3-hydorxyglutaric acid and β-caryophyllinic acid exhibit a strong correlation with the ambient temperature, largely due to the increased production of BSOA from enhanced emissions of BVOCs under the higher temperature conditions. The BSOA tracer concentrations are higher in daytime than in nighttime. As seen in Table 1, O_3 concentration during the sampling period is 50%

higher in daytime than in nighttime, clearly indicating that oxidation potential in daytime at the Mt. Tai site is stronger. Moreover, isoprene is only emitted by trees during daytime. Thus, we think the higher loadings of BSOA tracers in daytime are caused not only by stronger photochemical oxidation but also by enhanced emissions of BVOCs. In addition, oxalic acid and C_2/total diacids ratios correlated strongly with temperatures (Fig. 6b and Fig. 8f), because higher temperature conditions can promote photochemical formation of oxalic acid. Such a temperature dependence is also observed in other regions such as Mt. Hua (Meng et al., 2014) and Beijing (Wang et al., 2017) in China.

Online measurements, field observations and chamber studies (Cheng et al., 2017; Gao et al., 2004; McNeill, 2015; Meng et al., 2014; Wang et al., 2012, 2017) have suggested that oxalic acid is primarily derived from the acid-catalyzed heterogeneous oxidation of glyoxal and related precursors in the aqueous phase. Here we investigate the impact of LWC and pH_{IS} on the formation of oxalic acid in Mt. Tai aerosols. Because the sampling site is far from agricultural sources, most of the sulfate is assumed to be acidic. As shown in Fig.6c, a strong linear correlation between C_2 and SO_4^{2-} was found for the daytime (R^2=0.89) and nighttime (R^2=0.76) samples, respectively, which is consistent with the measurements observed in other mountainous region (Meng et al., 2014) and Chinese cities (Wang et al., 2012, 2017; Yu et al., 2005), indicating that oxalic acid and sulfate are formed via a similar formation pathway such as in-cloud or aqueous-phase (Warneck, 2003). In this study, oxalic acid does not exhibit correlations with relative humidity (RH) and LWC (Fig. 6d and 6e), but presents a significant negative correlation with pH_{IS} (R^2>0.60) (Fig. 6f), largely due to the fact that acidic conditions can promote the formation of oxalic acid and their precursors. Therefore, a robust negative correlation was obtained for pH_{IS} and the precursors of oxalic acid such as Gly, mGly and ωC_2 (R^2>0.50). A few studies have pointed out that aerosol acidity are favorable for the formation of biogenic SOA (BSOA) derived from isoprene oxidation such as 2-methylglyceric acid, which can be oxidized into Gly and mGly and then converted to oxalic acid (Meng et al., 2014; Surratt et al., 2007, 2010). Our previous studies have revealed that enhanced RH can reduce particle acidity (pH_{IS}) and is thus unfavorable for oxalic acid formation by acid-catalyzed reactions occurring in the aerosol aqueous phase (Meng et al., 2014). Both RH and aerosol composition are key factors controlling the aerosol LWC (Bikkina et al., 2017). Deshmukh et al. (2017) and Bikkina et al. (2017) also found that RH and LWC correlated well with oxalic acid, indicating that humid conditions are favorable for the aqueous phase formation of C_2. Nevertheless, Zhang et al. (2011) pointed out that low RH conditions can promote SOA yields via the oxidation of isoprene. Higher RH and LWC can promote the partitioning of water-soluble semi-volatile organic precursors of oxalic acid (e.g., Gly and mGly) into the aerosol aqueous phase but can also suppress acid-catalyzed formation of oxalic acid because of lower aerosol acidity due to dilution. Therefore, C_2 does not present any correlations with RH or LWC in Mt. Tai.

3.6 Stable carbon isotopic composition of oxalic acid and related SOA

To further understand the formation mechanism of C_2 and related SOA, the stable isotopic composition of major dicarboxylic acids and related SOA in the Mt. Tai aerosols were investigated (Table 5). Generally, an increase in $\delta^{13}C$ values was observed with a decrease in carbon numbers of dicarboxylic acids. The averaged $\delta^{13}C$ value (daytime: −15.8±1.9‰; nighttime: −17.2±1.7‰) of C_2 is higher than other dicarboxylic acid and related SOA in the Mt. Tai atmosphere, and also higher than those observed in urban regions such as Xi'an, China (−22.7‰ to −22.0‰) (Wang et al., 2012) and Sapporo, Japan (18.8±2.0‰) (Aggarwal and Kawamura, 2008) and rural regions such as Morogoro, Tanzania (18.3±1.7‰) (Mkoma et al., 2014), but lower than those (11.5±2.8‰) (Zhang et al., 2016) at a background site (the Korea Climate Observatory at Gosan) in East Asia during the summer. Pavuluri et al. (2016) have reported that the average $\delta^{13}C$ values of C_2 from biogenic aerosols are higher than those from anthropogenic aerosols. The relatively higher $\delta^{13}C$ values of C_2

observed in Mt. Tai further demonstrate that the contribution of biogenic sources to C_2 and related SOA is more significant than anthropogenic sources, which is consistent with our discussions above. The average δ^{13}C values of C_4 are more negative than C_2 and C_3 (Fig. 7). Such a phenomenon is also observed in other regions (Aggarwal and Kawamura, 2008; Wang et al., 2012; Zhang et al., 2016). Photochemical decomposition (or breakdown) of longer-chain diacarboxylic acids (e.g. C_3 or C_4) in aerosol aqueous phase can form C_2 (Wang et al., 2017), during which C_3 or C_4 release CO_2/CO by reaction with OH radical and other oxidants, resulting in C_2 more enriched in ^{13}C due to kinetic isotope effects (KIE) (Wang et al., 2012). The ^{13}C enrichment in C_2 is more distinguished in daytime than in nighttime (Table 5 and Fig. 7), largely due to the enhanced photochemical oxidation. However, such diurnal variation was not found for C_3 and C_4.

ωC_2 is an important intermediate of aqueous phase photochemical oxidation of precursors such as Gly, mGly, and Pyr during the C_2 formation process (Carlton et al., 2006; Fu et al., 2008). Thus, the higher mass ratios of $C_2/\omega C_2$, C_2/Gly and C_2/mGly indicate that organic aerosols are more aged (Wang et al., 2017). As shown in Fig. 8(g-i), δ^{13}C values of C_2 correlate robustly with C_2/Gly, C_2/mGly, and C_2/total diacids, suggesting an enrichment of ^{13}C during the organic aerosol ageing process. During the campaign, ωC_2 is less enriched in ^{13}C in comparison with Gly, mGly, and Pyr, because lighter isotope (^{12}C) is preferentially enriched in the products due to KIEs during the aqueous phase irreversible chemical reactions (Wang et al., 2012). As one of the major precursors of Gly, isoprene emitted directly from vegetation is depleted in ^{13}C with a range from –32‰ to –27‰ (Affek and Yakir, 2003), but during the transport process isoprene could gradually be enriched with ^{13}C (δ^{13}C value=–16.8‰) due to isotope fractionation associated with the reaction with OH radical (Rudolph et al., 2003). Moreover, chamber experiments have pointed out that *β*-pinene is preferably enriched with ^{13}C during its ozonolysis due to KIE (Fisseha et al., 2009). Therefore, the δ^{13}C values of Gly and mGly are relatively higher than fresh BVOCs such as isoprene, largely attributed to the secondary formation from the oxidation of isoprene and other biogenic precursors.

4. Summary and conclusions

$PM_{2.5}$ aerosols from the summit of Mt. Tai (15340 m a.s.l) in the North China Plain during the summer of 2016 were analyzed for dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls, EC, OC and WSOC. Molecular compositions of dicarboxylic acids and related compounds in the forested highland are similar to those on the ground and other mountainous regions. The concentrations of total dicarboxylic acids and ketocarboxylic acids are higher in daytime than those in daytime, but α-dicarbonyls presents lower values in daytime, suggesting the mountainous atmospheric environment is more photochemically aged in daytime than in nighttime. The concentrations of oxalic acid and BSOA traces and the mass ratios of C_2/Gly, C_2/mGly, and C_2/total diacids correlate positively with O_3 concentrations in the daytime during the campaign, but such correlations were not found at night. Moreover, C_2, C_2/total diacids ratios and BSOA tracers correlate strongly with temperatures, because higher temperature conditions can enhance the emissions of BVOCs and further promote the photochemical formation of C_2. C_2 has a robust correlation with pH_{IS} and SO_4^{2-} during the whole sampling period, indicating that acidic conditions can favor the formation of oxalic acid in aqueous phase.

