Measurement Report: Enhanced contribution of photooxidation to dicarboxylic acids in urban aerosols during the COVID-19 lockdown in Jinan, East China

Jingjing Meng[1,2], Yachen Wang[1], Yuanyuan Li[1], Tonglin Huang[1], Zhifei Wang[3], Yiqiu, Wang[4], Min Chen[1], Zhanfang Hou[1], Kimitaka Kawamura[5], Pingqing Fu[2]

[1]School of Geography and Environment, Liaocheng University, Liaocheng 252000, China
[2]Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China
[3]Jinan Environmental Monitoring Center of Shandong Province, Jinan 250101, China
[4]Liaocheng Environmental Information and Monitoring Center, Liaocheng, 252000, China
[5]Chubu Institute for Advanced Studies, Chubu University, Kasugai 487-8501, Japan

Correspondence to: Pingqing Fu (fupingqing@tju.edu.cn)

Abstract. To curb the spread of a novel coronavirus pandemic (COVID-19), a preventive lockdown (LCD) policy was first implemented across China in early 2020, resulting in a substantial drop-off in anthropogenic pollutant emissions and thus the amelioration of air quality. Unexpectedly, several haze events driven by enhanced secondary organic aerosols (SOA) still took place in eastern China during the LCD. To investigate the effect of LCD measures on the formation of SOA, $PM_{2.5}$ samples were collected before and during the LCD in Jinan, East China. The samples were analyzed for dicarboxylic acids (diacids) and related compounds, water-soluble inorganic ions, carbonaceous species, as well as the stable carbon isotopic compositions ($\delta^{13}C$) of major diacids. Our results show that despite the sharp decrease of primary pollutants (e.g., CO, SO_2, NO_2, and elemental carbon) during the LCD, the O_3 concentration, proportion of secondary inorganic aerosols, concentration levels, and relative abundance of diacid homologues in water-soluble organic compounds (WSOC) were still 2–4 times higher than those before the LCD. The ratios of oxalic acid (C_2) to diacids (C_2/diacids) and to total detected organic components were higher during the LCD than those before the LCD, suggesting the more aged organic aerosols during the LCD under the clearer sky conditions. The temporal changes, diurnal variations in major diacids, and their higher concentrations and contributions during the LCD than before the LCD are mainly due to the enhanced photochemical oxidation by the higher O_3 and the stronger solar radiation during the LCD. Interestingly, compound-specific stable carbon isotope ratios ($\delta^{13}C$) of C_2 and other major diacids show higher values in the nighttime than the daytime before the LCD, which indicates a significant contribution of organic acids via aqueous phase oxidation at night. Source apportionments using the molecular characteristics of organic compounds and positive matrix factorization (PMF) model suggest that the aqueous oxidation (45.2%) and coal combustion (16.7%) were the major sources before the LCD but the photochemical oxidation promoted by the higher O_3 concentration (48.8%) and aqueous oxidation (17.7%) were the dominant source during the LCD. The increased $\delta^{13}C$ values of oxalic acid and other major organic acids along with the high ratios of C_2/Gly, C_2/mGly, and C_2/diacids before and during the LCD confirm an isotopic fractionation effect during the precursor oxidation processes. Furthermore, more positive $\delta^{13}C$ values of diacids are observed in the daytime than the nighttime during the LCD, which suggests an enhanced photochemical oxidation in the urban atmosphere during this period.

1 Introduction

Water-soluble organic compounds (WSOC), constituting a great proportion of atmospheric fine particles, have attracted a growing attention for the adverse effects on haze formation and global climate change (Lv et al., 2022; Wang et al., 2016). Dicarboxylic acids (diacids) and their organic precursors such as oxocarboxylic acids (oxoacids) and α-dicarbonyls are ubiquitous in the atmosphere, accounting for 14% of WSOC in particulate matter of urban regions (Ho et al., 2007; Kawamura and Bikkina, 2016), and can be up to 52% in the marine area (Bikkina et al., 2015). Due to the high solubility and hygroscopic property, diacid homologues can not only modify the hygroscopic growth of aerosols, but also improve the cloud condensation nuclei (CCN) activation, thus they exert an important effect on radiative forcing of aerosols via scattering the solar radiation and cloud formation (Ding et al., 2021; Wang et al., 2015).

Diacids and related compounds can be emitted directly from biogenic sources (Rinaldi et al., 2011), vehicle exhausts (Kawamura and Kaplan, 1987), and combustions of biomass and fossil fuels (Cao et al., 2017; Narukawa et al., 1999), while their relative contribution to total aerosol mass is negligible (Shen et al., 2022; Wang et al., 2020a). A growing body of evidence from model studies, chamber experiments, cloud observations, and field measurements have highlighted that most of these water-soluble organic acids are predominantly generated from the photochemical oxidation of volatile organic compounds (VOCs) followed by partitioning into the aqueous phase in wet aerosols, fog, and cloud droplets (Carlton et al., 2007; Ervens et al., 2004, 2011; Fu et al., 2008; Lim et al., 2013; Shen et al., 2022; Wang et al., 2010). Therefore, diacid homologues have been regarded as essential indicators of SOA in the atmosphere to trace the aging processes and assess the oxidative capacity of atmosphere (Enami et al., 2015; Zhao et al., 2020). As the lowest molecular weight and the most abundant diacid, oxalic acid (C_2) has been proved to be mostly derived from two pathways: (1) photochemical breakdown (or decomposition) of longer-chain diacids (C_3–C_{11}) (Enami et al., 2015; Yu et al., 2021); and (2) secondary oxidation of VOCs via α-dicarbonyls including glyoxal (Gly) and methylglyoxal (mGly) in queous phase of aerosol and cloud droplets, which has been considered to dominate over the first pathway (Carlton et al., 2007; Xu et al., 2022).

More oxidized SOA are largely produced from aqueous oxidation, while less oxidized SOA are largely derived from gaseous photochemical oxidation (Hu et al., 2017; Yu et al., 2019). Modeling studies and laboratory experiments also demonstrate the in-cloud C_2 formation (Crahan et al., 2004; Lim et al., 2005; Warneck, 2003) from the oxidation of Gly (Carlton et al., 2007) and other gaseous "Gly-like" precursors such as glycolaldehyde (Perri et al., 2009) and mGly (Altieri et al., 2008) with $OH\cdot$ radical. Yu et al. (2019) reported that aqueous oxidation exerts a dominant effect on diacids and related compounds despite the increased contribution of photochemical oxidation in gas phase during the haze events in Beijing using multiple linear regression. A recent study by Xu et al. (2022) pointed out that a large portion of C_2 was derived from the aqueous process of organic precursors emitted from fossil fuel combustion. Laboratory simulation has demonstrated that C_2 can be photodegraded under the O_3 chemical pathway (Gligorovski et al., 2010), but field measurements have demonstrated that formation pathways influenced by O_3 are involved in the formation of C_2 (Meng et al., 2021; Mochizuki et al., 2017). The formation mechanism and influencing factors as well as the contribution of aqueous oxidation and gaseous photochemical oxidation are still not well understood. Therefore, further investigations on C_2 and related compounds are necessary to provide a knowledge base for better understanding SOA and improving the accuracy of model.

To curb the transmission of the novel coronavirus disease 2019 (COVID-19) in human society, a strict lockdown (LCD) measure was first implemented by the Chinese government starting at the end of January 2020 (Le et al., 2020). These dramatic restrictions resulted in a sharp drop-off of air pollutants (Li et al., 2021; Meng et al., 2021), for instance, the average concentrations of five parameters including CO, NO_2, SO_2, $PM_{2.5}$, and PM_{10} decreased by 4.6–24.7% in 44 cities of China because of the travel restrictions during the LCD (Bao and Zhang, 2020). Unexpectedly, a few haze episodes still occurred in China during the LCD. Online observations, model simulations, and satellite measurements have pointed out that the appearance of haze events during the LCD were mainly caused by the unfavorable meteorological conditions, continuous emissions of SO_2, NO_X, and VOCs from power plants and petrochemical refineries, and an enhanced SOA formation (Huang

et al., 2020; Li et al., 2020; Wang et al., 2020b; Shi et al., 2021; Zhong et al., 2021). These studies focused on the effect of the LCD policies on air quality and haze formation, for example, Le et al. (2020) and Huang et al. (2020) pointed out that the reduction of NO_X emissions lead to the enhanced ozone concentration, further improved the atmospheric oxidizing capacity and promoted the formation of secondary aerosol during the LCD. However, little is known about the impact of LCD measures on the molecular distributions, aging processes, and the formation mechanisms of SOA from field observations.

In order to understand the effect of the reduced anthropogenic emissions during the LCD and different meteorological parameters on the evolutionary process of homologous diacids and to investigate the relative contribution of aqueous oxidation versus gas-phase photochemical oxidation to total diacid homologues, we collected fine aerosol samples in urban Jinan, East China on a day/night basis before and during the LCD. We compare the differences in the molecular distributions, stable carbon isotopic compositions, and formation processes of C_2 and the related SOA before and during the LCD. Then, we investigate the effect of meteorological parameters (e.g., RH, temperature, and solar radiation) and aerosol aqueous properties (e.g., liquid water content (LWC) of aerosol and particle acidity (pH_{is})) on their formation processes in the urban atmosphere.

2 Experimental methods

2.1 Aerosol sampling

Fine aerosol ($PM_{2.5}$) sampling was conducted on the rooftop of a six-story building (36.67 °N, 117.06 °E, approximately 20 m above ground) that was about 40 m away from the Jinan Environment Monitoring Center (one of the State Controlling Air Sampling Sites in Jinan). The sampling site is in the center of Jinan city, which is located in the midwestern part of Shandong Province, China (Fig. S1). The sampling site lies in a typical urban setting surrounded by heavy traffic roads, residential areas, and commercial centers. $PM_{2.5}$ samples were collected using prebaked (450 ℃, 8 h) quartz fiber filters (8 in. × 10 in.) from 6 January to 17 February 2020. The government of Shandong Province first performed the preventive LCD starting on 24 January 2020; thus the whole sampling period was divided into two periods: (1) before the LCD from 6 to 23 January, (2) during the LCD from 31 January to 17 February. Each sample lasted for 12 h on a day/night basis using a high-volume air sampler (TISCH, USA) at an airflow rate of 1.013 m^3 min^{-1}. The daytime samples were collected from 8:00 to 20:00, while nighttime samples were collected from 20:00 to 8:00 the next day. The field blank is sampled to see whether the aerosol samples have been polluted during the operation process, including the placing and collecting processes of the filter, which takes about a few minutes. The operating procedure of collecting field blank samples for 10 min in this study is conventional and scientifically sound and was also confirmed in other studies (Qi et al., 2022; Yi et al., 2021). Therefore, field blank samples were also collected by mounting the blank filter onto the sampler for 10 min without turning on the sampler before, during, and after the sampling campaign, respectively. A total of 72 $PM_{2.5}$ samples (36 for daytime and 36 for nighttime) and 6 field blank samples were collected in the whole sampling period. After the collection, each filter was sealed in an aluminum foil bag and stored in a freezer (−20 ℃) for about 16 months prior to analysis. The concentrations of $PM_{2.5}$, PM_{10}, CO, SO_2, NO_2, and O_3, as well as meteorological parameters such as wind direction/speed, RH, temperature, and solar radiation were retrieved from the monitoring station in the Jinan Environment Monitoring Center (https://www.aqistudy.cn/). The detail information of quality assurance/quality control (QA/QC) of online data was described in Text S4. The inlet height of the air quality monitoring station was approximately 20 m above the ground level.

2.2 Chemical Analysis

2.2.1 Determination of diacids and related compounds as well as levoglucosan

The quantitative method for analyzing diacids, oxoacids, and α-dicarbonyls in $PM_{2.5}$ has been described previously (Fu et al.,

2013; Meng et al., 2020). Briefly, a quarter of the filter was extracted with 5 mL pure Milli-Q water under ultrasonication three times. The water extracts were concentrated to near dryness and then reacted with 14% BF_3/*n*-butanol at 100 ℃ for 1 hour. During this process, the carboxyl functional group was derivatized to butyl ester, and the aldehyde and keto groups were derivatized to dibutoxy acetal. After derivatization, *n*-hexane was added and washed with pure water three times. Finally, the hexane layer was determined by a gas chromatography-mass spectrometry (GC-MS) and quantitatively analyzed using a GC (Agilent 6980) coupled with an HP-5 column (0.2mm × 25m, 0.5 μm film thickness) and a flame ionization detector (FID). GC-MS was performed on a Hewlett-Packard model Agilent 7890A GC coupled to a Hewlett-Packard model Agilent 5975C mass selective detector (MSD). GC separation was equipped with a split/splitless injector and a fused silica capillary column (DB-5MS, 30 m × 0.25 mm i.d., 0.25 μm film thickness). The GC oven temperature was programmed from 50^{o}C for 2 min to 120^{o}C at a rate of 15^{o}C min^{-1}, and then to 300^{o}C at a rate of 5^{o}C min^{-1} with a final hold at 300^{o}C for 16 min. The mass spectrometer was operated on the electron impact (IE) mode at 70 eV and scanned from 50 to 650 Da. The same analytical method as described above was also applied for field blank filters. As described in previous studies, the recoveries of C_2 ranged from 70% to 83% and other target compounds were better than 80% (Ding et al., 2021; Kawamura et al., 2013; Kawamura and Yasui, 2005; Meng et al., 2020; Zhao et al., 2020). Recoveries of the target compounds in this study were 80% for C_2 and higher than 85% for other organic species. Therefore, the percent recoveries mentioned in this study were good enough for such analysis.

