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 $\delta^{13}C$ 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), $\delta^{13}C$ 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 ($\delta^{13}C$ 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 $\delta^{13}C$ 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.

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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)

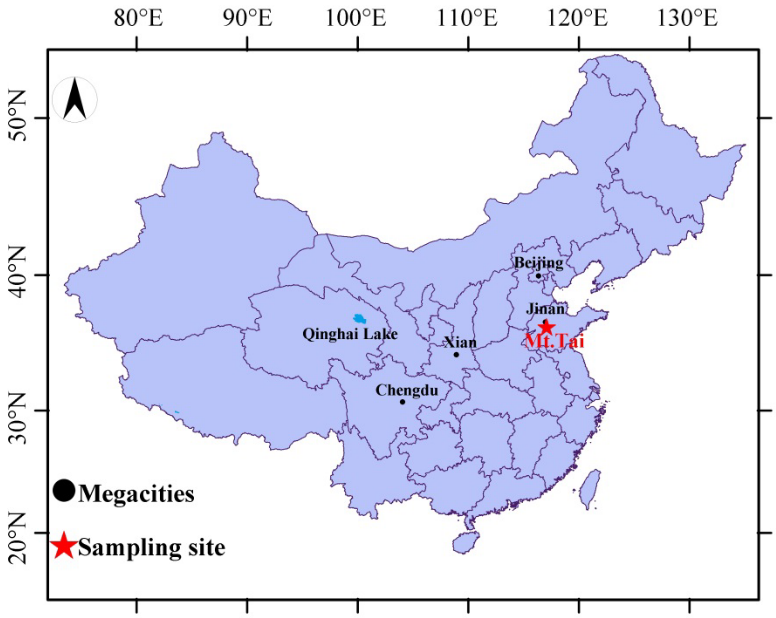
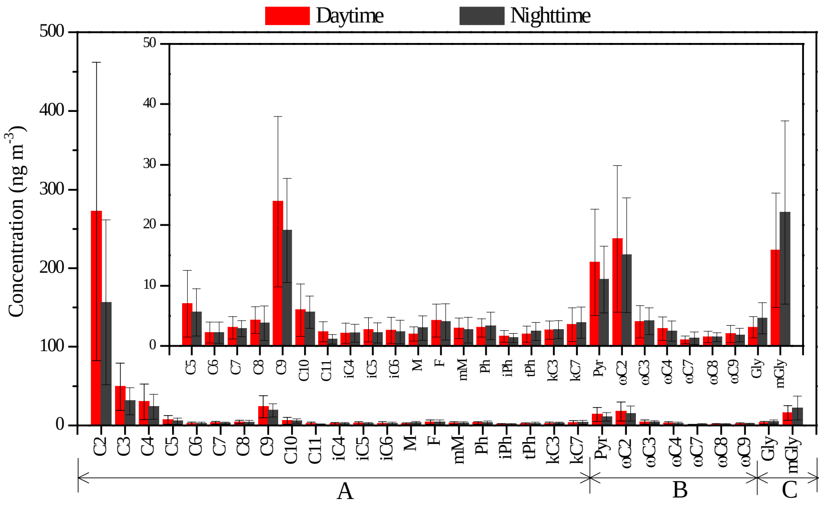


Fig.1. Location of the sampling site (Mt. Tai; 36.25° N, 117.10°E; 1534 m a.s.l.).