A significant enrichment of ^{13}C in dicarboxylic aicds was observed as a function of their carbon number. The observed larger $\delta^{13}C$ values of lower carbon numbered dicarboxylic acids can be explained by isotopic fractionations resulting from the atmospheric decomposition of relatively longer chain-diacids or their precursors. Increased $\delta^{13}C$ values of C_2 relative to C_2/Gly and C_2/mGly ratios also suggested an important effect of photochemical aging on the stable carbon isotopic composition of dicarboxylic acids.

Acknowledgements

This work was supported by China National Science Funds (Grant No. 41505112 and 41773117), Natural Science Foundation of Shandong Province (Grant No.

BS2015HZ002), the China National Natural Science Funds for Distinguished Young Scholars (No.41325014) and Open Funds of State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences (Grant Nos. SKLLQG1509 and SKLLQG1504).

References

Affek, H. P., and Yakir, D.: Natural Abundance Carbon Isotope Composition of Isoprene Reflects Incomplete Coupling between Isoprene Synthesis and Photosynthetic Carbon Flow, Plant Physiology, 131, 1727, 2003.

Aggarwal, S. G., and Kawamura, K.: Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport, J. Geophys. Res., 113, D14301, 10.1029/2007jd009365, 2008.

Bian, Q., Huang, X. H. H., and Yu, J. Z.: One-year observations of size distribution characteristics of major aerosol constituents at a coastal receptor site in Hong Kong – Part 1: Inorganic ions and oxalate, Atmos. Chem. Phys., 14, 9013-9027, 10.5194/acp-14-9013-2014, 2014.

Bikkina, S., Kawamura, K., and Sarin, M.: Secondary Organic Aerosol Formation over Coastal Ocean: Inferences from Atmospheric Water-Soluble Low Molecular Weight Organic Compounds, Environmental Science & Technology, 51, 4347-4357, 10.1021/acs.est.6b05986, 2017.

Bilde, M., Barsanti, K., Booth, M., Cappa, C. D., Donahue, N. M., Emanuelsson, E. U., McFiggans, G., Krieger, U. K., Marcolli, C., Topping, D., Ziemann, P., Barley, M., Clegg, S., Dennis-Smither, B., Hallquist, M., Hallquist, Å. M., Khlystov, A., Kulmala, M., Mogensen, D., Percival, C. J., Pope, F., Reid, J. P., Ribeiro da Silva, M. A. V., Rosenoern, T., Salo, K., Soonsin, V. P., Yli-Juuti, T., Prisle, N. L., Pagels, J., Rarey, J., Zardini, A. A., and Riipinen, I.: Saturation Vapor Pressures and Transition Enthalpies of Low-Volatility Organic Molecules of Atmospheric Relevance: From Dicarboxylic Acids to Complex Mixtures, Chemical Reviews, 115, 4115-4156, 10.1021/cr5005502, 2015.

Boreddy, S. K. R., Kawamura, K., and Tachibana, E.: Long-term (2001–2013) observations of water-soluble dicarboxylic acids and related compounds over the western North Pacific: trends, seasonality and source apportionment, Scientific Reports, 7, 8518, 10.1038/s41598-017-08745-w, 2017.

Carlton, A. G., Turpin, B. J., Lim, H.-J., Altieri, K. E., and Seitzinger, S.: Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, Geophysical Research Letters, 33, L06822, 10.1029/2005gl025374, 2006.

Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H.-J., and Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmospheric Environment, 41, 7588-7602, http://dx.doi.org/10.1016/j.atmosenv.2007.05.035, 2007.

Cheng, C., Wang, G., Zhou, B., Meng, J., Li, J., Cao, J., and Xiao, S.: Comparison of dicarboxylic acids and related compounds in aerosol samples collected in Xi'an, China during haze and clean periods, Atmospheric Environment, 81, 443-449, http://dx.doi.org/10.1016/j.atmosenv.2013.09.013, 2013.

Cheng, C., Wang, G., Meng, J., Wang, Q., Cao, J., Li, J., and Wang, J.: Size-resolved airborne particulate oxalic and related secondary organic aerosol species in the urban atmosphere of Chengdu, China, Atmospheric Research, 161–162, 134-142, http://dx.doi.org/10.1016/j.atmosres.2015.04.010, 2015.

Cheng, C., Li, M., Chan, C. K., Tong, H., Chen, C., Chen, D., Wu, D., Li, L., Wu, C., Cheng, P., Gao, W., Huang, Z., Li, X., Zhang, Z., Fu, Z., Bi, Y., and Zhou, Z.: Mixing state of oxalic acid containing particles in the rural area of Pearl River Delta, China: implications for the formation mechanism of oxalic acid, Atmos. Chem. Phys., 17, 9519-9533, 10.5194/acp-17-9519-2017, 2017.

Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmüller, H., and Fung, K.: Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols, Environmental Science & Technology, 38, 4414-4422, 10.1021/es034936u, 2004.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene, Science, 303, 1173-1176, 10.1126/science.1092805, 2004.

Edwards, P. M., Aikin, K. C., Dube, W. P., Fry, J. L., Gilman, J. B., de Gouw, J. A., Graus, M. G., Hanisco, T. F., Holloway, J., Huber, G., Kaiser, J., Keutsch, F. N., Lerner, B. M., Neuman, J. A., Parrish, D. D., Peischl, J., Pollack, I. B., Ravishankara, A. R., Roberts, J. M., Ryerson, T. B., Trainer, M., Veres, P. R., Wolfe, G. M., Warneke, C., and Brown, S. S.: Transition from high- to low-NOx control of night-time oxidation in the southeastern US, Nature Geoscience, 10, 490-496, 2017.

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, Nature, 506, 476, 10.1038/nature13032, 2014.

Ervens, B., Sorooshian, A., Lim, Y. B., and Turpin, B. J.: Key parameters controlling OH-initiated formation of secondary organic aerosol in the aqueous phase (aqSOA), Journal of Geophysical Research: Atmospheres, 119, 3997-4016, 10.1002/2013jd021021, 2014.

Fick, J., Pommer, L., Nilsson, C., and Andersson, B.: Effect of OH radicals, relative humidity, and time on the composition of the products formed in the ozonolysis of α-pinene, Atmospheric Environment, 37, 4087-4096, https://doi.org/10.1016/S1352-2310(03)00522-3, 2003.

Fisseha, R., Spahn, H., Wegener, R., Hohaus, T., Brasse, G., Wissel, H., Tillmann, R., Wahner, A., Koppmann, R., and Kiendler-Scharr, A.: Stable carbon isotope composition of secondary organic aerosol from β-pinene oxidation, Journal of Geophysical Research: Atmospheres, 114, n/a-n/a, 10.1029/2008jd011326, 2009.

Fu, P., Kawamura, K., Kanaya, Y., and Wang, Z.: Contributions of biogenic volatile organic compounds to the formation of secondary organic aerosols over Mt. Tai, Central East China, Atmospheric Environment, 44, 4817-4826, http://dx.doi.org/10.1016/j.atmosenv.2010.08.040, 2010.

Fu, P., Kawamura, K., Usukura, K., and Miura, K.: Dicarboxylic acids, ketocarboxylic acids and glyoxal in the marine aerosols collected during a round-the-world cruise, Marine Chemistry, 148, 22-32, http://dx.doi.org/10.1016/j.marchem.2012.11.002, 2013.

Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J. Geophys. Res., 113, D15303, 10.1029/2007jd009505, 2008.

Gao, S., Ng, N. L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J., Yoo, K. Y., Beauchamp, J. L., Hodyss, R. P., Flagan, R. C., and Seinfeld, J. H.: Particle Phase Acidity and Oligomer Formation in Secondary Organic Aerosol, Environmental Science & Technology, 38, 6582-6589, 10.1021/es049125k, 2004.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmospheric Chemistry and Physics, 9, 5155-5236, 2009.

Hatakeyama, S., Ohno, M., Weng, J., Takagi, H., and Akimoto, H.: Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air, Environmental Science & Technology, 21, 52-57, 10.1021/es00155a005, 1987.

He, N., Kawamura, K., Okuzawa, K., Pochanart, P., Liu, Y., Kanaya, Y., and Wang, Z. F.: Diurnal and temporal variations of water-soluble dicarboxylic acids and related compounds in aerosols from the northern vicinity of Beijing: Implication for photochemical aging during atmospheric transport, Science of The Total Environment, 499, 154-165, http://dx.doi.org/10.1016/j.scitotenv.2014.08.050, 2014.

Hegde, P., and Kawamura, K.: Seasonal variations of water-soluble organic carbon, dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls in Central Himalayan aerosols, Atmos. Chem. Phys., 12, 6645-6665, 10.5194/acp-12-6645-2012, 2012.

Herrmann, H., Ervens, B., Nowacki, P., Wolke, R., and Zellner, R.: A chemical aqueous phase radical mechanism for tropospheric chemistry, Chemosphere, 38, 1223-1232, https://doi.org/10.1016/S0045-6535(98)00520-7, 1999.