Additionally, another portion of each filter sample was extracted with a mixture of dichloromethane and methanol (2:1, *v/v*) under ultrasonication. After being derivatized with 60 μL mixture of N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine (5:1, *v/v*) at 70^{o}C for 3 h, the derivatized extracts were identified for levoglucosan using a GC-MS (Yi et al., 2021). The recovery rate of levoglucosan is higher than 95%. Compared with the ambient samples, the concentration of levoglucosan in the field blank samples was lower than 4%. The data of targeted organic species presented in this study were corrected for both recoveries and field blanks.

2.2.2 Stable carbon isotopic composition of diacids and related compounds

The stable carbon isotopic compositions (δ^{13}C) of major diacids and related compounds were measured using the method reported elsewhere (Kawamura and Watanabe, 2004). Briefly, 2 μL internal standard (*n*-C_{13} alkane, -27.24 ‰) was spiked to the ester fraction, and the δ^{13}C values of the derivatized samples relative to Pee Dee Belemnite (PDB) were identified using a GC-isotope ratio MS (GC-IR-MS, Thermo Fisher, Delta V Advantage). GC was installed with a HP manual on-column injector and a capillary column (CIP-Sil 8CB, 60 m × 0.32 mm × 0.25 μm) was used with a column oven temperature programmed from 50 to 120^{o}C at a rate of 30^{o}C min^{-1} and then to 300^{o}C at a rate of 6^{o}C min^{-1}. Flow rate of carrier gas (He) was maintained at 1.7 mL min^{-1}. Each sample was measured twice or three times to check the analytical error of the δ^{13}C values, which were less than 0.2‰. The δ^{13}C values were then calculated for free organic acids using an isotope mass balance equation based on the measured δ^{13}C values of derivatives and the derivatizing agent (BF_3/*n*-butanol), as detailed in Text S1 (Kawamura and Watanabe, 2004).

2.2.3 Elemental carbon (EC), organic carbon (OC), WSOC, and inorganic ions

EC and OC in the $PM_{2.5}$ samples were analyzed using a DRI Model 2015 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 each sample filter was extracted with 30 mL Milli-Q water using an ultrasonic bath three times, and then filtered through PTFE filters to remove particles and filter debris. The water extract was then divided into two parts. One part was analyzed for inorganic ions using an ion chromatography (Dionex 600, USA), and the other part was used to determine WSOC using a Total Carbon Analyzer (TOC-L CPH, Shimadzu, Japan).

2.3 Calculation of aerosol liquid water content (LWC) and particle in-situ pH (pH_{is})

As for the calculation of aerosol LWC and pH_{is}, the ISORROPIA-II model that treated the Na^+ - NH_4^+ - K^+ - Ca^{2+} - Mg^{2+} - SO_4^{2-} - NO_3^- - Cl^- system was applied. The forward mode with a metastable state in the ISORROPIA model was adopted (Fountoukis and Nenes, 2007).

3 Results and Discussion

3.1 Overview of observations

Temporal variations in the concentrations of $PM_{2.5}$, PM_{10}, gaseous pollutants, major chemical components of $PM_{2.5}$, and meteorological parameters before and during the LCD are summarized in Table 1 and presented in Fig. 1. Both temperature and solar radiation exhibited a continuously increasing trend, whereas RH before the LCD was 1.4 times higher than that during the LCD. Wind speed (3.0 ± 0.7 m s^{-1}) before the LCD was smaller than that (3.7 ± 1.1 m s^{-1}) during the LCD (Table 1), suggesting that air pollution caused by emissions from the local and surrounding regions of Jinan city before the LCD was greater than that during the LCD, which was supported by the results of backward trajectory and PSCF analysis (Fig. S1).

The parameters of air quality including $PM_{2.5}$, PM_{10}, CO, SO_2, and NO_2 reduced by 39–62% during the LCD (Table 1, Fig. 1), suggesting that the air quality was better during the LCD because of the substantial reduction of anthropogenic emissions. O_3 in Chinese megacities during the wintertime is primarily produced from the NO_x-saturated regime because of the lack of HO_x radical (Li et al., 2021). Being opposite to other five air-quality parameters, O_3 concentration (66 ± 21 μg m^{-3}) during the LCD increased by 2.3 times compared to that (29 ± 18 μg m^{-3}) before the LCD (Table 1). O_3 is produced from nonlinear processes, and O_3 in Chinese cities is largely produced from NO_x (NO + NO_2)-saturated regime attributed to the scared HO_x radicals during the wintertime (Le et al., 2020). The significant drop of NO_2 during the LCD resulted in the reduction of NO concentration (Xu et al., 2020), and further alleviated the efficient titration effect of O_3 (Levy et al., 2014). Thus, the lower concentration of NO_2 during the LCD could lead to an increase in O_3 concentration. Besides, O_3 exhibited a negative correlation with $PM_{2.5}$ mass concentration ($R^2 = 0.57$) during the LCD, due to the weakened aerosol radiative effect on the photochemical formation of O_3 (Wu et al., 2020) and the reduced precursors of O_3 (Li et al., 2019). The more favorable atmospheric conditions such as the higher temperature and stronger solar radiation during the LCD were beneficial for the generation and accumulation of O_3 (Li et al., 2019). A recent study using the WRF−Chem model found that about 80% of the increased O_3 level in eastern China was mainly due to meteorological changes, and only 20% resulted from the reduced pollutant emissions (Wang et al., 2022).

The decreased concentrations of EC, OC, and WSOC in $PM_{2.5}$ but the enhanced ratios of OC/EC and WSOC/OC during the LCD (Table 1, Fig. 1) indicated more SOA productions due to the stronger photochemical oxidation during the LCD (Zhong et al., 2021). As a key tracer for biomass burning, levoglucosan showed a positive relationship with OC, EC, and WSOC ($R^2 \geq 0.45$) before the LCD rather than during the LCD ($R^2 \leq 0.15$) (Table S1), suggesting that biomass burning played an important role on carbonaceous species before the LCD rather than during the LCD. Secondary inorganic ions (SIA, total concentration of SO_4^{2-}, NO_3^-, and NH_4^+) were dominant components of $PM_{2.5}$, which accounted for the higher percentages ($47 \pm 8\%$) in $PM_{2.5}$ mass during the LCD than that ($40 \pm 6\%$) before the LCD, indicating an enhanced formation of secondary aerosols during the LCD. The Results of backward trajectory analysis showed that air masses before and during the LCD in Jinan were different (Fig. S1). Thus, the differences in above chemical species and ratios may be not only because of different emission strengths and types of sources, but also due to different air masses between these two periods. The LWC concentration of aerosol is determined by RH and SIA concentration (Meng et al., 2020). Given the higher RH and SIA concentration before the LCD, the LWC concentration (35 ± 33 μg m^{-3}) before the LCD was 3.4 times higher than

that (10 ± 10 μg m^{-3}) during the LCD. However, pH_{is} remained similar before (3.2 ± 3.0) and during the LCD (3.5 ± 3.5) with no significant statistical difference ($p > 0.05$, Table S2), indicating an insignificant difference in atmospheric aerosol acidity before and during the LCD.

3.2 Molecular distributions of diacids and related species

A homogeneous series of diacids (C_2–C_{11}), oxoacids, and α-dicarbonyls identified in $PM_{2.5}$ samples before and during the LCD are summarized in Table 2. To avoid the effect of atmospheric dilution due to the boundary layer height variations, here we use the ratios of SOA species to EC or CO to explore the secondary production of organic species (Yu et al., 2021). As shown in Fig. 2, the ratio of total concentration of detected organic components (TDOCs) normalized by CO (TDOCs/CO) increased exponentially with the increase of temperature before ($y = 257.46e^{0.019x}$, $R^2 = 0.56$, Fig. 5a) and during ($y = 301.49e^{0.067x}$, $R^2 = 0.58$, Fig. 5c) the LCD, which was consistent with the Arrhennius Law, confirming that TDCOCs in this study were primarily derived from secondary formation and the contribution of primary emissions was insignificant. TDOCs are considered as stable products of secondary oxidation for a number of hydrocarbons (Martinelango et al., 2007). The loss of diacids (e.g., C_2) through the photolysis of iron oxalate complexes is a dominant sink from field observations and model studies (Cheng et al., 2017; Pavuluri and Kawamura, 2012; Weller et al., 2014; Zhou et al., 2015), while these species are stable in the absence of Fe (Kunwar et al., 2019). Previous studies have pointed out that diacids and related compounds presented a strong correlation with temperature, emphasizing the significance of secondary formation of those compounds with the increase of temperature (Kawamura and Bikkina, 2016; Kawamura and Yasui, 2005; Meng et al., 2014, 2018). Therefore, the loss of diacids and related compounds may be negligible when the temperature increases. Additionally, the exponent number (0.067) of the regression trend line during the LCD was 3.5 times higher ($p < 0.05$) than that (0.019) before the LCD, indicating that the oxidation rate during the LCD was larger. Different secondary formation rates of TDOCs between these two observation periods were largely due to different meteorological factors (e.g., temperature, solar radiation, and RH), oxidants (e.g., O_3 and OH · radical), emission strengths and types of organic precursors, physicochemical properties of aerosols (e.g., pH_{is} and LWC), and other influencing factors.

To verify if the concentrations of target compounds and major ratios were of significant difference, statistic tests were performed for $PM_{2.5}$ samples before and during the LCD (Table S2 and Table S3). As shown in Table S2, the concentrations of organic species (except for α-dicarbonyls) and major ratios in $PM_{2.5}$ before and during the LCD presented p values less than 0.05, indicating that the abundances and compositions of the major species before and during the LCD were statistically different. TDOCs exhibited an upward trend from 437 ± 117 ng m^{-3} (246 – 833 ng m^{-3}) before the LCD to 486 ± 144 ng m^{-3} (179 –825 ng m^{-3}) during the LCD (Table 2). The concentrations of diacids and oxoacids during the LCD increased by 1.1 and 2.1 times, respectively, while α-dicarbonyls during the LCD was almost the same as that before the LCD. The concentrations of diacids and TDOCs in this study were significantly lower than those in Xi'an (Cheng et al., 2013), Chengdu (Li et al., 2015), Tianjin (Devineni et al., 2023; Zhao et al., 2023), Liaocheng (Meng et al., 2020), 14 Chinese cities, and other Asian megacities such as Padori, Daejeon (Zhao et al., 2023), Ulaanbaatar (Jung et al., 2010), Chennai (Pavuluri et al., 2010), and Tokyo (Kawamura and Yasui, 2005), but similar to those in Beijing (Zhao et al., 2018) and Guangzhou (Ho et al., 2011) during the wintertime (Table S4).

The daytime concentration of diacids before the LCD was 17% lower than that at night, which was opposite to the diurnal variation of diacids concentration during the LCD (Fig. 3a). As the predominant species throughout the whole observation period, C_2 concentration increased from 181 ± 47 ng m^{-3} before the LCD to 239 ± 108 ng m^{-3} during the LCD (Table 2), despite of the significant decrease in the primary pollutants from anthropogenic emissions during the LCD. C_2 is an end product derived from photochemical decomposition of longer-chain diacids or secondary oxidation of α-dicarbonyls and oxoacids, thus the ratios of C_2/diacids and C_2/TDOCs can be considered essential tracers for aerosol aging (Wang et al., 2012; Zhao et al., 2020). Both ratios of C_2/diacids and C_2/TDOCs during the LCD were higher than those before the LCD (Fig. 3b),

reflecting the more aged organic aerosols during the LCD. Therefore, the concentration of C_2 as well as its relative abundance in total diacids and TDOCs were higher during the LCD than those before the LCD, mainly due to the accelerated formation of C_2 during the LCD, which could offset the drop of organic precursors from anthropogenic emissions (Huang et al., 2020). Moreover, the daytime concentration of C_2 and the ratios of C_2/TDOCs and C_2/diacids were lower than those at night before the LCD but the opposite trends were found during the LCD, being consistent with the diurnal changes of total diacids before and during the LCD (Fig. 3). The second most abundant diacid was succinic acid (C_4), followed by malonic acid (C_3) and azelaic acid (C_9) before the LCD, while the second dominant diacid during the LCD was C_3, followed by C_4 and phthalic acid (Ph) (Table 2). Our results suggest that these species had different sources and underwent different formation processes because of different concentration levels of organic precursors and meteorological conditions before and during the LCD. Both ratios of C_2/C_4 and C_3/C_4 have been used as indicators of photochemical aging of diacids, because the hydroxylation of C_4 can be photodegraded into C_3 through the decarboxylation process, and C_3 can be photochemically oxidized into C_2 via intermediates (e.g., ketomalonic (kC_3) and hydroxymalonic acids) (Kawamura and Bikkina, 2016; Wang et al., 2010). Both C_2/C_4 (8.4 ± 3.4) and C_3/C_4 (1.6 ± 0.4) ratios during the LCD were higher than those (3.9 ± 1.5, 0.3 ± 0.1) before the LCD (Fig. 3b), indicating the stronger photochemical transformation of organic aerosols during the LCD. The C_3/C_4 ratio before the LCD was lower than that in other Asian megacities such as 14 Chinese cities (Ho et al., 2007), Beijing (Zhao et al., 2018), Daejeon (Devineni et al., 2023), and Chennai (Pavuluri et al., 2010), but comparable to that in Tianjin where biomass burning, biogenic sources, and their aging contributed significantly to diacids and related compounds (Devineni et al., 2023) (Table S4). However, the C_3/C_4 ratio during the LCD was much higher than that in other Asian megacities (Table S4), again implying the significantly enhanced photochemical oxidation during the LCD. Previous studies have demonstrated that the C_3/C_4 ratio presented a strong correlation with temperature when the contribution of local sources predominates over long-distance transport (Kawamura and Usukura, 1993; Pavuluri et al., 2010a; Wang et al., 2020). In this study, the C_3/C_4 ratio was correlated strongly with temperature before the LCD (R^2 = 0.54, Fig. 4a), indicating that diacids before the LCD were largely influenced by local sources. However, the C_3/C_4 ratio was correlated moderately with temperature (R^2 = 0.33, Fig. 4b) during the LCD, suggesting that the contribution of local sources was equal to that of long-range transport to diacids during the LCD. These results were consistent with the results of backward trajectory and PSCF analysis (Fig. S1). The higher ratios of C_2/C_4 and C_3/C_4 during the LCD may be due to the local photooxidation and aging effects of long-distance transport.

