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Enhanced photochemical formation of secondary organic aerosols during the COVID-19 lockdown in Northern China

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**HIGHLIGHTS**
- The remarkable reductions in primary pollutant emissions during the lockdown
- Oxalic acid (C2) and its precursors increased significantly during the lockdown
- The significant impact of biomass burning on C2 before the lockdown
- The O3-dominated formation pathways of C2 during the lockdown

**ABSTRACT**

To eliminate the spread of a novel coronavirus breaking out in the end of 2019 (COVID-19), the Chinese government has implemented a nationwide lockdown policy after the Chinese lunar New Year of 2020, resulting in a sharp reduction in air pollutant emissions. To investigate the impact of the lockdown on aerosol chemistry, the number fraction, size distribution and formation process of oxalic acid (C2) containing particles and its precursors were studied using a single particle aerosol mass spectrometer (SPAMS) at the urban site of Liaocheng in the North China Plain (NCP). Our results showed that five air pollutants (i.e., PM2.5, PM10, SO2, NO2, and CO) decreased by 30.0–59.8% during the lockdown compared to those before the lockdown, while O3 increased by 63.9% during the lockdown mainly due to the inefficient titration effect of O3 via NO reduction. The increased O3 concentration can boost the atmospheric oxidizing capacity and further enhance the formation of secondary organic aerosols, thereby significantly enhancing the C2 particles and its precursors as observed during the lockdown. Before the lockdown, C2 particles were significantly originated from biomass burning emissions and their subsequent aqueous-phase oxidation. The hourly variation patterns and correlation analysis before the lockdown suggested that relative humidity (RH) and aerosol liquid water content (ALWC) played a key role in the formation of C2 particles and the increased aerosol acidity can promote the conversion of precursors such as glyoxal (Gly) and methyglyoxal (mGly) into C2 particles in the aqueous phase. RH and ALWC decreased sharply but O3 concentration and solar radiation increased remarkably during the lockdown, the O3-dominated photochemical pathways played an important role in the formation of C2 particles in which aerosol acidity was ineffective. Our study indicated that air pollution treatment sponges on a joint-control and balanced strategy for controlling numerous pollutants.

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1. Introduction

The outbreak of the novel coronavirus disease 2019 (COVID-19) has significantly impacted the world and become a substantial global threat to public health (Le et al., 2020; Wang et al., 2020a). To eliminate the spread of the virus among humans, the Chinese government first implemented effective regulatory policies such as urban lockdown, imposing traffic restrictions and suspending factory production, and required people to stay at home beginning at the end of January 2020 (Chen et al., 2020). These restrictions make the Chinese air quality improve remarkably compared to the corresponding period in the past years (Li et al., 2020a; Shahrzad et al., 2020). Five air pollutants in 44 cities of northern China including PM10, PM2.5, SO2, NOx, and CO decreased by 13.7%, 5.9%, 6.8%, 24.7%, and 4.6%, respectively, due to the travel restrictions during the COVID-19 pandemic (Bao and Zhang, 2020). However, a few severe haze events still occurred in China during the lockdown period in spite of a remarkable reduction in air pollutant emissions (Huang et al., 2020; Le et al., 2020). For example, model simulations and synergistic measurements have reported that the haze event during the COVID-19 lockdown was principally caused by increased aerosol heterogeneous reaction, stagnant airflow, together with fast secondary formation (Huang et al., 2020; Le et al., 2020; Li et al., 2020b). The enhanced secondary aerosols have been proposed as the dominant contributors to the haze pollution (Huang et al., 2020; Le et al., 2020). The remarkable reduction of NOx and PM2.5 concentrations can lead to the enhancement of O3, which can in turn improve the atmospheric oxidizing capacity and further promote the secondary organic aerosols (SOA) formation (Huang et al., 2020; Le et al., 2020; Li et al., 2020a; Xu et al., 2020b). However, the formation mechanism of increased SOA during the lockdown period is elusive especially at the molecular level.