Ho, K. F., Lee, S. C., Cao, J. J., Kawamura, K., Watanabe, T., Cheng, Y., and Chow, J. C.: Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong, Atmospheric Environment, 40, 3030-3040, http://dx.doi.org/10.1016/j.atmosenv.2005.11.069, 2006.

Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. G.: Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, Journal of Geophysical Research: Atmospheres, 112, D22S27, 10.1029/2006jd008011, 2007.

Hoque, M. M. M., Kawamura, K., and Uematsu, M.: Spatio-temporal distributions of dicarboxylic acids, ω-oxocarboxylic acids, pyruvic acid, α-dicarbonyls and fatty acids in the marine aerosols from the North and South Pacific, Atmospheric Research, 185, 158-168, http://dx.doi.org/10.1016/j.atmosres.2016.10.022, 2017.

Huang, D., Zhang, X., Chen, Z. M., Zhao, Y., and Shen, X. L.: The kinetics and mechanism of an aqueous phase isoprene reaction with hydroxyl radical, Atmos. Chem. Phys., 11, 7399-7415, 10.5194/acp-11-7399-2011, 2011.

Jung, J., Tsatsral, B., Kim, Y. J., and Kawamura, K.: Organic and inorganic aerosol compositions in Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008: Dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls, Journal of Geophysical Research: Atmospheres, 115, n/a-n/a, 10.1029/2010jd014339, 2010a.

Kawamura, K., and Kaplan, I. R.: Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, Environmental Science & Technology, 21, 105-110, 10.1021/es00155a014, 1987.

Kawamura, K., and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, Environmental Science & Technology, 27, 2227-2235, 10.1021/es00047a033, 1993.

Kawamura, K., and Usukura, K.: Distributions of low molecular weight dicarboxylic acids in the North Pacific aerosol samples, Journal of Oceanography, 49, 271-283, 10.1007/bf02269565, 1993.

Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, Atmospheric Environment, 30, 1709-1722, http://dx.doi.org/10.1016/1352-2310(95)00395-9, 1996.

Kawamura, K., and Watanabe, T.: Determination of Stable Carbon Isotopic Compositions of Low Molecular Weight Dicarboxylic Acids and Ketocarboxylic Acids in Atmospheric Aerosol and Snow Samples, Analytical Chemistry, 76, 5762-5768, 10.1021/ac049491m, 2004.

Kawamura, K., Okuzawa, K., Aggarwal, S. G., Irie, H., Kanaya, Y., and Wang, Z.: Determination of gaseous and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai, Atmos. Chem. Phys., 13, 5369-5380, 10.5194/acp-13-5369-2013, 2013a.

Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S. G., Kanaya, Y., and Wang, Z. F.: High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the mountain aerosols over the North China Plain during wheat burning season, Atmos. Chem. Phys. , 13, 3695-3734, 10.5194/acpd-13-3695-2013, 2013b.

Kawamura, K., and Bikkina, S.: A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation, Atmospheric Research, 170, 140-160, http://dx.doi.org/10.1016/j.atmosres.2015.11.018, 2016.

Kroll, J. H., and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, Atmospheric Environment, 42, 3593-3624, https://doi.org/10.1016/j.atmosenv.2008.01.003, 2008.

Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers, Atmos. Chem. Phys., 10, 2209-2225, 10.5194/acp-10-2209-2010, 2010a.

Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Diurnal variation in the water-soluble inorganic ions, organic carbon and isotopic compositions of total carbon and nitrogen in biomass burning aerosols from the LBA-SMOCC campaign in Rondônia, Brazil, Journal of Aerosol Science, 41, 118-133, http://dx.doi.org/10.1016/j.jaerosci.2009.08.006, 2010b.

Kunwar, B., Torii, K., and Kawamura, K.: Springtime influences of Asian outflow and photochemistry on the distributions of diacids, oxoacids and α-dicarbonyls in the aerosols from the western North Pacific Rim, Tellus B: Chemical and Physical Meteorology, 69, 1369341, 10.1080/16000889.2017.1369341, 2017.

Leaitch, W. R., Li, S. M., Liu, P. S. K., Banic, C. M., Macdonald, A. M., Isaac, G. A., Couture, M. D., and Strapp, J. W.: Relationships among ccn, aerosol size distribution and ion chemistry from airborne measurements over the bay of fundy in august-september, 1995 A2 - Kulmala, Markku, in: Nucleation and Atmospheric Aerosols 1996, edited by: Wagner, P. E., Pergamon, Amsterdam, 840-843, 1996.

Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, Journal of Geophysical Research: Atmospheres, 111, n/a-n/a, 10.1029/2006jd007050, 2006.

Li, J. J., Wang, G. H., Cao, J. J., Wang, X. M., and Zhang, R. J.: Observation of biogenic secondary organic aerosols in the atmosphere of a mountain site in central China: temperature and relative humidity effects, Atmos. Chem. Phys., 13, 11535-11549, 10.5194/acp-13-11535-2013, 2013.

Lim, H.-J., Carlton, A. G., and Turpin, B. J.: Isoprene Forms Secondary Organic Aerosol through Cloud Processing: Model Simulations, Environmental Science & Technology, 39, 4441-4446, 10.1021/es048039h, 2005.

McNeill, V. F.: Aqueous Organic Chemistry in the Atmosphere: Sources and Chemical Processing of Organic Aerosols, Environmental Science & Technology, 49, 1237-1244, 10.1021/es5043707, 2015.

Meng, J., Wang, G., Li, J., Cheng, C., and Cao, J.: Atmospheric oxalic acid and related secondary organic aerosols in Qinghai Lake, a continental background site in Tibet Plateau, Atmospheric Environment, 79, 582-589, http://dx.doi.org/10.1016/j.atmosenv.2013.07.024, 2013.

Meng, J., Wang, G., Li, J., Cheng, C., Ren, Y., Huang, Y., Cheng, Y., Cao, J., and Zhang, T.: Seasonal characteristics of oxalic acid and related SOA in the free troposphere of Mt. Hua, central China: Implications for sources and formation mechanisms, Science of The Total Environment, 493, 1088-1097, http://dx.doi.org/10.1016/j.scitotenv.2014.04.086, 2014.

Miyazaki, Y., Aggarwal, S. G., Singh, K., Gupta, P. K., and Kawamura, K.: Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and formation processes, Journal of Geophysical Research: Atmospheres, 114, D19206, 10.1029/2009jd011790, 2009.

Mkoma, S. L., Kawamura, K., and Tachibana, E.: Stable carbon isotopic compositions of low-molecular-weight dicarboxylic acids, glyoxylic acid and glyoxal in tropical aerosols: implications for photochemical processes of organic aerosols, Tellus B: Chemical and Physical Meteorology, 66, 23702, 10.3402/tellusb.v66.23702, 2014.

Mochizuki, T., Kawamura, K., Miyazaki, Y., Wada, R., Takahashi, Y., Saigusa, N., and Tani, A.: Secondary formation of oxalic acid and related organic species from biogenic sources in a larch forest at the northern slope of Mt. Fuji, Atmospheric Environment, 166, 255-262, https://doi.org/10.1016/j.atmosenv.2017.07.028, 2017.

Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, Atmos. Chem. Phys., 11, 5761-5782, 10.5194/acp-11-5761-2011, 2011.

Narukawa, M., Kawamura, K., Takeuchi, N., and Nakajima, T.: Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, Geophysical Research Letters, 26, 3101-3104, 10.1029/1999gl010810, 1999.

Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM2.5 ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere, Atmos. Chem. Phys., 9, 1711-1722, 10.5194/acp-9-1711-2009, 2009.

Pavuluri, C. M., Kawamura, K., and Swaminathan, T.: Water-soluble organic carbon, dicarboxylic acids, ketoacids, and α-dicarbonyls in the tropical Indian aerosols, Journal of Geophysical Research: Atmospheres, 115, D11302, 10.1029/2009jd012661, 2010.

Pavuluri, C. M., and Kawamura, K.: Enrichment of (13)C in diacids and related compounds during photochemical processing of aqueous aerosols: New proxy for organic aerosols aging, Scientific Reports, 6, 36467, 10.1038/srep36467, 2016.

Rapf, R. J., Dooley, M. R., Kappes, K., Perkins, R. J., and Vaida, V.: pH Dependence of the Aqueous Photochemistry of α-Keto Acids, The Journal of Physical Chemistry A, 121, 8368-8379, 10.1021/acs.jpca.7b08192, 2017.

Rudolph, J., Anderson, R. S., Czapiewski, K. V., Czuba, E., Ernst, D., Gillespie, T., Huang, L., Rigby, C., and Thompson, A. E.: The Stable Carbon Isotope Ratio of Biogenic Emissions of Isoprene and the Potential Use of Stable Isotope Ratio Measurements to Study Photochemical Processing of Isoprene in the Atmosphere, Journal of Atmospheric Chemistry, 44, 39-55, 10.1023/a:1022116304550, 2003.