Azelaic acid (C_9) is primarily derived from the secondary oxidation of unsaturated fatty acids (e.g., oleic acid) with a double bond at the C-9 position (Kawamura and Usukura, 1993), which is abundant in the fresh and aged aerosols emitted from biomass burning (Shen et al., 2022). It is noteworthy that C_9 concentration (12 ± 4.0) before the LCD was 2.0 times higher than that (5.9 ± 4.8) during the LCD (Table 2), which was consistent with the variation of levoglucosan concentration (Table 1). C_9 showed a more robust relationship with levoglucosan before the LCD (R^2 = 0.74) than that (R^2 = 0.06) during the LCD (Table S1), suggesting that biomass burning was an essential contributor to C_9 before the LCD rather than during the LCD. Ph is primarily derived from the photochemical degradation of aromatic hydrocarbons (e.g., naphthalene) emitted from anthropogenic sources (Kawamura and Usukura, 1993). Although Ph was the most abundant diacid except for $C_2 - C_4$ during the LCD, its concentration (8.8 ± 6.1 ng m^{-3}) and relative abundance (2.3 ± 2.2%) during the LCD were lower than those (11.0 ± 6.1 ng m^{-3}, 3.2 ± 1.5%) before the LCD (Table 2, Fig. 3), suggesting the remarkable drop of anthropogenic emissions during the LCD.

As the important intermediate compounds of mono-carboxylic acids, oxoacids can ultimately generate diacids through heterogeneous oxidation processes (Wang et al., 2012; Yu et al., 2021). The diurnal variations of oxoacids presented similar patterns with diacids in each period (Fig. 3a). Moreover, oxoacids were correlated well with total diacids in each period, respectively (R^2 > 0.5, Fig. 2), indicating that oxoacids are the important intermediate species of diacids. The molecular distributions of oxoacids were characterized by the predominance of glyoxylic acid (ωC_2) and pyruvic acid (Pyr) in each

period. Previous studies have demonstrated that C_2 in urban aerosols is mainly generated from ωC_2 via aqueous oxidation (Cheng et al., 2015; Zhao et al., 2018). Therefore, C_2 is positively correlated with ωC_2 before and during the LCD, respectively ($R^2 > 0.5$, Fig. 4).

As the two smallest molecular weight α-dicarbonyls in the aerosols, glyoxal (Gly) and methylglyoxal (mGly) are originated from the photochemical oxidation of volatile organic compounds such as aromatics, isoprene, and monoterpenes in the gaseous phase, which are then partitioned into the aqueous phase of aerosols, and ultimately are oxidized to relatively lower volatility organic acids (e.g., ωC_2, Pyr, and C_2) (Carlton et al., 2007; Fu et al., 2008). Although the anthropogenic source emissions of α-dicarbonyls decreased dramatically during the LCD, the higher temperature and O_3 concentration during the LCD provided a favorable condition for α-dicarbonyls productions via secondary oxidation, which could offset the drop of primary emissions. Therefore, the concentration (24.7 ± 10.0 ng m^{-3}) of α-dicarbonyls during the LCD was about equal to that (25.1 ± 13.5 ng m^{-3}) before the LCD.

3.3 Aqueous formation of SOA before the LCD

The nighttime concentrations of C_2, diacids, and TDOCs exhibited higher values than those during the daytime as discussed above. Such diurnal variations may be ascribed to the descended planetary boundary layer (PBL) height at night, which can cause the enhanced concentrations of C_2 and related SOA. However, the increase in the ratios of C_2/diacids and C_2/TDOCs at night indicated that the effect of lowered nighttime PBL height was minor, which could be supported by the insignificant diurnal differences of primary pollutant markers such as Na^+, Ca^{2+}, and Mg^{2+} ($p > 0.05$, Table S3) between the daytime and nighttime. Considering the higher RH and LWC concentration at night, the increased concentrations of C_2 and related SOA during the nighttime may be closely linked to the accelerated aqueous production (Cheng et al., 2015; Meng et al., 2020).

The molecular pattern of TDOCs was predominated by C_2 followed by C_4 and C_3 as discussed above, consistent with the molecular distribution in biomass burning smoke (Kawamura et al., 2013; Kundu et al., 2010; Meng et al., 2020; Sorathia et al., 2018). To explore the contribution of biomass burning to TDOCs, levoglucosan, and K^+ were proposed as reliable markers for biomass burning (Hoffmann et al., 2010; Huang et al., 2006). K^+ is abundant in aerosols emitted from biomass burning (Andreae, 1983), thus K^+ exhibited a close correlation with levoglucosan (R^2=0.77, Table S1) before the LCD. There was no obvious diurnal difference of levoglucosan and K^+ between daytime (140 ± 54.9 ng m^{-3}, 2.0 ± 0.1 μg m^{-3}) and nighttime (141 ± 84.4 ng m^{-3}, 2.1 ± 0.4 μg m^{-3}), suggesting that the higher concentrations of C_2 and related SOA at night were irrelevant to the difference in the emission strength of organic precursors from biomass burning in the daytime and nighttime. C_2, diacids, and TDOCs exhibited strong correlations with levoglucosan and K^+ before the LCD ($R^2 > 0.5$), while such correlations were not observed during the LCD ($R^2 < 0.2$, Table S1), suggesting that biomass burning was an essential contributor to C_2 and related SOA before the LCD rather than during the LCD. The ratio of C_2/levoglucosan (1.7 ± 0.6) at night before the LCD exhibited a larger value than that (1.3 ± 0.5) in the day, which was mainly ascribed to the accelerated aqueous formation of C_2 at night (see following discussions in Section 3.3). Moreover, the mean values of C_2/levoglucosan (1.5 ± 0.6), C_2/K^+ (0.2 ± 0.03), C_4/levoglucosan (0.4 ± 0.1), and C_4/K^+ (0.05 ± 0.02) ratios before the LCD were higher than those (0.05, 0.05, 0.03, 0.03) in fresh particles emitted from savanna fires of southern African (Gao et al., 2003). It is interesting to note that the average ratios of C_2/C_4 (3.9 ± 1.5), C_3/C_4 (0.3 ± 0.1), and C_2/diacids (0.52 ± 0.55) before the LCD were almost equal to those (3.8, 0.3, and 0.55) measured in the aerosols for two days aging biomass samples via chamber experiment (Shen et al., 2022), suggesting that C_2 and related SOA before the LCD were linked tightly to the secondary oxidation of organic precursors emitted from biomass burning.

To explore the formation pathways and contributing factors of C_2 and related SOA before the LCD, the temporal variations of major diacids, LWC, pH_{is}, and meteorological parameters (e.g., solar radiation, temperature, and RH) were illustrated in Fig. 5. The SO_4^{2-} formation was largely from aqueous phase oxidation (see Text S5), thus the correlation analysis between SO_4^{2-} and C_2 can be used to evaluate the formation process of C_2 mainly via aqueous phase pathways (Sorathia et al., 2018).

C_2 was correlated significantly with SO_4^{2-} in the daytime (R^2 = 0.53) and nighttime (R^2 = 0.66) (Fig. S2) before the LCD, confirming the dominant aqueous-phase formation pathway of C_2. It is worth noting that the slope of the regression line of C_2/SO_4^{2-} ratio (0.005) at night was 1.3 times higher than that (0.004) during the daytime (Fig. S2). Both the higher slop and C_2 concentrations indicate a more efficient formation of C_2 at night, largely because the C_2 production requires multiple steps of aqueous oxidation from VOCs while the formation of SO_4^{2-} requires fewer steps (Miyazaki et al., 2009). Noticeably, the concentrations of C_2 and diacids, as well as C_2/diacids ratio culminated on the nighttime of January 23, which was characterized by significantly higher LWC concentration (172 μg m^{-3}) and RH (86.9%) (Fig. 5). Gly and mGly are gaseous oxidation products of biogenic and anthropogenic VOCs, and both are highly water-soluble (Carlton et al., 2006). In the presence of liquid water, both species can dissolve in the aqueous phase following Henry's law (Myriokefalitakis et al., 2011). The higher RH and LWC concentration were favorable for the partitioning of Gly and mGly from gaseous phase to aqueous phase and forming C_2. As shown in Fig. 5, the enhanced concentrations of Gly and mGly in $PM_{2.5}$ before the LCD were observed when RH and LWC increased. Thus, C_2 and its precursors (including Gly and mGly) were positively correlated with RH and LWC, respectively (R^2 > 0.45, Fig. 4a). Moreover, the ratios of C_2/Gly and C_2/mGly also showed a significant correlation with RH and LWC (R^2 > 0.4, Fig. 4a). Such strong correlations suggest that the higher LWC concentration and RH could not only promote the formations of C_2 and its precursors, but also facilitate the transformation of C_2 from the organic precursors. Therefore, LWC and RH can be regarded as vitally important factors controlling the aqueous production of C_2. The nighttime concentrations of LWC and RH were higher than those during the daytime, which led to the higher concentration and percentage contribution of C_2 in the nighttime.

Previous studies have reported that C_2 can also be derived from the chain-breaking of longer-chain diacids in the aqueous phase (Kawamura and Usukura, 1993; Miyazaki et al., 2009). However, there was moderate or no serious correlation between C_2 and longer-chain diacids (e.g., C_3 and C_4), respectively (R^2 < 0.3, Fig. 4a). Furthermore, longer-chain diacids and the ratios of C_2/C_3 and C_2/C_4 exhibited no significant correlation with LWC or RH (R^2 < 0.24, Fig. 4a). It can be concluded the effect of chain-breaking of longer homologous diacids on aqueous formation mechanism of C_2 was negligible in this study. Numerous studies have reported that the acidic condition of aerosol is beneficial to the BSOA formation such as 2-methylglyceric acid from BVOCs (e.g., isoprene), and ultimately be transformed into C_2 via Gly, mGly, and ωC_2 in the aqueous phase by acid-catalyzed oxidation reactions (Surratt et al., 2007). Laboratory experiment has pointed out that the acidic environment of aerosol can accelerate the uptake and production of Gly and mGly via acidic-catalyzed heterogeneous oxidation (Jang et al., 2002; Surratt et al., 2007). As shown in Fig. 4a, pH_{is} exhibited pronounced negative relationships with C_2 and its precursors such as Gly and mGly ($R^2 \geq 0.45$), which was also found in other field studies (Cheng et al., 2017; Meng et al., 2014; Wang et al., 2016; Yu et al., 2021), possibly because of the fact that aerosol acidity could favor the productions of C_2 and its precursors. Therefore, we could conclude that C_2 before the LCD was dominantly derived from the acidic-catalyzed aqueous oxidation with α-dicarbonyls rather than longer-chain diacids determined by RH and LWC. The reaction rate constant (3.6×10^8 M^{-1} s^{-1}) of ωC_2 with OH ·radical to form C_2 is smaller than that (2.9×10^9 M^{-1} s^{-1}) of its anion, glyoxylate, thus the coarse particles during the dust period, which are alkaline, are favorable for the C_2 formation from ωC_2 (Wang et al., 2015). Tan et al. (2009) reported that acidity had a minor effect on C_2 formation at cloud- and fog-relevant conditions via online experiments. Those findings necessarily conflicted with each other, largely because the concentration levels of organic precursors, acidity, LWC, and other influencing factors were different from the aerosols in our filed observations. Therefore, further field measurements of wet aerosols, laboratory experiments, and model simulations are urgently necessary to elucidate the influencing mechanism of acidity on C_2 formation.