Oxalic acid (C2) and its precursors including glyoxal (Gly), methyglyoxal (mGly), glyoxylic acid (oC2), pyruvic acid (Pyr), and longer chain dicarboxylic acids (C-number > 2) have been regarded as significant SOA markers in the aerosol community (Meng et al., 2020). As the end product and the most abundant dicarboxylic acid, C2 is omnipresent in cloud water, precipitation and wet particles because of its high water-soluble nature and low vapor pressure (Lin et al., 2020; Zhang et al., 2017). Therefore, C2 plays a significant role in the hygroscopicity, acidity and cloud condensation nuclei (CCN) activity of atmospheric aerosols (Zhang et al., 2017). Although C2 can be emitted directly from primary sources including biogenic activity, fossil fuel combustion, and biomass burning, C2 is largely produced from the secondary oxidation of less oxygenated organic precursors such as Gly, mGly, oC2, and Pyr in the aqueous phase and the photochemical breakdown of longer chain di-acids (Carlton et al., 2007; Fu et al., 2008; Meng et al., 2018; Myriokefalitakis et al., 2011; Wang et al., 2012; Zhang et al., 2019; Zhao et al., 2020). Moreover, the aqueous-phase photooxidation of large multifunctional compounds can also be a significant source of C2 (Carlton et al., 2007). However, the formation mechanism of C2 is still incompletely understood because of oxidant levels and other influencing factors such as aerosol acidity, aerosol liquid water content (ALWC) and meteorological parameters. Some studies proposed that the enhanced acidity might suppress the C2 production during cloud processes (Sorooshian et al., 2007a, 2007b), but other studies claimed that more acidic conditions could promote the formation of C2 and its precursors (Lin et al., 2020; Meng et al., 2020). Field observations revealed that the photochemical decomposition of Fe-C2 complexes might result in the reduction of C2 through forming acetic acid (Cheng et al., 2017; Passanant et al., 2016). However, other field measurements and laboratory experiments argued that the presence of Fe could boost the production of C2 and its precursors due to Fe-driven Fenton reaction that can form OH radicals in liquid phase (Lin et al., 2018; Zhang et al., 2019). These controversies suggest the complexity of the formation mechanism of C2. Thus, further investigations on the formation process of C2 and related SOA are needed.

Online observations of the size distributions of C2-containing particles and the mixing state of C2 with other chemical species in single particles provide a useful tool to investigate the formation process of C2 and its precursors (Cheng et al., 2017). The dramatical shutdown of pollutant emissions during the COVID-19 lockdown provides a natural experiment to assess the contribution of SOA in the atmosphere and to evaluate the impact of the emissions and the meteorological conditions on the formation mechanism of SOA. In this study we analyzed the number fraction, size distribution, mixing state and formation process of C2 particles using a single particle aerosol mass spectrometer (SPAMS) before and during the lockdown to investigate the impact of emission controls on the chemistry of SOA in the urban region of Northern China.

2. Methods

2.1. Field measurements

Field measurements were performed at a national air quality monitoring station on the rooftop of a six-story building (36.43°N, 116.01°E; 25 m above ground) on the campus of Liaocheng University, which is situated in the southeast of Liaocheng (Fig. S1). Detailed information of the sampling site has been described elsewhere (Li et al., 2020b). Liaocheng is considered as one of the “2 + 26” air pollution transmission channel cities of China and located in the southwest of Shandong Province in the NCP. The sampling site is surrounded by main roads and residential communities, without significant industrial emissions or tall building nearby. Individual particles were collected hourly using the SPAMS (0515R Model, Hexin Analytical Instrument Co., Ltd., China) through a tygon tube of 3 m long at a flow rate of 75 mL·min−1. To explore the impact of COVID-19 lockdown on the formation mechanisms of oxalic acid (C2)-containing particles, the whole observation period was divided into “before the lockdown” ranging from January 3 to 23 and “during the lockdown” ranging from January 23 to February 19 in 2020. Six air pollutants including PM10, PM2.5, SO2, NOx, CO and O3, as well as meteorological parameters were obtained from the website of Environmental Protection Bureau of Liaocheng (http://www.lchbj.gov.cn).