Sorooshian, A., Lu, M.-L., Brechtel, F. J., Jonsson, H., Feingold, G., Flagan, R. C., and Seinfeld, J. H.: On the Source of Organic Acid Aerosol Layers above Clouds, Environmental Science & Technology, 41, 4647-4654, 10.1021/es0630442, 2007a.

Sorooshian, A., Ng, N. L., Chan, A. W. H., Feingold, G., Flagan, R. C., and Seinfeld, J. H.: Particulate organic acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), J. Geophys. Res., 112, D13201, 10.1029/2007jd008537, 2007b.

Tan, Y., Carlton, A. G., Seitzinger, S. P., and Turpin, B. J.: SOA from methylglyoxal in clouds and wet aerosols: Measurement and prediction of key products, Atmospheric Environment, 44, 5218-5226, http://dx.doi.org/10.1016/j.atmosenv.2010.08.045, 2010.

Wang, G., Kawamura, K., Umemoto, N., Xie, M., Hu, S., and Wang, Z.: Water-soluble organic compounds in PM2.5 and size-segregated aerosols over Mount Tai in North China Plain, Journal of Geophysical Research: Atmospheres, 114, D19208, 10.1029/2008jd011390, 2009.

Wang, G., Xie, M., Hu, S., Gao, S., Tachibana, E., and Kawamura, K.: Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation, Atmos. Chem. Phys., 10, 6087-6096, 10.5194/acp-10-6087-2010, 2010.

Wang, G., Kawamura, K., Cheng, C., Li, J., Cao, J., Zhang, R., Zhang, T., Liu, S., and Zhao, Z.: Molecular Distribution and Stable Carbon Isotopic Composition of Dicarboxylic Acids, Ketocarboxylic Acids, and α-Dicarbonyls in Size-Resolved Atmospheric Particles From Xi’an City, China, Environmental Science & Technology, 46, 4783-4791, 10.1021/es204322c, 2012.

Wang, G., Cheng, C., Meng, J., Huang, Y., Li, J., and Ren, Y.: Field observation on secondary organic aerosols during Asian dust storm periods: Formation mechanism of oxalic acid and related compounds on dust surface, Atmospheric Environment, 113, 169-176, http://dx.doi.org/10.1016/j.atmosenv.2015.05.013, 2015.

Wang, G., Zhang, F., Peng, J., Duan, L., Ji, Y., Marrero-Ortiz, W., Wang, J., Li, J., Wu, C., Cao, C., Wang, Y., Zheng, J., Secrest, J., Li, Y., Wang, Y., Li, H., Li, N., and Zhang, R.: Particle acidity and sulfate production during severe haze events in China cannot be reliably inferred by assuming a mixture of inorganic salts, Atmospheric Chemistry and Physics, 18, 10123-10132, 2018.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, Proceedings of the National Academy of Sciences, 113, 13630-13635, 10.1073/pnas.1616540113, 2016.

Wang, J., Wang, G., Gao, J., Wang, H., Ren, Y., Li, J., Zhou, B., Wu, C., Zhang, L., Wang, S., and Chai, F.: Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during, and after the 2014 APEC, Atmos. Chem. Phys., 17, 981-992, 10.5194/acp-17-981-2017, 2017.

Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, Atmospheric Environment, 37, 2423-2427, http://dx.doi.org/10.1016/S1352-2310(03)00136-5, 2003.

Yang, X., Xue, L., Yao, L., Li, Q., Wen, L., Zhu, Y., Chen, T., Wang, X., Yang, L., Wang, T., Lee, S., Chen, J., and Wang, W.: Carbonyl compounds at Mount Tai in the North China Plain: Characteristics, sources, and effects on ozone formation, Atmospheric Research, 196, 53-61, https://doi.org/10.1016/j.atmosres.2017.06.005, 2017.

Yu, J. Z., Huang, X.-F., Xu, J., and Hu, M.: When Aerosol Sulfate Goes Up, So Does Oxalate: Implication for the Formation Mechanisms of Oxalate, Environmental Science & Technology, 39, 128-133, 10.1021/es049559f, 2005.

Zhang, H., Surratt, J. D., Lin, Y. H., Bapat, J., and Kamens, R. M.: Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions, Atmos. Chem. Phys., 11, 6411-6424, 10.5194/acp-11-6411-2011, 2011.

Zhang, R., Wang, G., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., Wang, W., Hu, M., and Wang, Y.: Formation of urban fine particulate matter, Chemical Reviews, 115, 3803-3855,DOI: 3810.1021/acs.chemrev.3805b00067, 2015.

Zhang, Y.-L., Kawamura, K., Cao, F., and Lee, M.: Stable carbon isotopic compositions of low-molecular-weight dicarboxylic acids, oxocarboxylic acids, α-dicarbonyls, and fatty acids: Implications for atmospheric processing of organic aerosols, Journal of Geophysical Research: Atmospheres, 121, 3707-3717, 10.1002/2015jd024081, 2016.

Zhao, W., Kawamura, K., Yue, S., Wei, L., Ren, H., Yan, Y., Kang, M., Li, L., Ren, L., Lai, S., Li, J., Sun, Y., Wang, Z., and Fu, P.: Molecular distribution and compound-specific stable carbon isotopic composition of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in PM2.5 from Beijing, China, Atmos. Chem. Phys., 18, 2749-2767, 10.5194/acp-18-2749-2018, 2018.

Zhu, Y., Yang, L., Chen, J., Kawamura, K., Sato, M., Tilgner, A., van Pinxteren, D., Chen, Y., Xue, L., Wang, X., Herrmann, H., and Wang, W.: Molecular distributions of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in PM2.5 collected at Mt. Tai, in North China in 2014, Atmos. Chem. Phys. Discuss., 2018, 1-31, 10.5194/acp-2017-1240, 2018.

Table 1. Meteorological parameters and concentrations of inorganic ions, ozone, water soluble organic carbon (WSOC), organic carbon (OC), elemental carbon (EC), liquid water content (LWC), and in-situ pH (pH_{IS}) of $PM_{2.5}$ from Mt. Tai in the summer.

	Daytime (*n*=28)	Nighttime (*n*=29)	Total (*n*=57)
I. Meteorological parameters and ozone			
Temperature (°C)	23 ± 2.9 (17–28)	19 ± 2.9 (12–25)	21 ± 3.6 (12–28)
Relative humidity (%)	92 ± 5.0 (80–98)	77 ± 8.2 (65–93)	84 ± 9.9 (65–98)
O_3 (ppb)	32 ± 16 (7.8–61)	22 ± 12 (6.0–48)	27 ± 15 (6.0–61)
II. Inorganic ions (μg m^{-3})			
K^+	0.4 ± 0.2 (0.1–0.8)	0.4 ± 0.2 (0.1–0.7)	0.4 ± 0.2 (0.1–0.8)
Na^+	0.3 ± 0.1 (0.1–0.9)	0.3 ± 0.2 (0.1–1.0)	0.3 ± 0.2 (0.1–1.0)
NH_4^+	5.3 ± 2.9 (0.5–12)	6.6 ± 2.5 (1.2–11)	5.9 ± 2.8 (0.5–12)
Mg^{2+}	0.2 ± 0.1 (0–0.3)	0.2 ± 0.1 (0.1–0.3)	0.2 ± 0.1 (0–0.3)
Ca^{2+}	0.3 ± 0.1 (0–0.5)	0.3 ± 0.2 (0.1–0.7)	0.3 ± 0.2 (0–0.7)
NO_3^-	3.0 ± 2.1 (0.1–8.4)	4.2 ± 2.3 (0.9–10)	3.6 ± 2.3 (0.1–10)
SO_4^{2-}	13 ± 6.9 (3.0–33)	9.6 ± 3.7 (2.9–18)	12 ± 5.8 (2.9–33)
Subtotal	23 ± 12 (4.6–54)	22 ± 8.2 (6.6–40)	22 ± 10 (4.6–54)
Ⅲ. Other species (μg m^{-3})			
EC	0.2 ± 0.2 (0–0.6)	0.2 ± 0.2 (0–0.8)	0.2 ± 0.2 (0–0.8)
OC	2.4 ± 0.8 (1.1–3.9)	2.1 ± 0.3 (1.5–2.8)	2.2 ± 0.6 (1.1–3.9)
WSOC	1.9 ± 0.8 (0.8–3.6)	1.4 ± 0.5 (0.7–2.3)	1.7 ± 0.7 (0.7–3.6)
pH_{IS}	-0.04 ± 0.5 (-0.9–1.0)	0.4 ± 0.6 (-1.0–1.2)	0.2 ± 0.6 (-1.0–1.2)
LWC	94 ± 100 (10–313)	75 ± 69 (6.3–199)	84 ± 86 (6.3–313)
$PM_{2.5}$	38 ± 19 (6.1–83)	36 ± 14 (11–66)	37 ± 16 (6.1–83)

Table 2. Concentrations (ng m^{-3}) of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls of PM$_{2.5}$ from Mt. Tai in the summer.