3.4 Enhanced photochemical formation of SOA during the LCD

As discussed in Section 3.2, the concentrations of C_2, diacids, and TDOCs as well as the ratio of C_2/diacids during the LCD were higher than those before the LCD, despite the anthropogenic source strength dropping dramatically during the LCD.

Given the higher O_3 concentration and stronger solar radiation during the LCD (Table 1), it can be expected that the enhanced concentration and contribution of C_2 were driven by the promoted photochemical oxidation, which was supported by the significantly higher C_3/C_4 ratio (1.6 ± 0.4) during the LCD than that (0.3 ± 0.1) before the LCD. Since C_3 can be generated from photochemical oxidation of C_4 in the atmosphere (Kawamura and Bikkina, 2016), the relatively high C_3/C_4 ratio during the LCD (Fig. 3b) indicates that aerosols during the LCD experienced more substantial photochemical aging. Field measurements and chamber experiments have reported that C_2 can be principally originated from photochemical oxidation of α-dicarbonyls from VOCs driven by O_3 and OH ·radical (Meng et al., 2021; Mochizuki et al., 2017). Bikkina et al. (2021) reported a laboratory production of oxalic and other LMW diacids together with intermediate oxoacids and α-dicarbonyls by ozonolysis of isoprene. A few studies have observed that the OH ·radical in the North China Plain (e.g., Shandong Province) was higher during the LCD (e.g., in February 2020) than that before the LCD (Gaubert et al., 2021; Kang et al., 2021; Li et al., 2021). The reduced NO_x during the LCD could lead to higher OH · radical, because less OH · radical could be consumed with NO_2 to produce nitric acid (Gaubert et al., 2021). Besides, the elevated O_3 concentration during the LCD could result in the enhanced OH ·radical, as OH ·radical is mainly from the O_3 photolysis with the water vapor in the atmosphere (Kang et al., 2021). It could be concluded that the OH ·radical during the LCD was higher than before the LCD, being consistent with O_3 concentration. Because OH · radical was unavailable in this work, O_3 was used here as a marker for the oxidant concentration of photochemical oxidation. In addition, solar radiation could also be used as a reliable proxy for photochemical productions of C_2 and other diacids (Deshmukh et al., 2018). In view of the significant escalation of O_3 concentration and solar radiation during the LCD, it could be concluded that the productions of C_2 and related compounds may be closely involved in the photochemical pathways driven by the higher O_3 concentration and stronger solar radiation.

To investigate the formation mechanism and potential sources of C_2 and related SOA during the LCD, the temporal variations in C_2 and its precursors, O_3, as well as meteorological factors are presented in Fig. 5. It is interesting to note that the highest O_3 concentration was observed on the daytime of January 31 when the concentrations of C_2 and diacids reached their peaks. Moreover, both C_2 and diacids concentrations as well as the C_2/diacids ratio exhibited robust correlations with O_3 ($R^2 > 0.5$, Fig. 4b), respectively, suggesting that O_3 played an important role in the formation of C_2 and other diacids. Additionally, C_2 and diacids concentrations exhibited similar patterns of variations (Fig. 5) and strong correlations ($R^2 > 0.5$, Fig. 4b) with solar radiation during the daytime. However, such similarities and strong correlations of those were not observed with temperature ($R^2 < 0.2$, Fig. 4b and Fig. 5), suggesting that the effect of temperature on the photochemical formation of C_2 was negligible. The enhancement of temperature can promote the productions of C_2 and its precursors (Meng et al., 2018), while the increase in the temperature can accelerate the volatilization of C_2, leading to the drop of C_2 concentration in the aerosol phase (Bilde et al., 2015). These results confirmed that C_2 and other diacids were overwhelmingly derived from the photochemical processes driven by the stronger solar radiation, O_3, and other oxidants such as OH ·radical.

Numerous studies have demonstrated that the longer-chain diacids can be photochemically degraded into C_2 (Kawamura and Bikkina, 2016; Zhao et al., 2020). It is worth noting that C_2 was correlated strongly with longer-chain diacids such as C_3 and C_4, respectively ($R^2 > 0.5$, Fig. 4b). The ratio of C_2/diacids was correlated strongly with the ratios of C_3/C_4 ($R^2 = 0.68$) and C_2/C_4 ($R^2 = 0.58$, Fig. 4b), indicating that C_2 may be largely derived from the photochemical degradation of higher molecular weight homologues of diacids. However, the correlation of the C_2/diacids ratio with (C_3–C_{11})-C/WSOC ($R^2 = 0.12$) was weak, primarily because the supply rates of longer-chain diacids have been demonstrated to be faster than their degradation rates of forming C_2 (Zhao et al., 2020). C_2/diacids ratio was correlated robustly with solar radiation during the daytime ($R^2 = 0.76$, Fig. 4b). Previous study suggested that the correlation analysis of C_2/diacids, C_2/C_4, and C_3/C_4 with O_3 could indicate the photochemical chain-breaking of longer-chain diacids producing C_2 (Liu et al., 2021). These ratios were observed to be correlated significantly with O_3 ($R^2 > 0.45$, Fig. 4b). These results confirm that C_2 during the LCD was

primarily originated from the photochemical degradation of longer-chain homologous diacids that was driven by stronger solar radiation and higher O_3 concentration and other oxidants rather than higher temperature.

The photochemical oxidation of Gly and mGly has been proposed as a considerable regional and global source of C_2 (Carlton et al., 2007; Fu et al., 2008). Gly can be firstly oxidized to ωC_2 and subsequently to C_2, while mGly can be oxidized to C_2 via Pyr (Wang et al., 2012; Warneck, 2003). The correlations of C_2 with Gly (R^2 = 0.51) and ωC_2 (R^2 = 0.53) were stronger than those with mGly (R^2 = 0.38) and Pyr (R^2 = 0.04) (Fig. 4b). Moreover, the C_2/Gly ratio was correlated significantly with O_3 (R^2 = 0.49, Fig. 4b), whereas C_2/mGly ratio exhibited no correlation with O_3 (R^2 = 0.03, Fig. 4b). These results suggest that the photochemical oxidation of Gly via ωC_2 contributed more to the formation of C_2 than the oxidation of mGly via Pyr, in which O_3 and other oxidants may be important influencing factors.

3.5 Stable carbon isotopic compositions of diacids

$\delta^{13}C$ of specific organic acids can provide insights into the photochemical aging (or processing) of organic aerosols due to isotopic fractionation of carbon during the phase partitioning and/or photochemical oxidation (Wang et al., 2020a; Zhang et al., 2016). On average, most of the detected diacid homologues exhibited higher $\delta^{13}C$ values during the LCD than those before the LCD (Table 3, Fig. 6). A previous study demonstrated that the enhanced $\delta^{13}C$ values in diacid homologues were found with UV irradiation time (Pavuluri and Kawamura, 2016). Additionally, Shen et al. (2022) reported that the $\delta^{13}C$ value for C_2 in the 7-d aged biomass samples was higher than in the 2-d aged biomass samples using the combustion chamber. Thus, the enrichment of $\delta^{13}C$ values in diacid homologues during the LCD was mainly due to the promoted photochemical oxidation driven by the higher O_3 and the stronger solar radiation during the LCD. Similar to the diurnal variations in major diacids' concentrations, the nighttime $\delta^{13}C$ values of these detected diacids were more positive (or more negative) than those in the daytime before (or during) the LCD, which was ascribed to their different sources and formation processes in these two observation periods. In brief, the $\delta^{13}C$ values exhibited a decreasing trend as the carbon numbers of diacids increased (Fig. 6), consistent with other observation campaigns elsewhere (Meng et al., 2020; Pavuluri and Kawamura, 2016; Wang and Kawamura, 2006). The mean $\delta^{13}C$ value (−20 ± 2.5‰) of C_2 was the heaviest in each period (Table 3), which was comparable to that (−20 ± 3.5‰) observed in its surrounding city such as Liaocheng (Meng et al., 2020), and higher than the values obtained in other China's megacities such as Beijing (−23 ± 3.4‰) (Zhao et al., 2018) and Xi'an ($PM_{2.1}$: from −21 to −24‰) (Wang et al., 2012), but smaller than the values measured in the Korea Climate Observatory at Gosan (−16 ± 4.3‰) of East Asia (Zhang et al., 2016) and western Pacific and Southern Ocean (−17 ± 0.8‰) (Wang and Kawamura, 2006) in the winter (Fig. 7). It is worth noting that the average $\delta^{13}C$ value of C_2 (−22 ± 1.9‰) before the LCD was equal to that (−22 ± 1.2‰) determined in the 2 d biomass samples (Shen et al., 2022) (Fig. 7), confirming that biomass burning and subsequent oxidation exerted an important effect on C_2 before the LCD.

As mentioned above, C_2 can be not only originated from the photochemical breakdown (or decomposition) of C_3 and C_4 via kC_3 and hydroxymalonic acids (hC_4), but also be derived from the photochemical oxidation of aromatic hydrocarbons via ωC_2. The positive correlations of the ^{13}C values of C_2 with mass ratios of $C_2/\omega C_2$ ($R^2 \geq 0.39$) and C_2/kC_3 ($R^2 \geq 0.37$) during the LCD were observed, whereas such robust relations only with $C_2/\omega C_2$ ($R^2 \geq 0.47$) rather than C_2/kC_3 ($R^2 \geq 0.01$) before the LCD were observed (Fig. 8). These results imply that the effect of photochemical decomposition of higher diacid homologues on C_2 before the LCD was minor, which was consistent with the discussions in Section 3.3. The isotopic values of diacids followed the order of $C_2 > C_3 > C_4$ in each period (Fig. 6), primarily because diacids containing more carbon numbers may be more reactive to oxidants such as O_3 and OH radical in the atmosphere (Aggarwal and Kawamura, 2008). On the other hand, the removal of CO_2/CO in the processes of C_3 and C_4 reacting with atmospheric oxidants can generate more ^{13}C-enriched C_2 due to the KIEs (Wang and Kawamura, 2006). The isotopic values of C_9 ranged from −25 to −30‰ before the LCD, whose difference was less distinguished than those of C_2−C_4 (Table 3). It is worth noting that the $\delta^{13}C$ values of organic species from marine plankton (−20‰) are higher than those from terrestrial higher plants (C_3 plants:

−27‰). The $\delta^{13}C$ values of C_9 and the strong correlation of C_9 with levoglucosan before the LCD as discussed above indicate that biomass burning emitting unsaturated fatty acids and subsequent aqueous oxidation was an important contributor to C_9 in Jinan during the wintertime. The most negative $\delta^{13}C$ value among the identified organic species was tPh throughout the entire period, whose $\delta^{13}C$ value (−35 ± 3.1‰) was approximately equal to that (−35 ± 5.3‰) in Liaocheng (Meng et al., 2020) and lighter than that (−34 ± 3.4‰) in Beijing (Zhao et al., 2018) of China where the primary emissions from the combustion of plastic wastes is an essential source of tPh. Moreover, the $\delta^{13}C$ value of tPh was negatively (one outlier that possessed a relatively high relative abundance of tPh in diacids was removed) in the daytime or poorly correlated with the ratio of tPh/diacids at night before the LCD (Fig. 8f). The $\delta^{13}C$ value of tPh presented a negative correlation with the tPh/diacids during the LCD (Fig. 8l). These results suggest that the primary sources of plastic wastes burning exerted a significant impact on tPh in the atmosphere of Jinan.

Similarly, the $\delta^{13}C$ value of oxoacids increases as carbon number decreases (Table 3, Fig. 6). ωC_2 has the highest $\delta^{13}C$ value, followed by Pyr, and ωC_3 before and during the LCD. The more pronounced enhancement of $\delta^{13}C$ values in C_2 and ωC_2 in each period suggests that C_2 in Jinan aerosols was mainly originated from aqueous oxidation of ωC_2 (Meng et al., 2020). However, the lighter isotope (^{12}C) was more enriched in ωC_2 than both Gly and mGly (Table 3) in each period. ωC_2 is largely derived from the photochemical oxidation of organic precursors such as α-dicarbonyls and acetic acid (Carlton et al., 2007). ^{12}C can be preferentially accumulated in the products in the non-reversible chemical processes (Wang et al., 2012), resulting in the lighter $\delta^{13}C$ values of ωC_2 than its precursors. mGly was less enriched in ^{13}C than Gly (Table 3, Fig. 6) in each period, which was attributed to the lower vapor pressure and higher carbon numbers of mGly that may lead to the weaker isotopic fractionation (Zhang et al., 2016).