2.2. Detection and classification of oxalate-containing particles

SPAMS was designed to determine the size distribution and chemical composition of ambient single particles at 1 h resolution. A detailed description has been described in previous studies (Li et al., 2020b; Yang et al., 2009). Based on (Cheng et al., 2017), oxalic acid (C2) particles are identified if the peak area of m/z = 89 was larger than 0.5% of the total signal in the negative mass spectrum. In the current work, 31,361 and 83,732 C2 particles were obtained before and during the lockdown, respectively. In addition, the organic precursors of C2 particles were queried by searching for given m/z ratios (Table 1) based on previous studies (Lin et al., 2020; Zhou et al., 2015).

| SPAMS markers used to search for the precursors of oxalic acid (C2) containing particles. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Species                          | m/z             | Marker ion       | Relative area peak | Function                        |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| α-Dicarboxyls                    |                 |                 |                 |                 |
| Gly                             | 73              | [C,H,O]4        | >0.005          | Not containing 113/115 [K,C]2 | 213/215          |
|                                 |                 |                 |                 | [K2SO4] with a relative peak area of more than 0.5%. |
| Ketocarboxylic acids            |                 |                 |                 |                 |
| oC2                             | 57              | [C,H,O]4        | >0.005          |                 |
|                                 |                 |                 |                 |                 |
| Dicarboxylic acids              |                 |                 |                 |                 |
| C2                              | 103             | [C,H,O]4        | >0.005          |                 |
|                                 | 117             | [C,H,O]4        | >0.005          |                 |
|                                 | 131             | [C,H,O]4        | >0.005          |                 |
The C2 particles were categorized into five groups as follows: (1) C2-biomass burning (BB), (2) C2-secondary (Sec), (3) C2-carbonaceous species (CS), (4) C2-heavy metal (HM), and (5) C2-other. Different types of particles were identified based on both the characteristic ion markers and predominant chemical species. Briefly, (1) particles containing strong signals of 39[K]+ (peak area $> 1500$) with a relative peak area of more than 0.5% are classified as C2-BB type; (2) remaining particles containing abundant signals of 18$\text{NH}_4^+$ with peak area $> 50$, $-62\text{NO}_3^-$ and $-97\text{HSO}_4^-$ with a peak area $> 100$ are considered as C2-Sec type; (3) remaining particles containing abundant signals of carbon clusters (e.g., $±12\text{C}^+/−$, $±24\text{C}^+/−$, and $±36\text{C}^+/−$) and hydrocarbon clusters (e.g., $27\text{C}_2\text{H}_4^+$, $37\text{C}_2\text{H}_7^+$, and $43\text{C}_2\text{H}_6\text{O}^+$) with a relative peak area of higher than 0.5% are classified as C2-CS type; (4) remaining particles containing signals of 55[Mn]$^+$, 56[Fe]$^+$, 63/65[Cu]$^+$, and 206/207/208[Pb]$^+$ with a relative peak area of more than 0.5% are classified as C2-HM type; (5) remaining particles are classified as C2-other type. The classification methods of C2 particles in this study have been shown in previous studies (Cheng et al., 2017; Lin et al., 2020).

2.3. Aerosol liquid water content (ALWC) and in situ particle pH ($pH_{fs}$)

Water-soluble inorganic ions were measured hourly using an online analyzer (WARGA, Hangzhou Juguang Analytical Company) with a PM$_{2.5}$ sampling inlet during the whole observation period. Aerosol liquid water content (ALWC) and in situ particle pH ($pH_{fs}$) in PM$_{2.5}$ samples were calculated using the ISORROPIA-II model, which treated the Na$^+$ - $\text{NH}_4^+$ - K$^+$ - $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ - $\text{SO}_4^{2−}$ - $\text{NO}_3^−$ - $\text{Cl}^−$ system (Wu et al., 2018). The forward mode with a metastable state in the ISORROPIA model was employed.