Compounds	Daytime (*n*=28)	Nighttime (*n*=29)	Total (*n*=57)
I. Dicarboxylic acids			
Oxalic, C$_2$	272± 190 (11–623)	156 ± 105 (34–415)	213 ± 162 (11–623)
Malonic,C$_3$	49 ± 30 (4.0–101)	31 ±17 (7.4–69)	40 ± 26 (4.0–101)
Succinic, C$_4$	30 ± 23 (2.0–83)	24 ± 16 (4.7–67)	27 ± 20 (2.0–83)
Glutaric, C$_5$	7.0 ± 5.5 (0.4–19)	5.6 ± 3.9 (1.1–14)	6.3 ± 4.8 (0.4–19)
Adipic, C$_6$	2.2 ± 1.7 (0.1–5.6)	2.2 ± 1.8 (0.2–7.7)	2.2 ± 1.7 (0.1–7.7)
Pimelic, C$_7$	3.0 ±1.9 (0.3–7.3)	2.9 ± 1.3 (0.3–6.1)	3.0 ± 1.6 (0.3–7.3)
Suberic, C$_8$	4.3 ± 2.2 (0.9–9.0)	3.8 ± 2.8 (0.4–13)	4.0 ± 2.5 (0.4–13)
Azelaic, C$_9$	24 ± 14 (4.2–55)	19 ± 8.6 (4.5–41)	22 ± 12 (4.2–55)
Sebacic, C$_{10}$	5.9 ± 4.3 (0.1–14)	5.6 ± 2.7 (0.7–11)	5.8 ± 3.6 (0.1–14)
Undecanedioic, C$_{11}$	2.4 ± 1.7 (0.2–5.8)	1.1 ± 0.8 (0–3.8)	1.7 ± 1.4 (0–5.8)
Methylmalonic, iC$_4$	2.1 ±1.7 (0.1–5.2)	2.1 ± 1.5 (0–5.3)	2.1 ± 1.6 (0–5.3)
Mehtylsuccinic, iC$_5$	2.7 ± 2.0 (0.1–7.1)	2.2 ± 1.7 (0.2–6.1)	2.4 ± 1.8 (0.1–7.1)
Methyglutaric, iC$_6$	2.6 ± 2.1 (0.5–9.1)	2.3 ± 1.9 (0–9.0)	2.5 ± 2.0 (0–9.1)
Maleic, M	2.0 ±1.2 (0.1–4.3)	3.0 ± 2.0 (0.7–8.2)	2.5 ± 1.7 (0.1–8.2)
Fumaric, F	4.2 ± 2.7 (0.2–9.4)	4.0 ± 3.0 (0.5–13)	4.1 ± 2.8 (0.2–13)
Methylmaleic, mM	2.9 ± 1.7 (0.1–6.6)	2.7 ± 2.1 (0.5–9.9)	2.8 ± 1.9 (0.1–9.9)
Phthalic, Ph	3.0 ± 1.5 (0.6–5.6)	3.3 ± 2.3 (0.7–11.2)	3.2 ± 1.9 (0.6–11.2)
Isophthalic, iPh	1.6 ± 1.0 (0.1–3.3)	1.3 ± 0.8 (0.2–3.5)	1.4 ± 0.9 (0.1–3.5)
Terephthalic, tPh	1.9 ± 1.3 (0.1–5.0)	2.4 ±1.5 (0.1–6.1)	2.2 ± 1.4 (0.1–6.1)
Ketomalonic, kC$_3$	2.6 ± 1.5 (0–5.8)	2.7 ± 1.5 (0.5–6.4)	2.7 ± 1.5 (0–6.4)
Ketopimelic, kC$_7$	3.6 ± 2.8 (0.2–9.3)	3.9 ± 2.6 (0.2–12)	3.7 ± 2.7 (0.2–12)
Subtotal	430 ± 282 (27–944)	282 ± 161 (73–671)	354 ± 239 (27–944)
II. Ketocarboxylic acids			
Pyruvic, Pyr	14 ± 8.8 (1.4–28)	11 ± 5.5 (2.2–23)	12 ± 7.4 (1.4–28)
Glyoxylic, ωC$_2$	18 ± 12 (0.9–38)	15 ± 9.5 (3.5–35)	16 ± 11(0.9–38)
3-Oxopropanoic, ωC$_3$	4.0 ± 2.7 (0.1–7.7)	4.1 ± 2.2 (0.5–8.3)	4.1 ± 2.4 (0.1–8.3)
4-Oxobutanoic, ωC$_4$	2.9 ± 1.9 (0.2–6.8)	2.5 ± 1.7 (0.6–7.1)	2.7 ± 1.8 (0.2–7.1)
7-Oxoheptanoic, ωC7	1.0 ±0.6 (0–2.7)	1.3 ± 1.0 (0.1–4.8)	1.2 ± 0.9 (0.0–4.8)
8-Oxooctanoic, ωC$_8$	1.5 ± 0.9 (0.1–3.3)	1.5 ± 0.7 (0.2–3.4)	1.5 ± 0.8 (0.1–3.4)
9-Oxononanoic, ωC$_9$	2.0 ± 1.4 (0.1–4.4)	1.8 ± 1.1 (0.2–4.3)	1.9 ± 1.3 (0.1–4.4)
Subtotal	43 ± 28 (2.9–88)	37 ± 19 (7.6–77)	40 ± 24 (2.9–88)
III. α-Dicarbonyls			
Glyoxal, Gly	3.1 ± 1.8 (0.3–6.0)	4.6 ± 2.6 (0.4–12)	3.8 ± 2.3 (0.3–12)
Methyglyoxal, mGly	16 ± 9.5 (1.8–33)	22 ± 15 (1.4–62)	19 ± 13 (1.4–62)
Subtotal	19 ± 11 (2.6–39)	27 ± 17 (2.1–69)	23 ± 15 (2.1–69)
Total detected	491 ± 320 (33–1060)	346 ± 194 (96–807)	417 ± 271 (33–1060)

Table 3. Concentrations of α-dicarbonyls in $PM_{2.5}$ from Mt. Tai and Mt. Hua in China and the global budgets of atmospheric Gly and mGly.

Site	Sources/Season	Abundance		Mass ratio
		Gly	mGly	Gly/mGly
Global budget (Tg a^{-1})	Biogenic	22.8[a]	113.5[a]	1:5
	Anthropogenic	22.2[a]	26.5[a]	1:1
Mt. Hua (ngm^{-3})	Biogenic, Summer	2.3[b]	10[b]	1:4.4
	Anthropogenic, Winter	8.8[b]	1.3[b]	1:1.5
Mt. Tai (ngm^{-3}, this study)	Summer, Daytime	3.1	15.8	1:5.1
	Summer, Nighttime	4.6	22.1	1:4.8

Note: [a] Data are calculated from Fu et al., 2008;

[b] Data are cited from Meng et al., 2014.

Table 4. Correlation coefficients (*R*) matrix among major low molecular weight dicarboxylic acids and related SOA, BSOA tracers, temperature (T), and O_3 concentrations in Mt. Tai during the summer campaign.