It is well established that the ^{13}C values of diacids and related compounds become isotopically heavier in the aging process of organic aerosols (Pavuluri and Kawamura, 2016; Zhang et al., 2016). As mentioned above, the ratios of C_2/Gly, C_2/mGly, and C_2/diacids are usually considered significant proxies to evaluate the aging of organic aerosols. These ratios exhibited strong correlations with the ^{13}C values of C_2 in each period ($R^2 > 0.4$, Fig. 8), indicating the production of more ^{13}C-enriched C_2 during the aging processes. The less depletion of ^{13}C in C_2 of aged organic aerosols conformed to the actual secondary KIE on activated H-atom abstraction by OH radical rather than to the mass dependence of collision frequencies in the gas phase (Enami et al., 2015). Organic species can react with OH radical and other atmospheric oxidants in the atmospheric oxidation reactions, which result in the removal of CO_2/CO containing ^{12}C and cause the oxidation products more enriched with the heavier isotope ^{13}C (Narukawa et al., 1999). Therefore, the ^{13}C values of major diacids and the related compounds during the LCD were less negative than those before the LCD, again demonstrating that the photochemical oxidation was promoted during the LCD because of the higher temperature and O_3 concentration under the more clear sky conditions.

3.6 Comparison of the source fingerprinting before and during the LCD

To further investigate the crucial sources of diacids and related compounds, positive matrix factorization (PMF) was adopted. Detailed information about PMF analysis was described in Text S3. The model stability of the five-factor solution and error estimation diagnostics were detailed in Table S5 and Table S6, respectively. The PMF-resolved source profiles for the five factors before and during the LCD were shown in Fig. 9. Before the LCD, C_2, C_3, ωC_2, Pyr, Gly, mGly, LWC, WSOC, NO_3^-, SO_4^{2-}, and NH_4^+ exhibited the relatively higher loadings in the first factor (Fig. 9a). SO_4^{2-} is a representative product of secondary oxidation in the aqueous phase, and LWC had been proved to be a significant influencing factor during the aqueous oxidation as discussed above. Therefore, the first factor was considered the sources from aqueous phase oxidation. The second factor was characterized by the stronger loadings of C_3, C_4, Ph, and EC. Ph is generated from the photochemical oxidation of polycyclic aromatic hydrocarbons (e.g., naphthalene) that are primarily emitted from the domestic coal combustion in China's megacities (Zhao et al., 2018), thus the second factor was categorized as a coal combustion source. O_3 had been confirmed to be a reliable proxy for gaseous photochemical oxidation, thus the robust relationships of O_3,

α-dicarbonyls, and ωC_2 with the third factor indicated the contribution of gaseous photochemical oxidation. The fourth factor was significantly associated with Mg^{2+} and Ca^{2+}, which represented dust emission. As an important indicator of biomass burning, levoglucosan was strongly correlated with C_9 and EC in the fifth factor. Although diacids and related compounds can be produced from the secondary oxidation of organic precursors from biomass burning (Cao et al., 2017; Kawamura et al., 2013), biomass burning can directly emit those compounds (Fu et al., 2008; Gao et al., 2003; Kundu et al., 2010; Narukawa et al., 1999; Shen et al., 2022). Thus, the fifth factor could be regarded as a primary source of biomass burning.

During the LCD, the first factor was dominated by O_3, major diacids, and α-dicarbonyls (Fig. 9b), which represented gaseous photochemical oxidation. The second factor was strongly correlated with C_2, C_4, LWC, WSOC, NO_3^-, SO_4^{2-}, and NH_4^+, suggesting a significant contribution of aqueous oxidation. Levoglucosan, C_9, EC, and OC presented the stronger loadings in the third factor, indicating a primary source of biomass burning. Mg^{2+} and Ca^{2+} exhibited strong correlations with the fourth factor, suggesting the sources from dust emission. Ph and EC presented strong correlations with the fifth factor, representing a coal combustion source.

The PMF-resolved relative contributions to the detected species before and during the LCD were presented in Fig. 9c and Fig. 9d, respectively. The aqueous oxidation made the greatest contribution (47.2%) to C_2 and related compounds before the LCD, while it accounted for only 16.1% in the total identified sources during the LCD. The gaseous photochemical oxidation contributed the largest percentage (50.5%) to the total identified sources, confirming that such a source exerted a leading role in the formation of homologous diacids during the LCD, which was in agreement with the results as discussed above. The contribution of biomass burning increased from 11.4% before the LCD to 13.6% during the LCD. However, the contribution of coal combustion decreased from 16.2% before the LCD to 7.2% during the LCD, largely because of the decreased usage of coal for the industry during the LCD.

4 Summary and conclusions

To explore the impact of LCD on the SOA, $PM_{2.5}$ aerosols from Jinan, a megacity in East China, before and during the LCD were analyzed for OC, EC, WSOC, inorganic ions, diacids, oxoacids, and α-dicarbonyls. Due to the sharp dropping in human activities, the air pollutants including $PM_{2.5}$, PM_{10}, CO, SO_2, and NO_2 during the LCD reduced by 39.3–62.4% than those before the LCD. However, the O_3 concentration increased by 1.3 times synchronously during the LCD. The concentrations of diacids and oxoacids during the LCD exhibited upward trends, while α-dicarbonyls during the LCD was almost equal to that before the LCD. C_2 before the LCD was significantly derived from the acid-catalyzed aqueous phase oxidation of organic precursors emitted from biomass burning where RH and LWC played a significant role. However, C_2 during the LCD was dominantly generated from the photochemical degradation of longer-chain homologous diacids driven by stronger solar radiation and higher O_3 concentration rather than higher temperature. The $\delta^{13}C$ values of major detected diacids were more positive during the LCD than before the LCD, with the largest value (-20 ± 2.5‰) for C_2 and the smallest (-35 ± 3.1‰) for tPh. The ratios of C_2/Gly, C_2/mGly, and C_2/diacids exhibited strong correlations with ^{13}C values of C_2, indicating the more enriched ^{13}C in C_2 during the aging processes of organic aerosols. The molecular distributions of diacid homologues and PMF results suggest that TDOCs in Jinan were primarily derived from the aqueous mechanisms of organic precursors emitted from coal combustion and biomass burning before the LCD, while these species were principally derived from the photochemical pathways during the LCD.

Data availability. The data in this study are available at: https://doi.org/10.5281/zenodo.7533247 (Meng et al., 2023).

Author contribution. PF designed the study. WY, LY, HT, and CM carried out the experiments and performed the data analysis. JM prepared the manuscript with contributions from all co-authors.

Competing interests. The authors have the following competing interests: One of the coauthors, Prof. Kimitaka Kawamura is one of the editorial members of this journal.

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835 **Table 1. Meteorological parameters, liquid water content (LWC) of aerosol, in-situ pH (pH_{is}), and chemical compositions of $PM_{2.5}$ before (January 6 – 23, 2020) and during the lockdown (LCD) (January 31 – February 17, 2020) in Jinan, China.**

	Before the LCD (*n*=36)	During the LCD (*n*=36)	Whole period (*n*=72)
I. Meteorological parameters			
Temperature (^oC)	0.07 ±5.9 (-16–13)	6.8 ±5.2 (-3.4–16)	3.4 ±6.5 (-16–16)
Relative humidity (%)	52 ±10 (30–87)	39 ±18 (17–85)	45 ±16 (17–87)
Solar radiation (W m^{-2})	164 ±70 (32–282)	255 ±117 (18–423)	209 ±106 (18–423)
Wind speed (m s^{-1})	3.0 ±0.7 (1.6–4.6)	3.7 ±1.1 (1.2–6.6)	3.3 ±1.0 (1.2–6.6)
II. Gaseous pollutants (μg m^{-3})			
SO_2	23 ±8.9 (8.3–49)	14 ±4.9 (4.9–29)	18 ±8.5 (4.9–49)
NO_2	56 ±12 (38–82)	21 ±5.9 (9.3–34)	38 ±20 (9.3–81)
CO	1.6 ±0.3 (0.9–2.5)	0.9 ±0.2 (0.5–1.6)	1.3 ±0.5 (0.5–2.5)
O_3	29 ±18 (5.3–74)	66 ±21 (25–109)	48 ±27 (5.3–109)
III. Inorganic ions (μg m^{-3})			
K^+	1.0 ±0.1 (0.9–1.7)	1.3 ±0.6 (0.5–2.9)	1.1 ±0.4 (0.5–2.9)
Na^+	0.3 ±0.1 (0.1–0.6)	0.2 ±0.1 (0.1–0.8)	0.2 ±0.1 (0.1–0.8)
Ca^{2+}	0.4 ±0.2 (0.1–0.9)	0.5 ±0.2 (0.2–1.1)	0.5 ±0.2 (0.1–1.1)
Mg^{2+}	0.1 ±0.03 (0–0.1)	0.1 ±0.1 (0.1–0.4)	0.1 ±0.1 (0–0.4)
NH_4^+	11 ±5.7 (4.4–26)	7.7 ±4.7 (0.4–16)	9.6 ±5.5 (0.4–26)
NO_3^-	19 ±11 (5.4–49)	9.6 ±4.9 (1.2–18)	14 ±9.7 (1.2–49)
SO_4^{2-}	13 ±6.9 (3.8–31)	9.4 ±5.3 (1.1–18)	11 ±6.4 (1.1–31)
SNA[a]	44 ±23 (15–105)	27 ±15 (2.8–50)	35 ±21 (2.8–105)
Subtotal	49 ±24 (18–113)	35 ±18 (6.1–67)	42 ±22 (6.1–113)
IV. Carbonaceous species (μg m^{-3})			
EC	4.3 ±2.4 (0.9–11)	1.9 ±1.0 (0.3–3.8)	3.1 ±2.2 (0.3–11)
OC	10 ±3.0 (5.2–19)	6.4 ±2.6 (2.0–11)	8.3 ±3.4 (2.0–19)
WSOC	3.9 ±1.9 (1.2–10)	3.2 ±1.4 (1.0–7.0)	3.5 ±1.7 (1.0–10)
OC/EC	2.9 ±1.3 (1.5–6.9)	4.0 ±1.5 (2.4–8.4)	3.5 ±1.5 (1.5–8.4)
WSOC/OC	0.4 ±0.1 (0.2–0.7)	0.5 ±0.1 (0.3–0.8)	0.4 ±0.1 (0.2–0.8)
V. Other species			
$PM_{2.5}$ (μg m^{-3})	106 ±45 (35–202)	56 ±29 (10–111)	81 ±46 (10–202)
PM_{10} (μg m^{-3})	147 ±58 (38–285)	72 ±33 (19–129)	109 ±60 (19–285)
Levoglucosan (ng m^{-3})	141 ±70 (50–370)	102 ±29 (61–186)	121 ±57 (50–370)
pH_{is}	3.2 ±3.0 (2.3–7.7)	3.5 ±3.5(2.8–4.9)	3.3 ±3.1 (2.3–7.7)
LWC (μg m^{-3})	35 ±33 (4.3–172)	10 ±10 (0.2–45)	24 ±30 (0.2–172)
$SNA/PM_{2.5}$ (%)	40 ±6.5 (29–54)	47 ±8.2 (28–60)	43 ±8.1 (28–60)
N/S[b]	1.5 ±0.3 (0.9–2.4)	1.1 ±0.2 (0.7–1.5)	1.3 ±0.4 (0.7–2.4)

[a]Total concentration of SO_4^{2-}, NO_3^-, and NH_4^+.
[b]The ratio of NO_3^-/SO_4^{2-}.

840 **Table 2. Concentrations (ng m^{-3}) of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in $PM_{2.5}$ before and during the LCD in Jinan.**