3. Results and discussion

3.1. Variations in air quality and meteorological conditions

Temporal variations in the concentration of PM$_{2.5}$, PM$_{10}$, and gaseous pollutants (e.g., SO$_2$, NO$_2$, O$_3$, and CO) along with meteorological parameters in the whole observation period are presented in Fig. 1. PM$_{2.5}$ and PM$_{10}$ concentration were 63.8 ± 44.9 μg m$^{-3}$ and 174 ± 67.2 μg m$^{-3}$ during the lockdown, which decreased by 53.8% and 56.9% compared to those (138.2 ± 56.9 μg m$^{-3}$ for PM$_{2.5}$, 75.1 ± 46.5 μg m$^{-3}$ for PM$_{10}$) before the lockdown, reflecting that the air quality was significantly improved due to the dramatic reduction of pollutant emissions during the lockdown (Le et al., 2020; Li et al., 2020a). Similarly, the concentrations of SO$_2$, NO$_2$ and CO during the lockdown decreased by 30.0%, 69.8% and 50.0% than those before the lockdown. It is a remarkable fact that the drop of the NO$_2$ was the most prominent, which was also observed in other urban regions in the Yangtze River Delta Region (Li et al., 2020a) and Central China (Xu et al., 2020b), due to the drastic decrease of on-road vehicular traffic and industrial exhausts during the lockdown (Li et al., 2020a). On the contrary, the drop of the SO$_2$ was relatively smaller, which is attributed to the ongoing emissions from petrochemical facilities and power plants that cannot be shut down during the COVID-19 event (Le et al., 2020). O$_3$ is mainly originated from the photochemical formation of NO$_x$ and volatile organic compounds (VOCs), thus it can be used to evaluate the atmospheric oxidation capacity (Fu et al., 2020). It is noteworthy that O$_3$ concentration (64.8 ± 23.6 μg m$^{-3}$) was 63.9% higher during the lockdown than that (27.5 ± 23.4 μg m$^{-3}$) before the lockdown, which was completely opposite to the variations of the other five air pollutants, suggesting the stronger atmospheric oxidation capacity during the lockdown. The formation of O$_3$ in the urban regions of China is mostly derived from NO$_x$ (the sum of NO and NO$_2$)-saturated regime because of the scarce of HO$_x$ radicals in the winter (Seinfeld and Pandis, 1998). Moreover, the sharp reduction of NO$_2$ concentration during the lockdown can lead to the lower concentration level of NO (Xu et al., 2020b), and then alleviated the titration of O$_3$ (Seinfeld and Pandis, 1998; Zou et al., 2019). Therefore, the sink of NO$_2$ can result in an enhancement of O$_3$ during the lockdown. Previous studies have demonstrated that the negative relationship between O$_3$ and PM$_{2.5}$ mass can be ascribed to the aerosol radiative effect on the photochemistry production of O$_3$ (Wu et al., 2020) and the decreased precursors of O$_3$ (Li et al., 2019). Moreover, the stronger solar radiation and higher temperature conditions during the lockdown (Fig. 1) were favorable for the formation and cumulation of O$_3$ (Xu et al., 2020b).