	BSOA tracer	C_2	C_3	C_4	ωC_2	Pyr	Gly	mGly	O_3	T
					(a) Daytime					
Isoprene derived SOA	2-methylglyceric acid	0.98[a]	0.96[a]	0.86[a]	0.95[a]	0.73[a]	0.96[a]	0.94[a]	0.92[a]	0.85[a]
	2-methylthreitol	0.83[a]	0.80[a]	0.64[a]	0.74[a]	0.77[a]	0.77[a]	0.82[a]	0.85[a]	0.72[a]
	2-methylerthritol	0.84[a]	0.87[a]	0.70[a]	0.78[a]	0.83[a]	0.83[a]	0.84[a]	0.80[a]	0.71[a]
α-/*β*-pinene derived SOA	*cis*-pinonic acid	0.83[a]	0.75[a]	0.73[a]	0.75[a]	0.74[a]	0.71[a]	0.77[a]	0.80[a]	0.72[a]
	3-hydroxyglutaric acid	0.81[a]	0.76[a]	0.69[a]	0.74[a]	0.78[a]	0.74[a]	0.73[a]	0.73[a]	0.75[a]
	MBTCA[c]	0.84[a]	0.77[a]	0.83[a]	0.82[a]	0.75[a]	0.74[a]	0.77[a]	0.82[a]	0.67[a]
β-caryophyllene derived SOA	*β*-caryophyllinic acid	0.75[a]	0.70[a]	0.79[a]	0.70[a]	0.70[a]	0.71[a]	0.72[a]	0.65[a]	0.57[a]
					(b) Nighttime					
Isoprene derived SOA	2-methylglyceric acid	0.87[a]	0.72[a]	0.74[a]	0.70[a]	0.64[a]	0.44[b]	0.51[a]	0.09	0.59[a]
	2-methylthreitol	0.81[a]	0.71[a]	0.58[a]	0.71[a]	0.66[a]	0.60[a]	0.47[b]	0.05[a]	0.65[a]
	2-methylerthritol	0.83[a]	0.72[a]	0.62[a]	0.79[a]	0.73[a]	0.67[a]	0.61[a]	0.23	0.74[a]
α-/*β*-pinene derived SOA	*cis*-pinonic acid	0.83[a]	0.65[a]	0.57[a]	0.75[a]	0.61[a]	0.56[a]	0.54[a]	0.22	0.63[a]
	3-hydroxyglutaric acid	0.79[a]	0.62[a]	0.69[a]	0.71[a]	0.60[a]	0.58[a]	0.50[a]	0.43[b]	0.62[a]
	MBTCA[c]	0.82[a]	0.80[a]	0.78[a]	0.73[a]	0.75[a]	0.61[a]	0.55[a]	0.30	0.60[a]
β-caryophyllene derived SOA	*β*-caryophyllinic acid	0.68[a]	0.74[a]	0.61[a]	0.73[a]	0.71[a]	0.73[a]	0.58[a]	0.32[a]	0.53[a]

[a] $P<0.01$; [b] $P<0.05$.

[c] MBTCA: 3-Methyl-1,2,3-butanetricarboxylic acid.

Table 5. Stable carbon isotopic compositions (δ^{13}C, ‰) of major dicarboxylic acids and related SOA in $PM_{2.5}$ of Mt. Tai in the North China Plain.

Compounds	Daytime (*n*=28)	Nighttime (*n*=29)	Total (*n*=57)
I. Dicarboxylic acids			
Oxalic, C_2	−15.8±1.9 (−19.4 to −13.0)	−17.2±1.7 (−20.1 to −12.1)	−16.5±1.9 (−20.1 to −12.1)
Malonic,C_3	−19.1±2.3 (−23.8 to−15.9)	−18.5±1.8 (−21.1 to−15.3)	−18.8±2.0 (−23.8 to−15.3)
Succinic, C_4	−22.0±2.3 (−25.6 to−18.5)	−21.4±2.2 (−24.6 to −18.4)	−21.7±2.2 (−25.6 to −18.4)
Adipic, C_6	−23.7±2.5 (−27.3 to −19.9)	−24.8±2.4 (−27.9 to −21.4)	−24.2±2.5 (−27.9 to −19.9)
Azelaic, C_9	−24.7±2.6 (−28.7 to−21.0)	−25.7±2.7 (−30.3 to−21.9)	−25.2±2.7 (−30.3 to −21.0)
Phthalic, Ph	−24.3±2.5 (−28.1 to−20.6)	−25.2±2.6 (−29.2 to−20.9)	−24.8±2.5 (−29.2 to −20.6)
II. Ketocarboxylic acids			
Pyruvic, Pyr	−19.4±2.1 (−23.1 to −16.5)	−21.2±2.2 (−24.5 to −17.8)	−20.3±2.3 (−24.5 to −16.5)
Glyoxylic, ωC_2	−18.6.8±1.9 (−21.5 to	−20.2±2.1 (−23.1 to−16.9)	−19.4±2.2 (−23.1 to−15.6)
3-Oxopropanoic, ωC_3	−20.2±2.1 (−23.5 to−17.0)	−24.0±2.5 (−27.7 to − 20.8)	−22.2±3.0 (−27.7 to−17.0)
III. *α*-Dicarbonyls			
Glyoxal, Gly	−16.7±1.7 (−19.4 to−14.0)	−18.1±1.8(−21.3 to −15.2)	−17.4±1.9 (−21.3 to −14.0)
Methyglyoxal, mGly	−17.9±1.8 (−21.0 to−15.0)	−19.6±2.0 (−22.5 to−16.5)	−18.8±2.1 (−22.5 to−15.0)

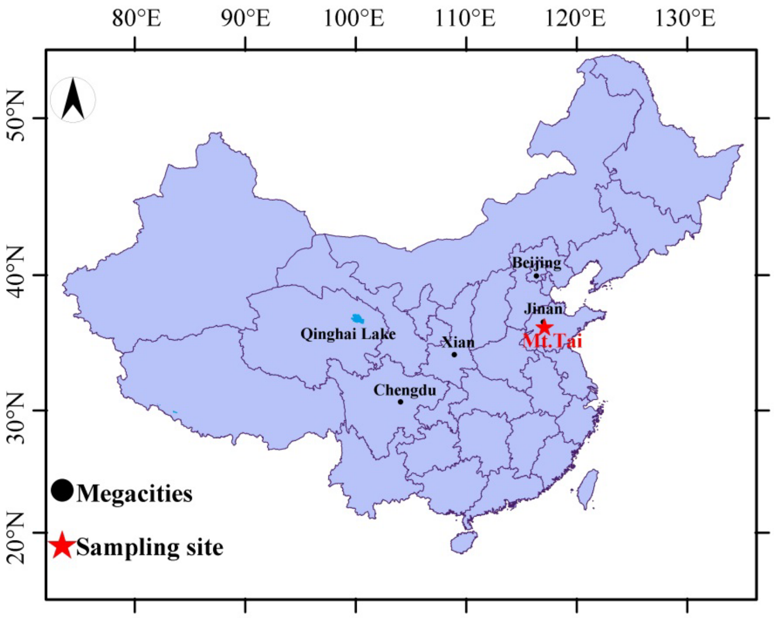

Fig.1. Location of the sampling site (Mt. Tai; 36.25° N, 117.10°E; 1534 m a.s.l.).

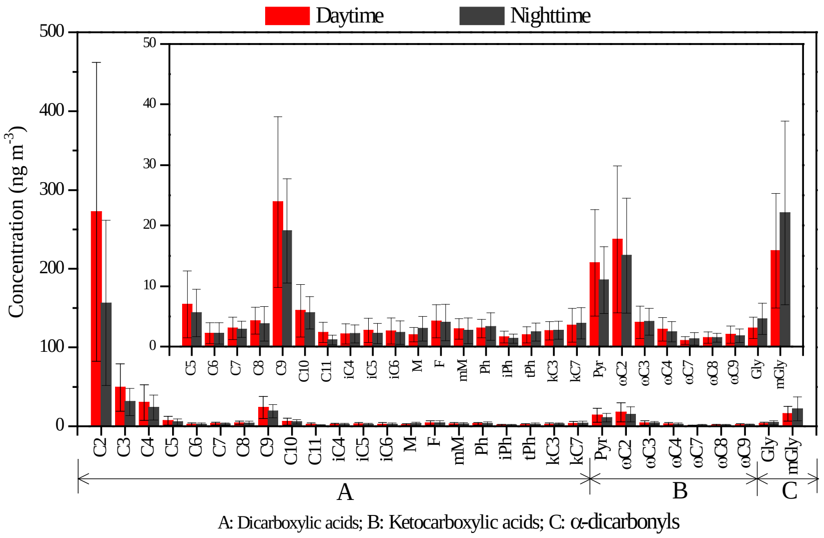

Fig.2. Molecular distributions of dicarboxylic acids and related compounds in $PM_{2.5}$ of Mt. Tai in North China Plain.