Compounds	Before the LCD (*n* = 36)	During the LCD (*n* = 36)	Whole period (*n* = 72)
I. Dicarboxylic acids			
Oxalic, C_2	181 ±48 (110–381)	239 ±108 (46–478)	210 ±88 (46–478)
Malonic, C_3	15 ±4.3 (5.2–26)	45 ±14 (18–79)	30 ±19 (5.2–79)
Succinic, C_4	54 ±29 (15–178)	30 ±13 (11–66)	42 ±25 (11–178)
Glutaric, C_5	6.7 ±4.5 (0.6–20)	7.5 ±4.0 (0.7–15)	7.1 ±4.2 (0.6–20)
Adipic, C_6	9.2 ±8.6 (1.7–41)	6.1 ±3.3 (0.9–14)	7.6 ±6.7 (0.9–41)
Pimelic, C_7	2.3 ±1.5 (0.2–7.4)	1.9 ±1.4 (0–5.1)	2.1 ±1.5 (0–7.4)
Suberic, C_8	7.7 ±4.7 (1.9–23)	3.0 ±2.4 (0.1–13)	5.4 ±4.4 (0.1–23)
Azelaic, C_9	12 ±4.0 (5.8–24)	5.9 ±4.8 (0.4–23)	9.0 ±5.3 (0.4–24)
Sebacic, C_{10}	3.9 ±2.3 (1.3–9.9)	2.6 ±1.5 (0.2– 5.1)	3.3 ±2.0 (0.2– 9.9)
Undecanedioic, C_{11}	4.0 ±2.9 (0.5–15)	3.5 ±1.9 (0.3–8.6)	3.8 ±2.4 (0.3–15)
Methylmalonic, iC_4	3.5 ±4.1 (0.2–13)	4.8 ±4.6 (0–17)	4.1 ±4.4 (0–17)
Mehtylsuccinic, iC_5	4.2 ±3.5 (0.4–12)	3.4 ±1.6 (0.4–6.1)	3.8 ±2.7 (0.4–12)
Methyglutaric, iC_6	2.2 ±1.1 (0.4–5.6)	2.4 ±1.4 (0–6.6)	2.3 ±1.3 (0–6.6)
Maleic, M	6.9 ±6.2 (0.8–34)	5.0 ±2.3 (0.6–11.0)	5.9 ±4.7 (0.6–34)
Fumaric, F	10 ±7.6 (2.3–44)	1.5 ±0.9 (0.2–4.8)	5.8 ±6.9 (0.2–44)
Methylmaleic, mM	5.5 ±4.3 (1.4–22)	4.2 ±3.3 (0–16)	4.9 ±3.9 (0–22)
Phthalic, Ph	11 ±6.1 (2.9–34)	8.8 ±6.1 (1.2–25)	9.9 ±6.2 (1.2–34)
Isophthalic, iPh	3.0 ±3.9 (0.2–24)	1.8 ±2.4 (0–9.9)	2.4 ±3.3 (0–24)
Terephthalic, tPh	2.0 ±1.4 (0.2–7.5)	1.3 ±0.8 (0.1–2.6)	1.6 ±1.2 (0.1–7.5)
Ketomalonic, kC_3	2.1 ±1.4 (0.3–6.3)	3.0 ±1.7 (0.2–7.4)	2.6 ±1.6 (0.2–7.4)
Ketopimelic, kC_7	5.1 ±4.7 (0.8–20)	5.7 ±4.2 (0.2–17)	5.4 ±4.4 (0.2–20)
Subtotal	351 ±92 (212–672)	386 ±127 (121–707)	369 ±112 (121–707)
II. Oxocarboxylic acids			
Pyruvic, Pyr	13 ±4.9 (4.4–25)	21 ±8.8 (7.3–43)	17 ±8.2 (4.4–43)
Glyoxylic, ωC_2	24 ±9.1 (6.6–43)	29 ±8.5 (10–43)	26 ±9.0 (6.6–43)
3-Oxopropanoic, ωC_3	4.5 ±4.6 (0.8–25)	12 ±6.5 (0.6–27)	8.4 ±6.9 (0.6–27)
4-Oxobutanoic, ωC_4	7.1 ±6.4 (0.8–38)	3.1 ±2.7 (0–12)	5.1 ±5.3 (0–38)
7-Oxoheptanoic, ωC_7	2.3 ±2.2 (0.2–8.6)	1.9 ±2.0 (0–8.6)	2.1 ±2.1 (0–8.6)
8-Oxooctanoic, ωC_8	3.2 ±2.8 (0.4–16)	3.7 ±2.1 (0.1–9.3)	3.4 ±2.4 (0.1–16)
9-Oxononanoic, ωC_9	6.9 ±3.0 (1.5–15)	3.4 ±2.9 (0–9.0)	5.2 ±3.4 (0–15)
Subtotal	61 ±20 (25–106)	75 ±17 (37–104)	68 ±19 (25–106)
III. α-Dicarbonyls			
Glyoxal, Gly	13 ±6.3 (4.4–32)	13 ±5.3 (2.0–28)	13 ±5.8 (2.0–32)
Methylglyoxal, mGly	12 ±7.6 (2.6–30)	12 ±4.8 (2.4–21)	12 ±6.0 (2.4–30)
Subtotal	25 ±14 (7.8–62)	25 ±10 (4.4–49)	25 ±12 (4.4–62)
Total detected species	437 ±117 (246–833)	486 ±144 (179–825)	461 ±132 (179–833)

Table 3. Differences in the stable carbon isotopic compositions ($\delta^{13}C$, ‰) of major detected diacids and related compounds before and during the LCD.

Compounds	Before the LCD (*n* = 36)	During the LCD (*n* = 36)	Whole period (*n* = 72)
	I. Dicarboxylic acids		
C_2	−22 ± 1.9 (−26 to −17)	−19 ± 2.5 (−24 to −14)	−20 ± 2.5 (−26 to −14)
C_3	−25 ±4.2 (−36 to −19)	−23 ± 2.2 (−26 to −18)	−24 ± 3.6 (−36 to −18)
C_4	−28 ± 4.6 (−39 to −22)	−25 ± 2.4 (−29 to −20)	−26 ± 4.0 (−39 to −20)
C_6	−29 ± 3.4 (−38 to −23)	−27 ± 2.8 (−31 to −22)	−28 ± 3.3 (−38 to −22)
C_9	−27 ± 1.2 (−30 to −25)	−27 ± 2.3 (−32 to −24)	−27 ± 1.8 (−32 to −24)
Ph	−39 ± 6.4 (−51 to −27)	−30 ± 2.6 (−36 to −26)	−34 ± 6.4 (−51 to −26)
tPh	−37 ± 4.1 (−46 to −26)	−34 ± 0.9 (−36 to −32)	−35 ± 3.1 (−46 to −26)
	II. Oxocarboxylic acids		
Pyr	−28 ± 4.0 (−39 to −22)	−24 ± 2.3 (−29 to −20)	−26 ±3.9 (−39 to −20)
ωC_2	−27 ± 3.6 (−38 to −22)	−23 ± 2.2 (−26 to −19)	−25 ± 3.6 (−38 to −19)
ωC_3	−29 ± 4.0 (−40 to −24)	−26 ± 2.3 (−30 to −22)	−28 ± 3.7 (−40 to −22)
	III. α-Dicarbonyls		
Gly	−23 ± 3.7 (−36 to −19)	−20 ± 2.2 (−24 to −16)	−21 ± 3.5 (−36 to −16)
mGly	−25± 3.8 (−37 to −21)	−21 ± 2.0 (−25 to −18)	−23 ± 3.6 (−37 to −18)

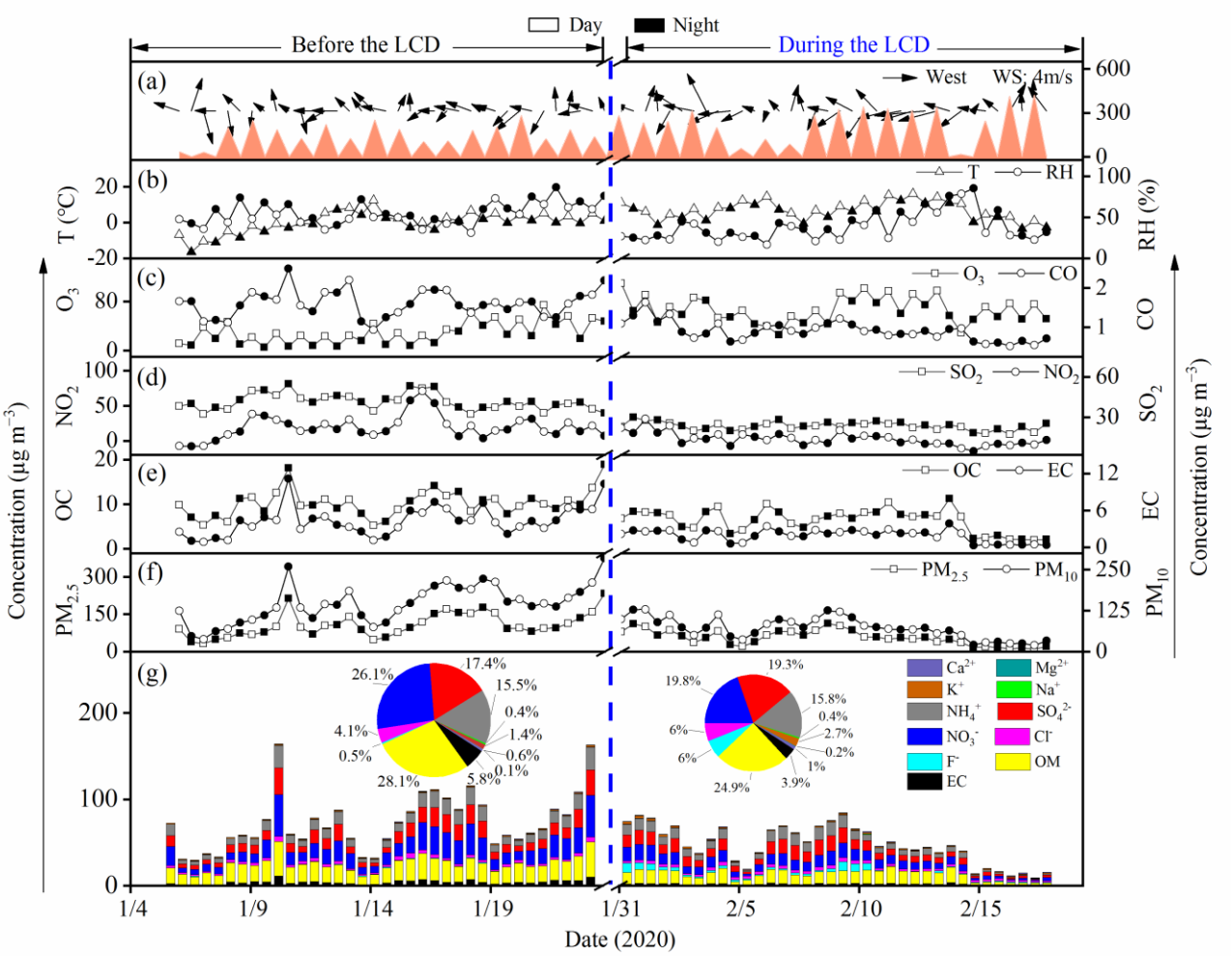

Figure 1. Temporal variations of gaseous pollutants, meteorological parameters, and chemical compositions of $PM_{2.5}$ before and during the LCD.

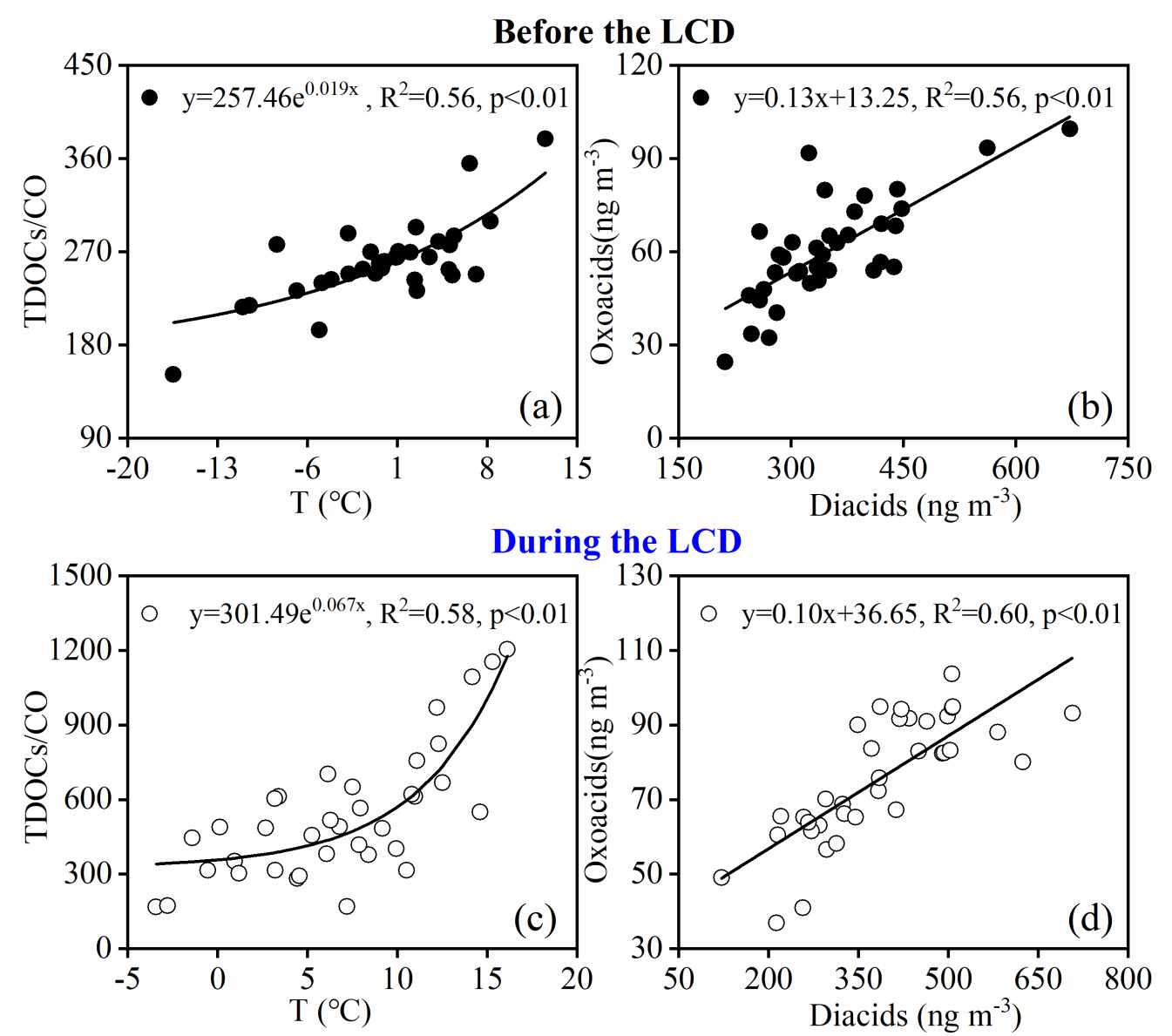

Figure 2. Correlation analysis between the ratio of total concentration of detected organic components (TDOCs) normalized by CO (TDOCs/CO) and temperature, and between diacids and oxoacids (a) and (b) before the LCD, (c) and (d) during the LCD.