A: Dicarboxylic acids; B: Ketocarboxylic acids; C: α-dicarbonyls

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

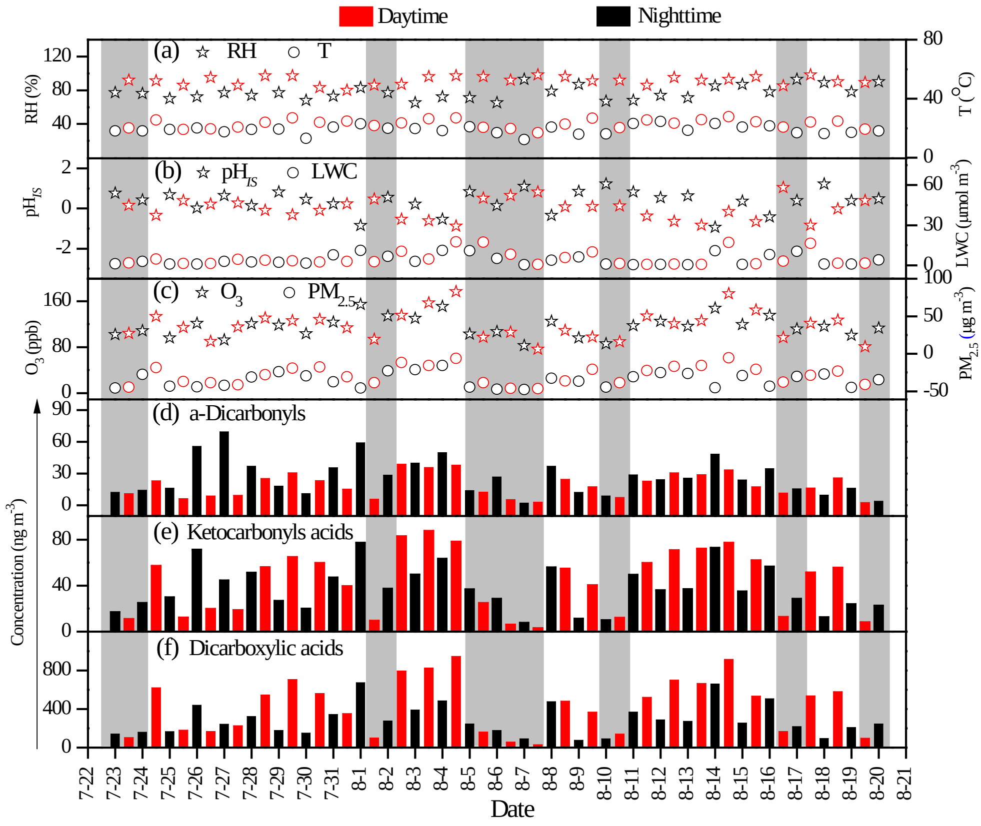


Fig.3. Diurnal variations of relative humidity (RH), temperature (T), in-situ acidity of particles (pH$_{IS}$), liquid water content of particles (LWC), concentrations of O$_{3,}$ PM$_{2.5}$, α-dicarbonyls, ketocarboxylic acids, and dicarboxylic acids (rainy days are highlighted in shadow).

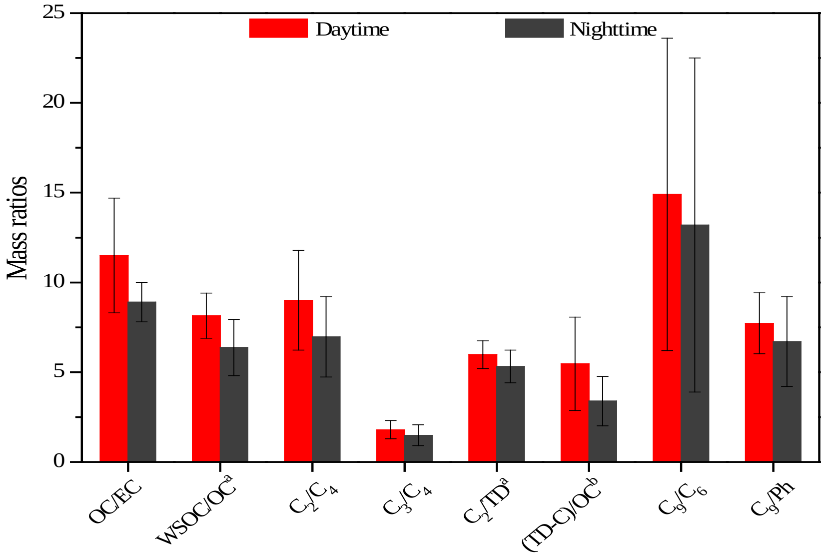


Fig.4. Diurnal variations of mass ratios of OC/EC, WSOC/OC, C_2/C_4, C_3/C_4, C_2/TD, (TD-C)/OC, C_9/C_6, C_9/Ph. (TD: total dicarboxylic acids; TD-C: the carbon concentration of total dicarboxylic acids; ^{a} the mass ratios expanding 10 times; ^{b} the mass ratios expanding 100 times).

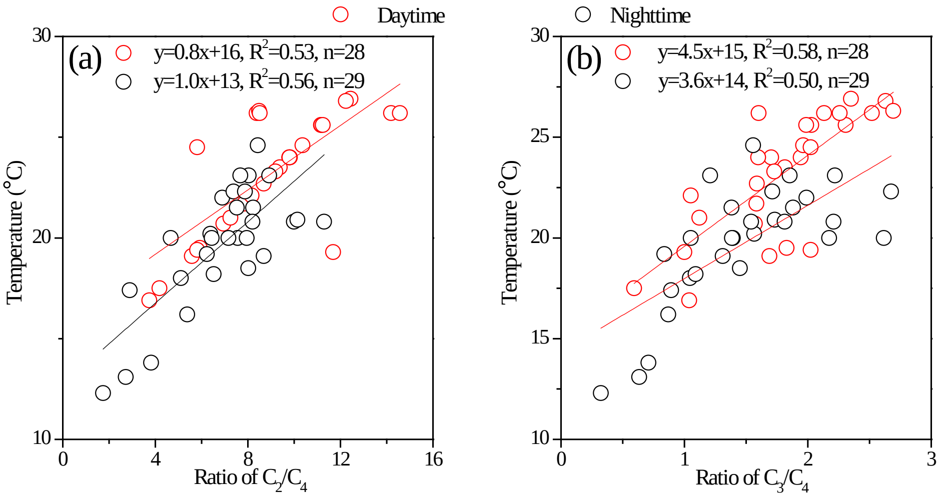


Fig.5. Linear fit regression for temperature (T) with mass ratios of (**a**) C_2/C_4 and (**b**) C_3/C_4 (See the abbreviations in Table 1).