Secondary inorganic aerosols (SIA, i.e., SO$_4^{2−}$, NO$_3^{−}$, and NH$_4^+$) are major components of PM$_{2.5}$, which exhibited a similar pattern of variation with PM$_{2.5}$ mass (Fig. 1). SO$_4^{2−}$, NO$_3^{−}$, and NH$_4^+$ before the lockdown were 23.55 ± 10.2 μg m$^{-3}$, 36.2 ± 18.7 μg m$^{-3}$, and 17.1 ± 7.0 μg m$^{-3}$, respectively (138.2 ± 56.9 μg m$^{-3}$ for PM$_{2.5}$, 75.1 ± 46.5 μg m$^{-3}$ for PM$_{10}$) before the lockdown, reflecting that the air quality was significantly improved due to the dramatic reduction of pollutant emissions during the lockdown (Le et al., 2020; Li et al., 2020a). Similarly, the concentrations of SO$_2$, NO$_2$ and CO during the lockdown decreased by 30.0%, 69.8% and 50.0% than those before the lockdown. It is a remarkable fact that the drop of the NO$_2$ was the most prominent, which was also observed in other urban regions in the Yangtze River Delta Region (Li et al., 2020a) and Central China (Xu et al., 2020b), due to the drastic decrease of on-road vehicular traffic and industrial exhausts during the lockdown (Li et al., 2020a). On the contrary, the drop of the SO$_2$ was relatively smaller, which is attributed to the ongoing emissions from petrochemical facilities and power plants that cannot be shut down during the COVID-19 event (Le et al., 2020). O$_3$ is mainly originated from the photochemical formation of NO$_x$ and volatile organic compounds (VOCs), thus it can be used to evaluate the atmospheric oxidation capacity (Fu et al., 2020). It is noteworthy that O$_3$ concentration (64.8 ± 23.6 μg m$^{-3}$) was 63.9% higher during the lockdown than that (27.5 ± 23.4 μg m$^{-3}$) before the lockdown, which was completely opposite to the variations of the other five air pollutants, suggesting the stronger atmospheric oxidation capacity during the lockdown. The formation of O$_3$ in the urban regions of China is mostly derived from NO$_x$ (the sum of NO and NO$_2$)-saturated regime because of the scarce of HO$_x$ radicals in the winter (Seinfeld and Pandis, 1998). Moreover, the sharp reduction of NO$_2$ concentration during the lockdown can lead to the lower concentration level of NO (Xu et al., 2020b), and then alleviated the titration of O$_3$ (Seinfeld and Pandis, 1998; Zou et al., 2019). Therefore, the sink of NO$_2$ can result in an enhancement of O$_3$ during the lockdown. Previous studies have demonstrated that the negative relationship between O$_3$ and PM$_{2.5}$ mass can be ascribed to the aerosol radiative effect on the photochemistry production of O$_3$ (Wu et al., 2020) and the decreased precursors of O$_3$ (Li et al., 2019). Moreover, the stronger solar radiation and higher temperature conditions during the lockdown (Fig. 1) were favorable for the formation and cumulation of O$_3$ (Xu et al., 2020b).

Fig. 1. Temporal variations of meteorological parameters and the concentrations of PM$_{2.5}$, PM$_{10}$, gaseous pollutants and major inorganic ions of PM$_{2.5}$ in the whole period.
accounting for 17.7, 26.2, and 13.0% of PM$_{2.5}$ mass, respectively. Their concentrations dropped to 8.8 ± 6.6 μg m$^{-3}$, 9.9 ± 6.0 μg m$^{-3}$, and 5.4 ± 3.5 μg m$^{-3}$ during the lockdown with the contributions to PM$_{2.5}$ mass reduced to 14.6, 17.2, and 9.8%, respectively. Temperature increased dramatically from 0.8 ± 3.1 °C before the lockdown to 5.0 ± 5.2 °C during the lockdown, and solar radiation (242.0 ± 191.5 W m$^{-2}$) was much stronger during the lockdown than that (150.5 ± 133.6 W m$^{-2}$) before the lockdown. In contrast, relative humidity (RH) showed a decreasing trend, with an average of 81.4 ± 15.1% before the lockdown and 64.9 ± 20.7% during the lockdown. The ALWC is determined by SNA (Faust et al., 2017) and RH (Clegg et al., 1998). Both SNA concentrations and RH were higher before the lockdown compared to those during the lockdown, resulting in the ALWC before the lockdown (236 ± 190 μg m$^{-3}$) 4.6 times higher than that (52 ± 101 μg m$^{-3}$) during the lockdown. In contrast, pH$_{b}$ increased from 0.9 ± 2.0 before the lockdown to 2.7 ± 2.1 during the lockdown, suggesting that the aerosols were less acidic during the lockdown than before the lockdown.