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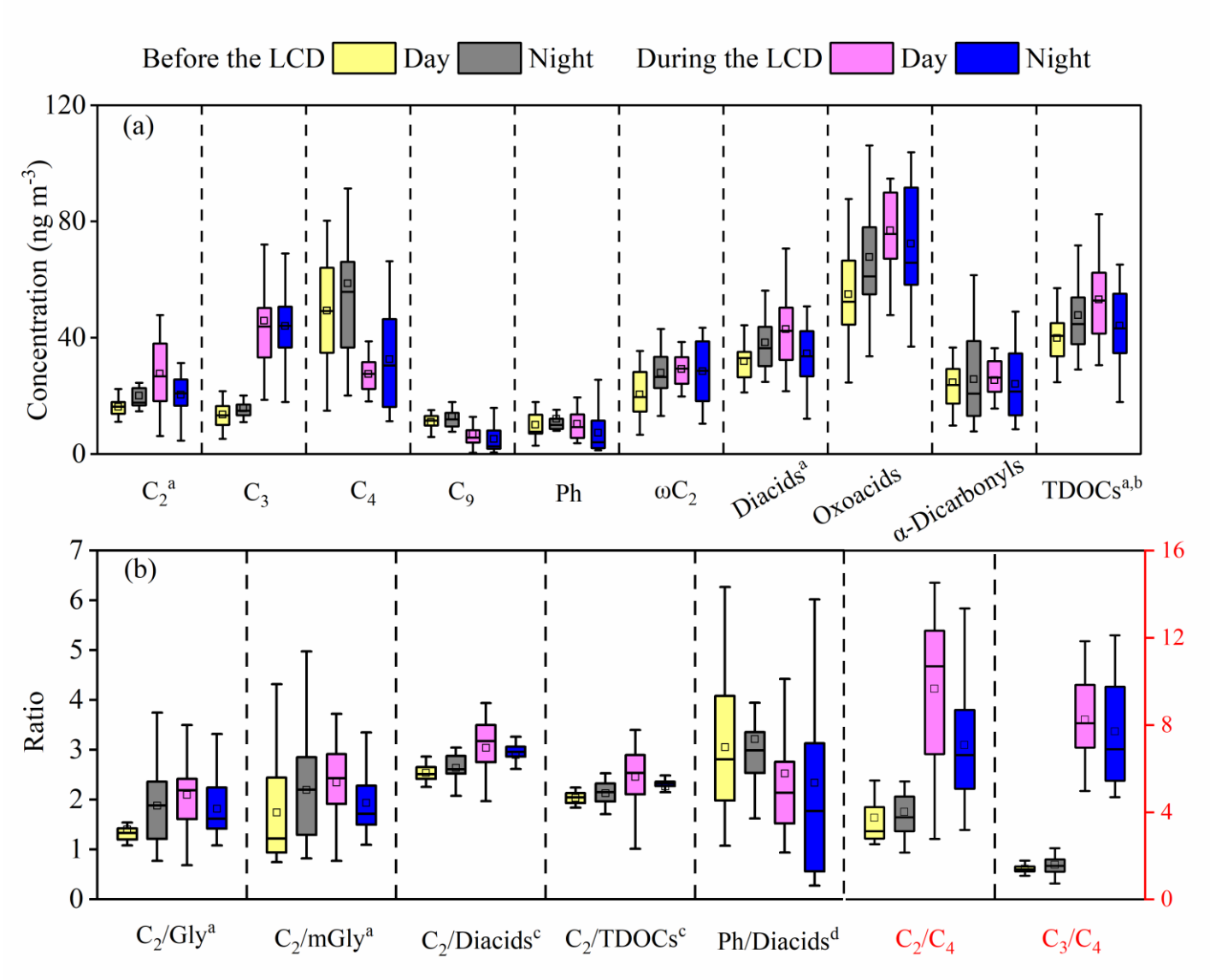

Figure 3. Diurnal changes of (a) major organic compounds and (b) selected mass ratios before and during the LCD ([a] the concentrations reduced by 10 times; [b] TDOCs: total detected organic components; [c] the mass ratios enlarged by 5 times; [d] the mass ratio enlarged by 100 times).

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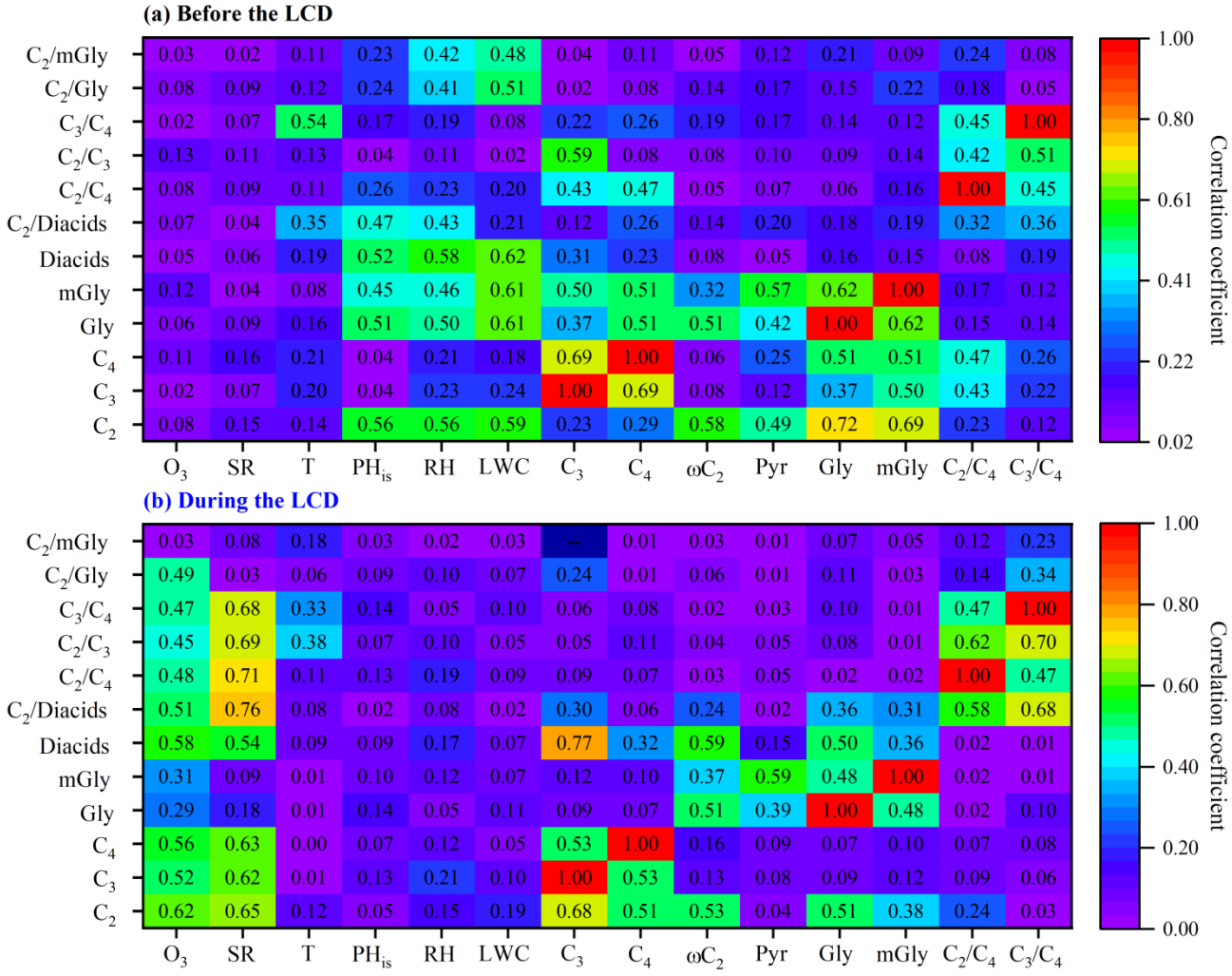

Figure 4. Correlation coefficients (R^2) of concentrations of C_2 and its organic precursors and selected ratios with influencing factors (a) before the LCD and (b) during the LCD.

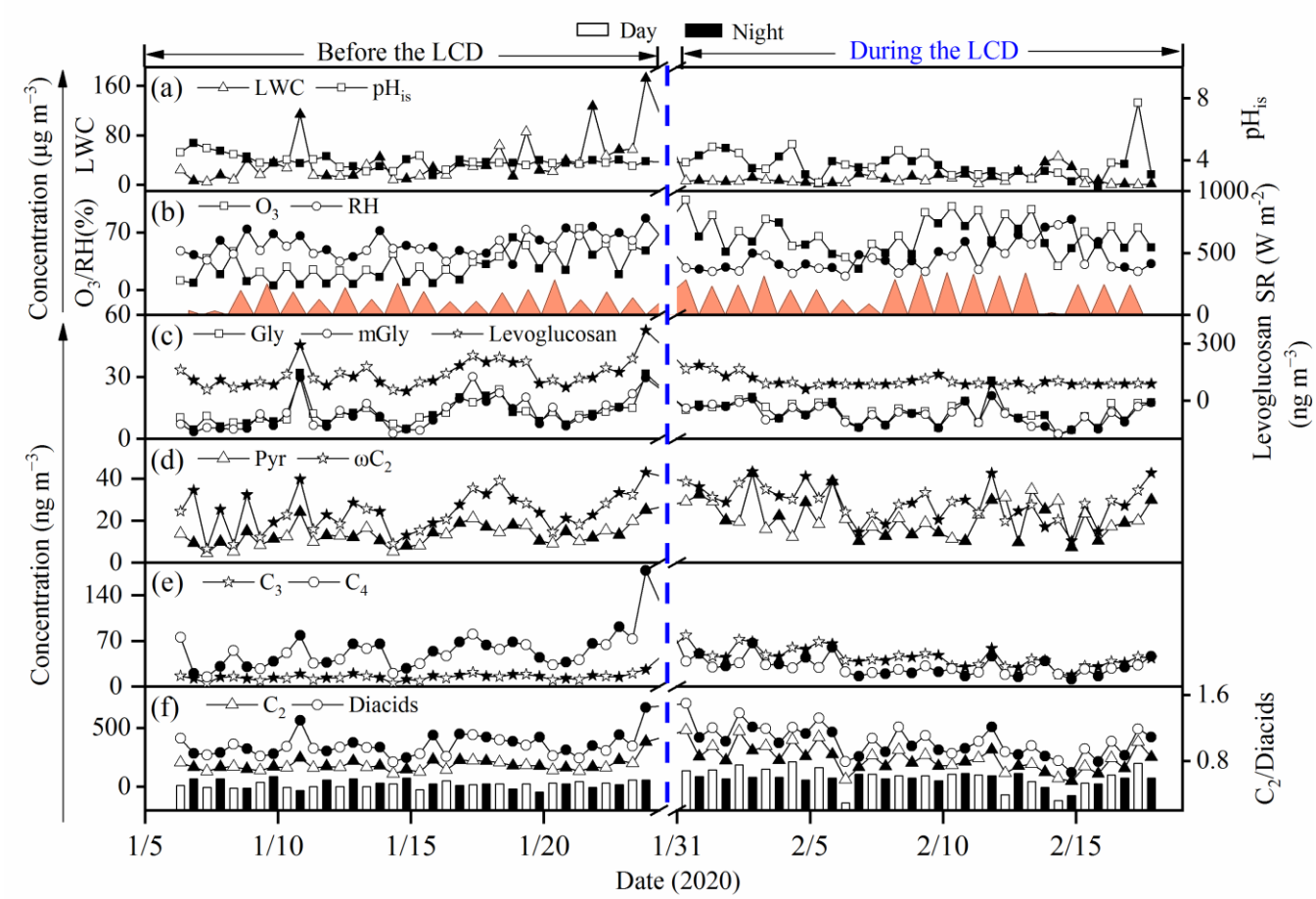

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Figure 5. Temporal variations in the concentrations of levoglucosan, diacids, C_2 and its major precursors, the ratios of C_2/Diacids, as well as liquid water content (LWC), in-situ pH (pH_{is}), temperature, relative humidity (RH), solar radiation, and O_3 before and during the LCD.