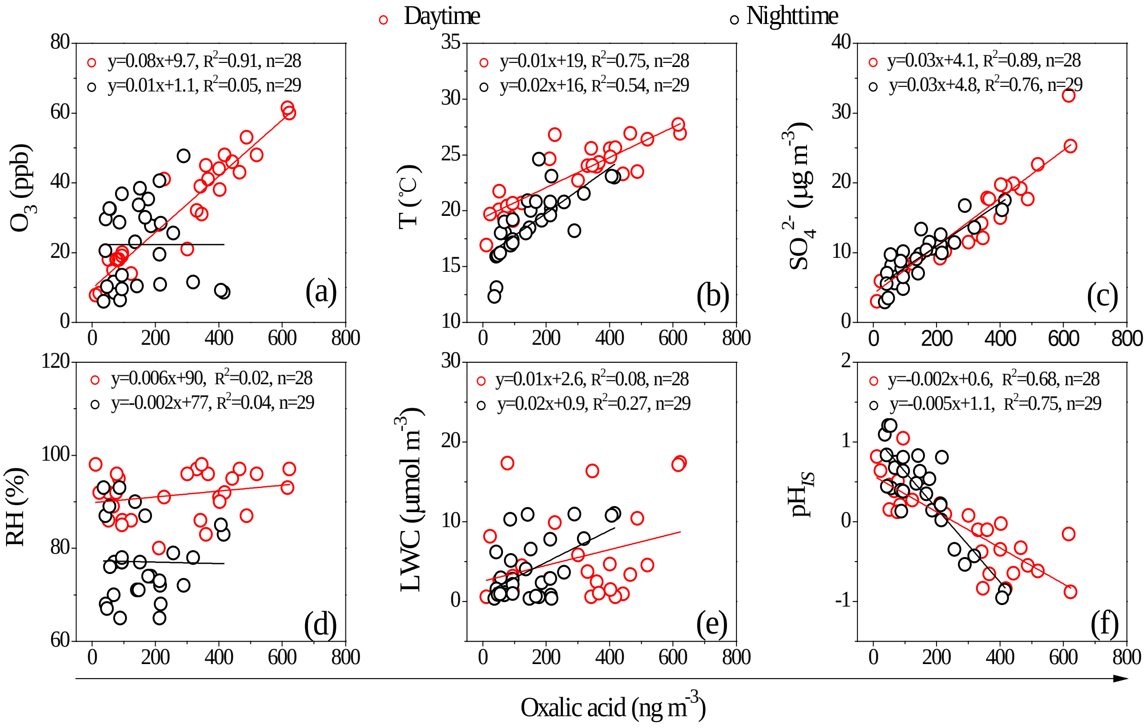


Fig.6. Linear fit regressions of oxalic acid (C_2) with (**a**) O_3, (**b**) temperature (T), (**c**)SO_4^{2-}, (**d**) relative humidity (RH), (**e**) aerosol liquid water content (LWC), and (**f**) in-situ acidity of particles (pH_{IS}).