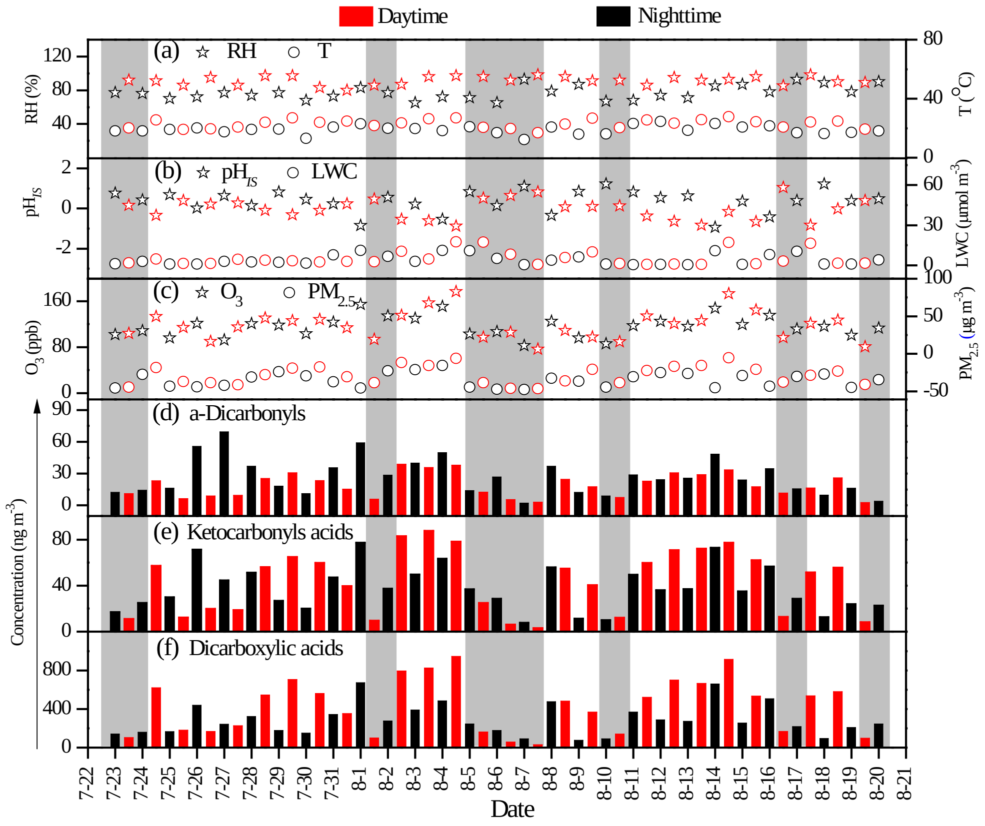

Fig.3. Diurnal variations of relative humidity (RH), temperature (T), in-situ acidity of particles (pH$_{IS}$), liquid water content of particles (LWC), concentrations of O$_3$, PM$_{2.5}$, α-dicarbonyls, ketocarboxylic acids, and dicarboxylic acids (rainy days are highlighted in shadow).

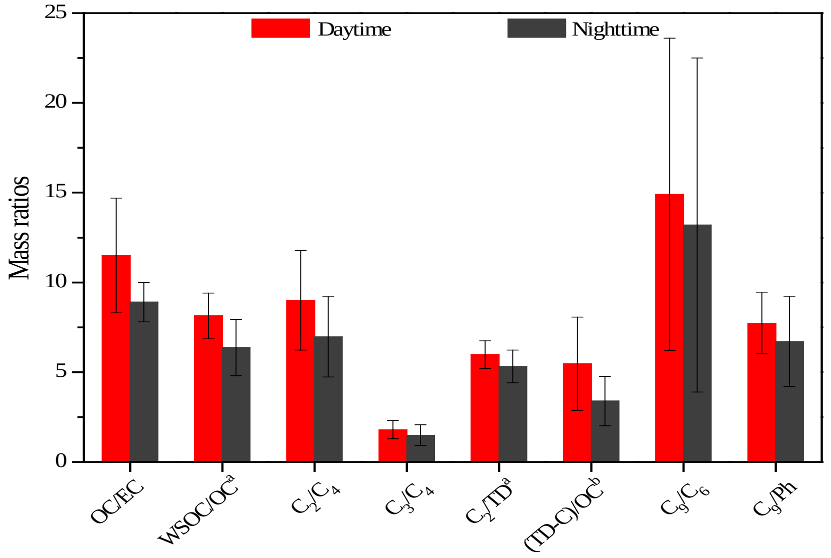

Fig.4. Diurnal variations of mass ratios of OC/EC, WSOC/OC, C_2/C_4, C_3/C_4, C_2/TD, (TD-C)/OC, C_9/C_6, C_9/Ph. (TD: total dicarboxylic acids; TD-C: the carbon concentration of total dicarboxylic acids; [a] the mass ratios expanding 10 times; [b] the mass ratios expanding 100 times).

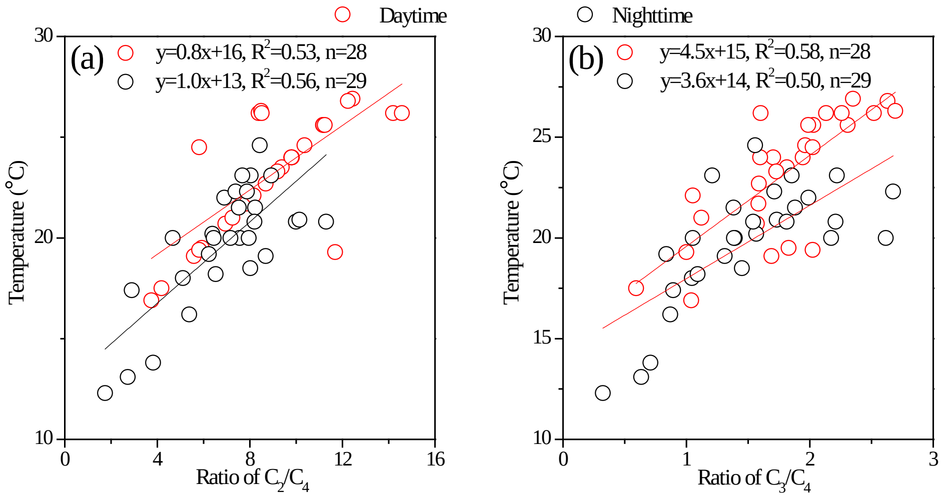

Fig.5. Linear fit regression for temperature (T) with mass ratios of (**a**) C_2/C_4 and (**b**) C_3/C_4 (See the abbreviations in Table 1).

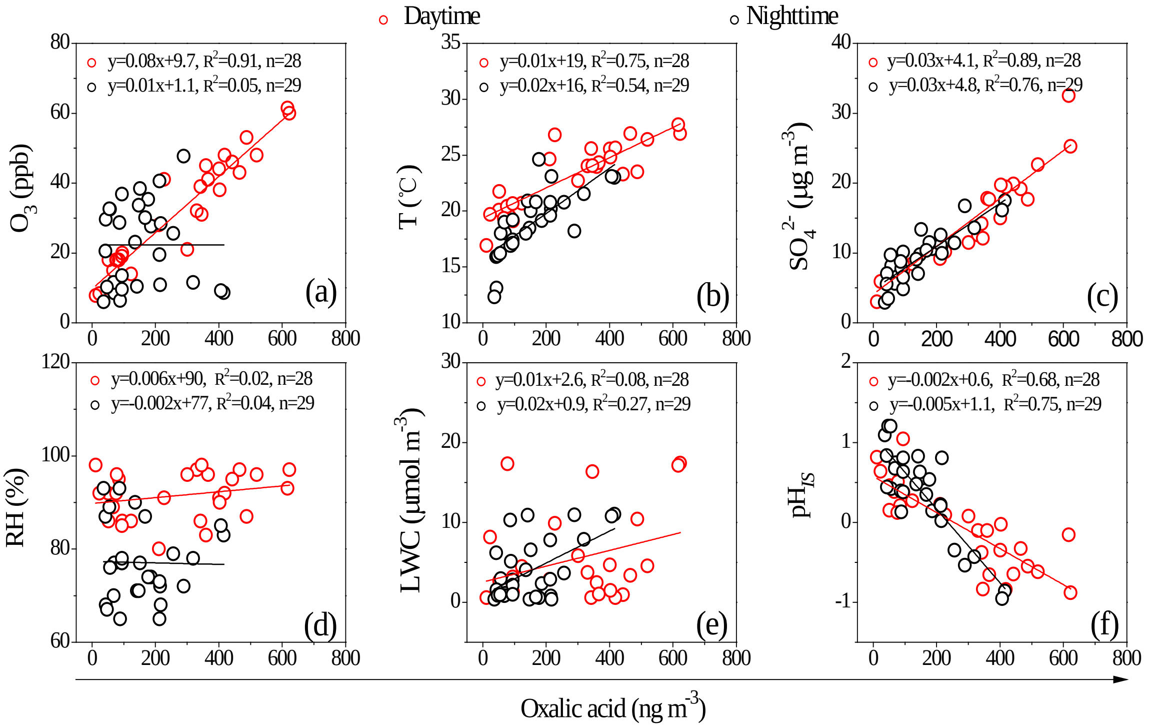

Fig.6. Linear fit regressions of oxalic acid (C_2) with **(a)** O_3, **(b)** temperature (T), **(c)**SO_4^{2-}, **(d)** relative humidity (RH), **(e)** aerosol liquid water content (LWC), and **(f)** in-situ acidity of particles (pH_{IS}).