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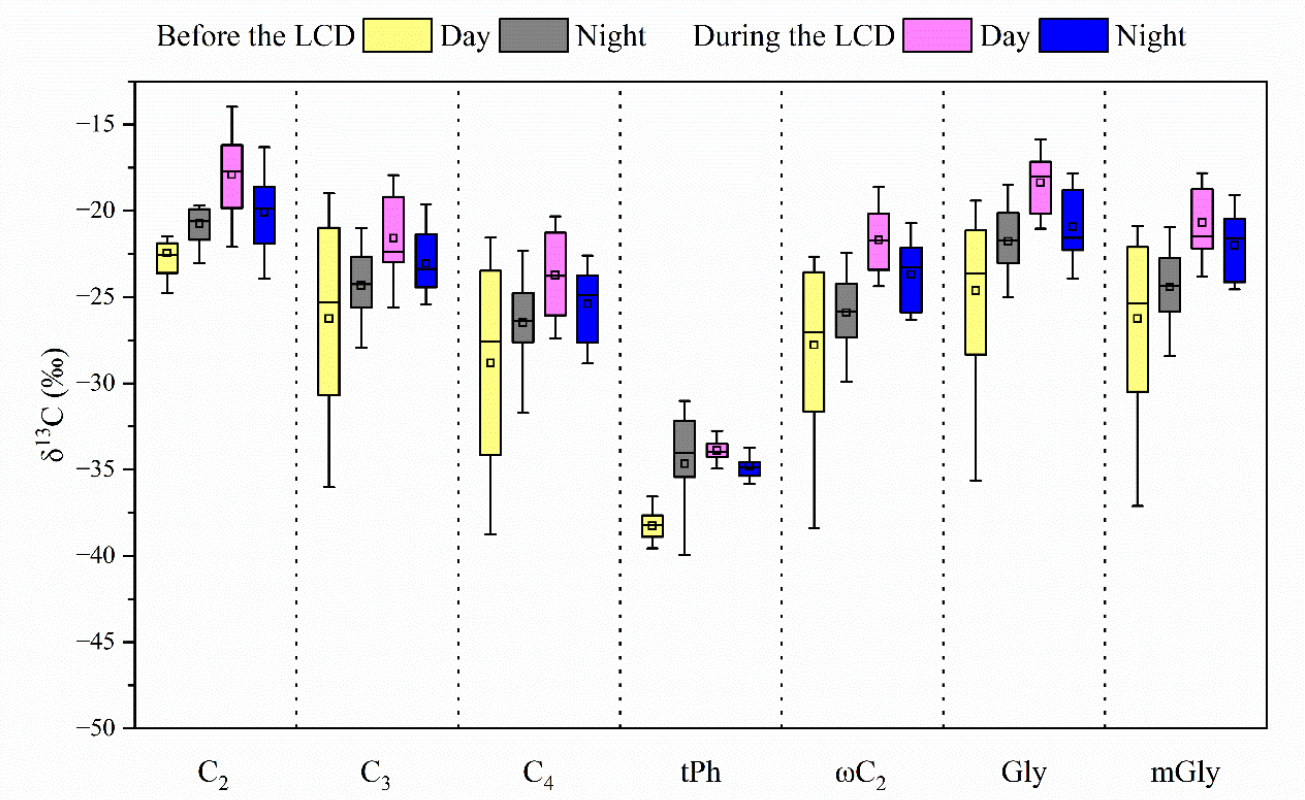

Figure 6. Differences in the stable carbon isotope compositions of major detected diacids (C_2−C_4, tPh), the smallest oxoacids (ωC_2), and α-dicarbonyls including Gly and mGly before and during the LCD in the atmosphere of Jinan.

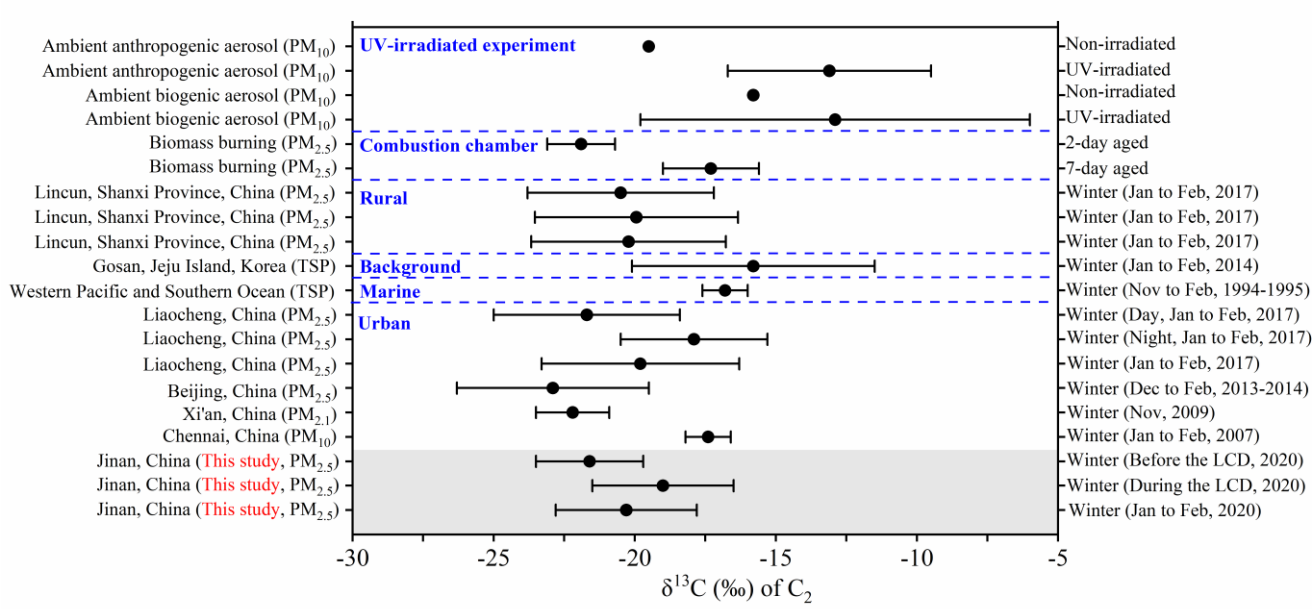

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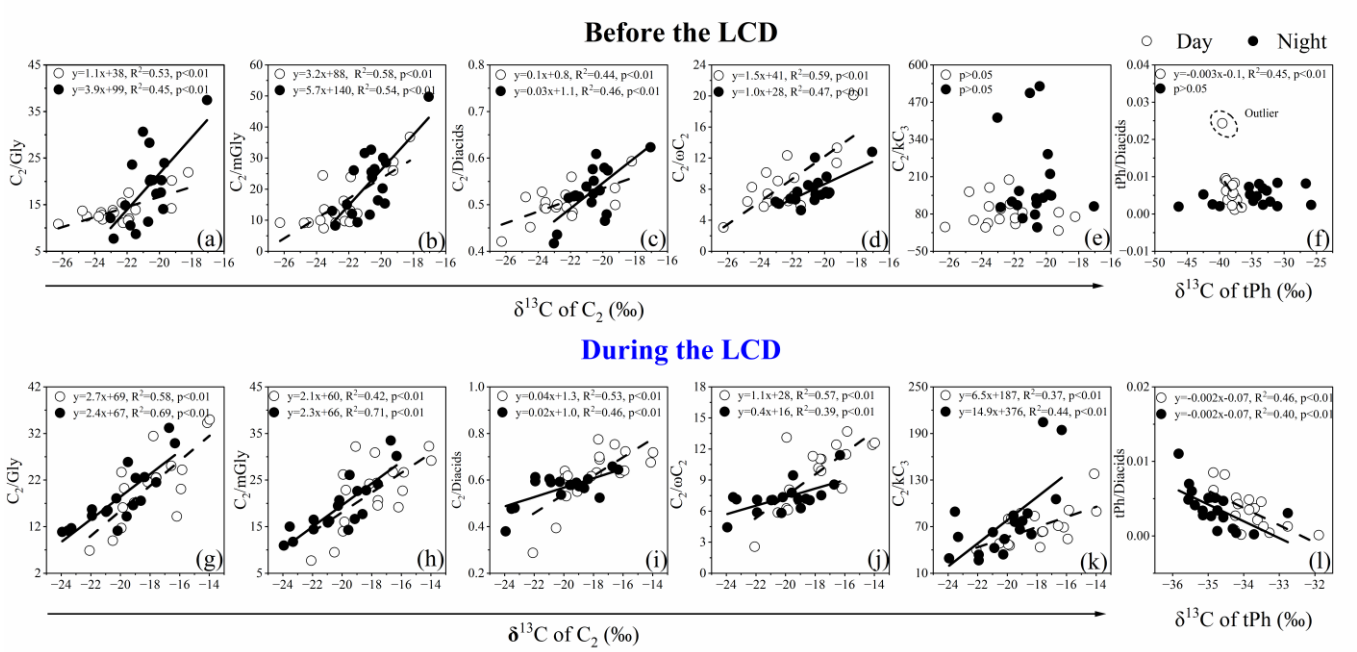
Figure 7. Comparison of stable carbon isotopic compositions ($\delta^{13}C$, ‰) of C_2 in aerosols of Jinan with those in other regions in the winter.



880 **Figure 8. Correlations of the $\delta^{13}C$ of C_2 with the mass ratios of C_2/Gly, C_2/mGly, C_2/Diacids, $C_2/\omega C_2$, and C_2/kC_3, and the $\delta^{13}C$ of tPh with the mass ratio of tPh/Diacids before and during the LCD in January to February 2020.**

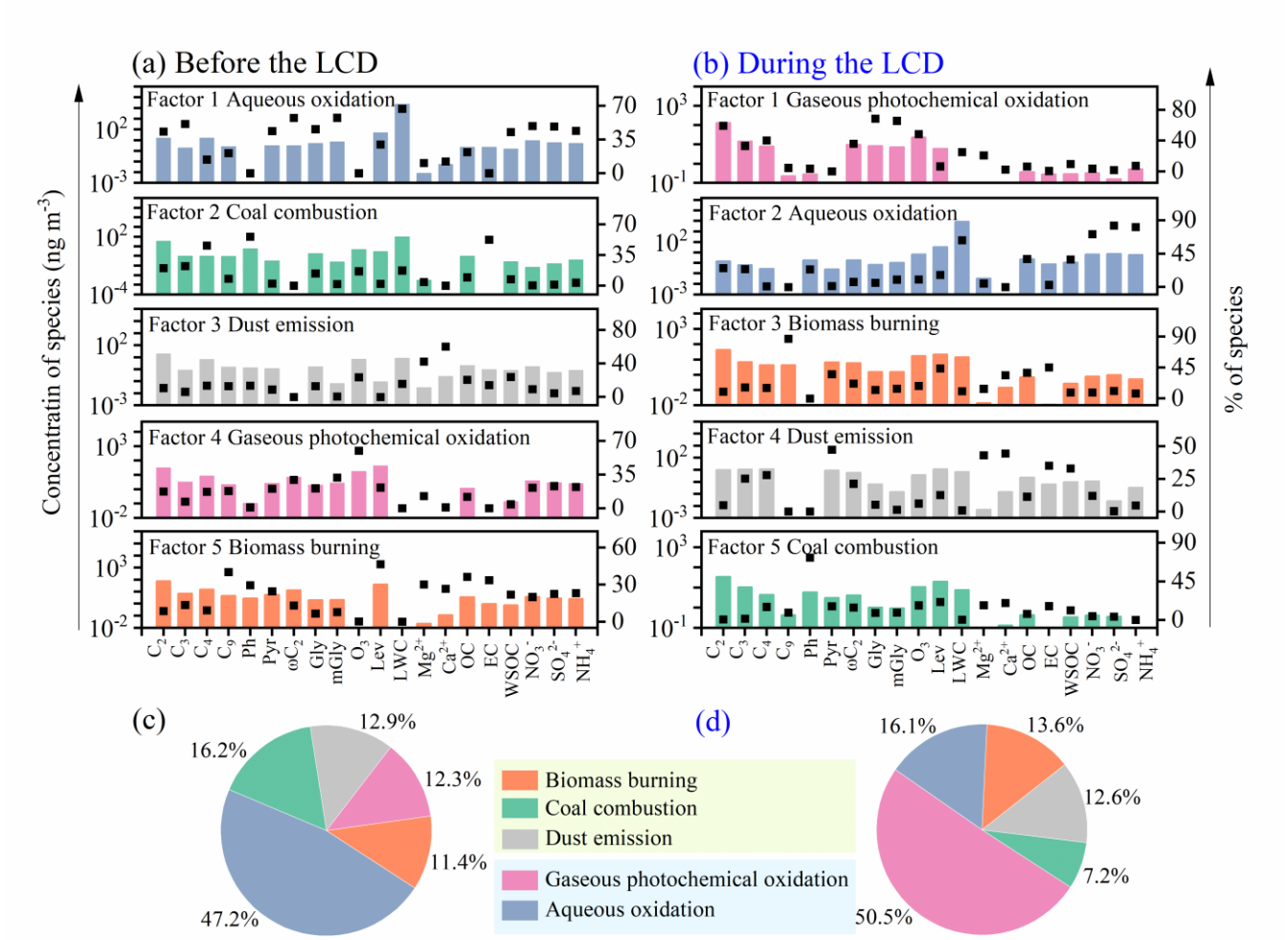


Figure 9. Source profiles of major chemical components in the $PM_{2.5}$ samples from Jinan (a, c) before the LCD and (b, d) during the LCD (BB: biomass burning).