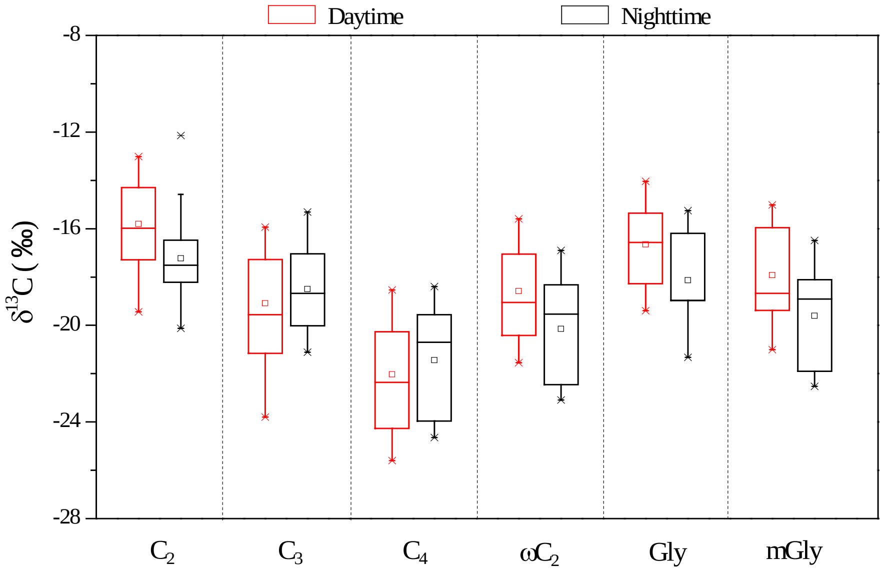


Fig.7. Diurnal variations of stable carbon isotope composition of low molecular weight dicarboxylic acids (C_2–C_4), the smallest ketocarboxylic acids (ωC_2) and α-dicarbonyls (Gly, mGly) in $PM_{2.5}$ collected at the summit of Mt. Tai during the summer.

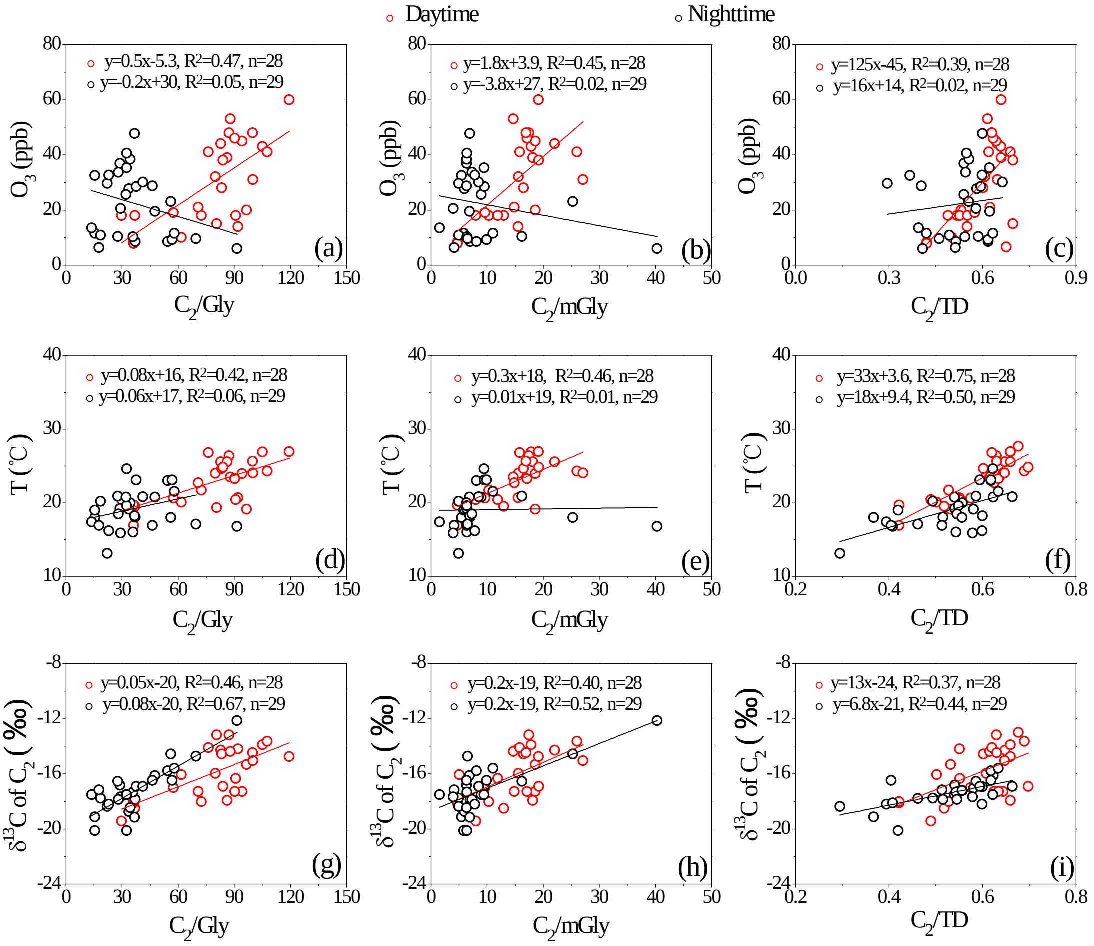


Fig.8. Correlation analysis for the mass ratios of C_2/Gly, C_2/mGly and C_2/TD with (**a-c**) concentrations of O_3; (**d-f**) temperature and (**g-i**) $\delta^{13}C$ of C_2 during the daytime and nighttime (C_2/TD: mass ratio of oxalic acid to total dicarboxylic acids; T: temperature).