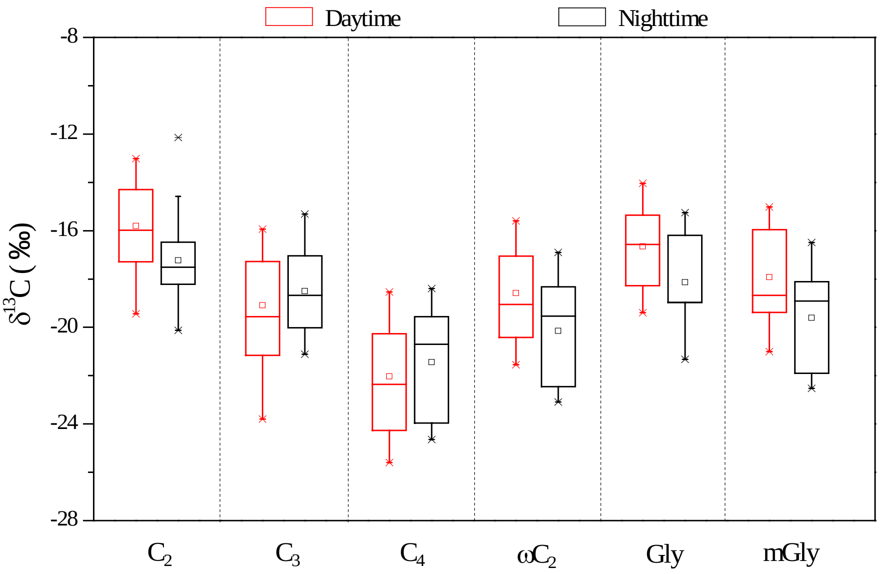

Fig.7. Diurnal variations of stable carbon isotope composition of low molecular weight dicarboxylic acids (C_2–C_4), the smallest ketocarboxylic acids (ωC_2) and α-dicarbonyls (Gly, mGly) in $PM_{2.5}$ collected at the summit of Mt. Tai during the summer.

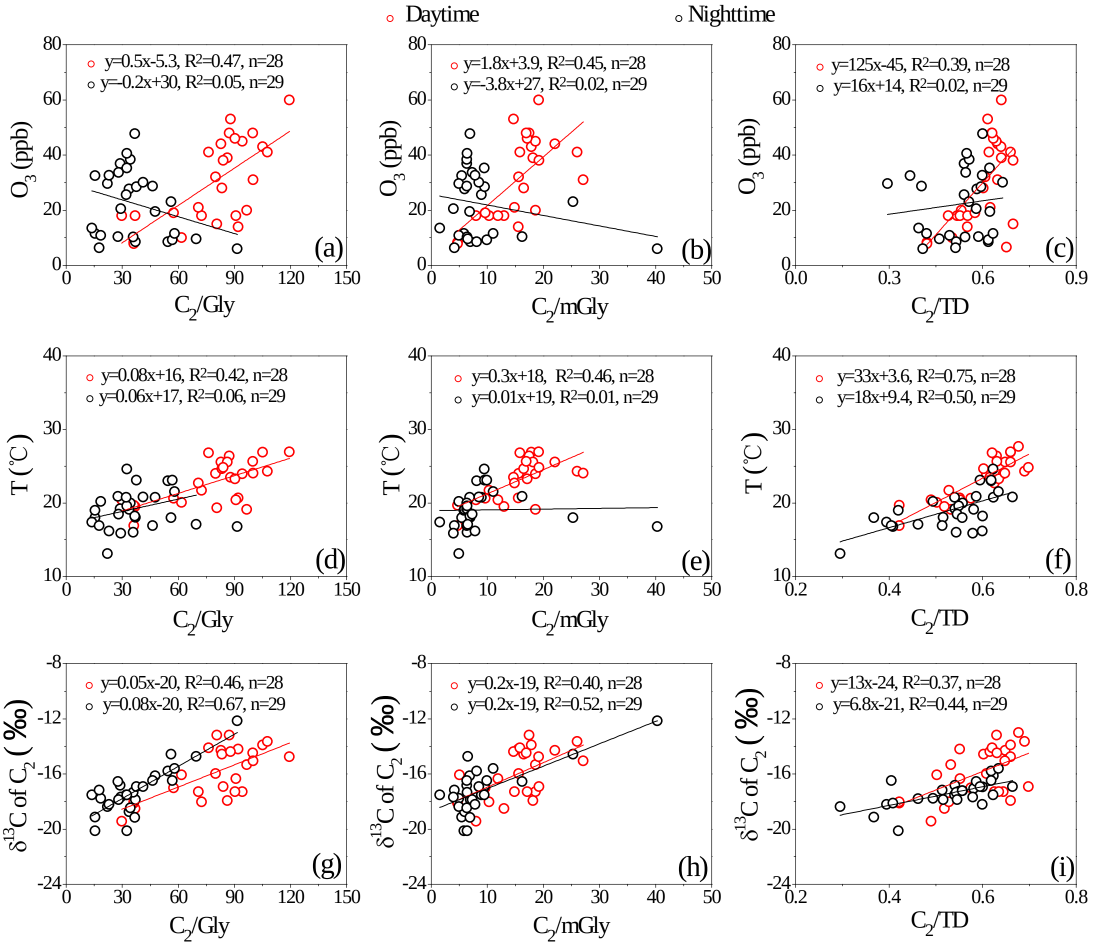

Fig.8. Correlation analysis for the mass ratios of C$_2$/Gly, C$_2$/mGly and C$_2$/TD with (**a-c**) concentrations of O$_3$; (**d-f**) temperature and (**g-i**) δ^{13}C of C$_2$ during the daytime and nighttime (C$_2$/TD: mass ratio of oxalic acid to total dicarboxylic acids; T: temperature).

Supporting information

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

Jingjing Meng[1,3], Gehui Wang[2,3,4*], Zhanfang Hou[1,3], Xiaodi Liu[1], Benjie Wei[1],
Can Wu[3], Cong Cao[3], Jiayuan Wang[3], Jianjun Li[3], Junji Cao[3], Erxun Zhang[1], Jie Dong[1],
Jiazhen Liu[1,] Shuangshuang Ge[2], Yuning Xie[2]

[1] School of Environment and Planning, Liaocheng University, Liaocheng 252000, China
[2] Key Lab of Geographic Information Science of the Ministry of Education, School of Geographic Sciences, East China Normal University, Shanghai 200241, China
[3] State Key Laboratory of Loess and Quaternary Geology, Key Lab of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China
[4] School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an 710049, China

*Corresponding author: Prof. Gehui Wang
E-mail address: wanggh@ieecas.cn, or ghwang@geo.ecnu.edu.cn

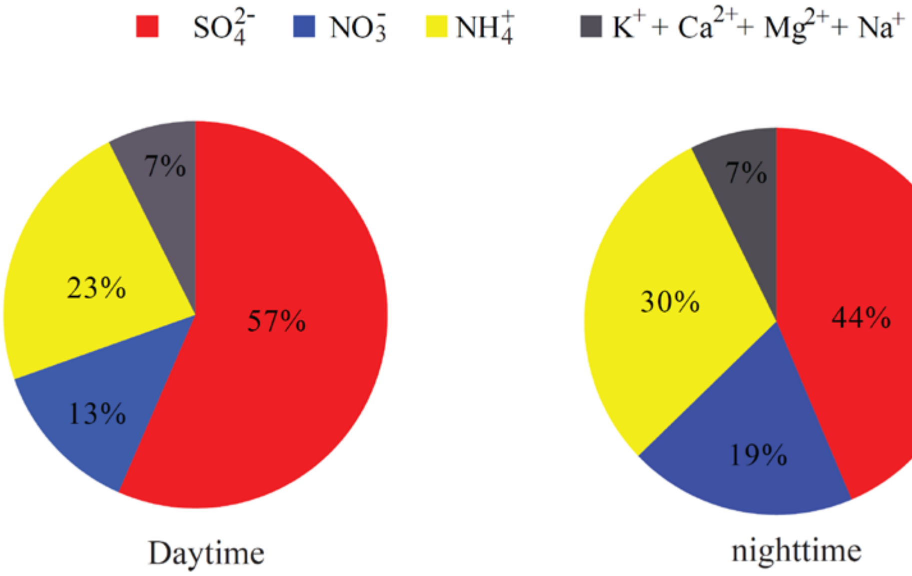

Fig. S1. Abundances of major ions relative to the total inorganic ions of PM$_{2.5}$ during the day and night at Mt. Tai.

Table S1. Statistic *t*-test for the differences in concentrations and mass ratios of major species of PM$_{2.5}$ during the day and night at Mt. Tai (2-tailed test).

	P
C_2	0.004
DCAs	0.002
Dicarbonyls	0.001
SO_4^{2-}	0.000
NO_3^-	0.004
NH_4^+	0.003
WSOC	0.000
OC	0.001
WSOC/OC	0.000
C_2/C_4	0.001
C_3/C_4	0.001
C_2/total diacids	0.002
Total(Diacids-C)/OC	0.001
C_2/Gly	0.000
C_2/mGly	0.003
$C_2/\omega C_2$	0.001