3.2. The effect of lockdown on oxalic acid and its precursors

As shown in Fig. 2a and b, the number concentration of oxalic acid (C$_2$) particles increased markedly from 31,361 before the lockdown to 83,732 during the lockdown, accounting for 1.1 and 4.6% of the total number of detected particles, respectively. Thus, both the number concentration of C$_2$ particles and its percentage contribution of total particles (C$_2$/total) were higher during the lockdown than those before the lockdown, which could be ascribed to the enhanced secondary formation of C$_2$ particles during the lockdown (detailed discussions will be described in Sections 3.3 and 3.4). Similarly, the counts and percentages of the precursors of C$_2$ particles, including α-dicarboxyls (e.g., Gly and mGly), ketocarboxylic acids (e.g., ωC$_2$ and Pyr) as well as some longer chain dicarboxylic acids including malonic (C$_3$), succinic (C$_4$), and glutaric acids (C$_5$) were all higher during the lockdown than those before the lockdown (Fig. 2a and b), indicating an increased production of these precursors during the lockdown. Previous studies demonstrated that C$_3$ is an end product formed via photochemical oxidation of less oxygenated organic precursors including Gly, mGly, Pyr, and ωC$_2$ in wet aerosols or fog droplets and/or clouds, thus the ratios of C$_2$/Gly, C$_2$/mGly, C$_2$/ωC$_2$, and C$_2$/Pyr can be considered as key indicators to evaluate the aging degree of organic aerosols (Ervens et al., 2004a; Wang et al., 2012, 2015; Zhao et al., 2020). These four ratios all exhibited the bigger values during the lockdown than those before the lockdown (Fig. 2c), further demonstrating that the organic aerosols during the lockdown were more aged. It has been reported that large signals of secondary inorganic species during the lockdown indicated C$_2$ particles undergone an aging process during the whole period (Fig. 3). Moreover, the stronger signal intensity of secondary inorganic species during the lockdown than before the lockdown revealed the more aged C$_2$ particles during the lockdown (Fig. 3).

Previous studies have reported that C$_4$ can be photochemically degraded to C$_3$ in the atmosphere, thus the C$_3$/C$_4$ ratio can be proposed as a key marker to assess the photochemical formation of SOA (Kawamura and Ikushima, 1993; Meng et al., 2020). The higher C$_3$/C$_4$ ratios during the day (day: 2.4; night: 1.9) were observed than those (day: 2.1; night: 1.3) before the lockdown (Fig. 2c), which further suggested the more photochemical formation of SOA during the lockdown due to the stronger solar radiation and higher O$_3$ concentration.

![Fig. 2. Differences in (a) the counts of oxalic acid (C$_2$) containing particles and its precursors, (b) the relative abundance of C$_2$ particles and its precursors in the total detected particles, (c) major ratios of C$_2$ particles to total detected particles or its major precursors between before the lockdown and during the lockdown (*exaggerated by 10 times; **exaggerated by 100 times).](image-url)

As shown in Fig. 4, the C$_2$-BB particles made up as high as 38.3% of the total C$_2$ particles, followed by C$_2$-CS (24.2%) and C$_2$-Sec particles (19.8%) before the lockdown. It’s worth noting that total C$_2$ particles exhibited a similar diurnal pattern with BB particles before the lockdown, indicating that BB was a significant source of C$_2$ particles. However, the contribution of C$_2$-BB particles decreased significantly to only 12% during the lockdown, when the C$_2$-Sec particles were the most abundant and contributed 35.4% to total C$_2$ particles during the lockdown, followed by CS (25.6%) and HM (17.8%) particles. During the lockdown, total C$_2$ particles and HM particles presented very similar diurnal patterns of variation (Fig. 4b), reflecting that the possible formation of C$_2$ particles was closely related to the transition metals such as Fe and Cu (Cheng et al., 2017; Zhou et al., 2015). Interestingly, the contribution of C$_2$-BB particles before the lockdown was 3.2 times higher than that during the lockdown, mainly because large amounts of organic compounds serving as precursors for C$_2$ particles emitted from BB decreased substantially due to the shutdown of power plants that use biomass as fuel in Liaocheng and its surrounding regions. Instead, all the electricity was mad by power plants, resulting in the percentage of C$_2$-EC particles during the lockdown increased by 2.1 times compared to that before the lockdown (Le et al., 2020; Li et al., 2020b).

The different peak modes suggest a heterogeneity in the atmospheric evolution process of C$_2$ particles (Cheng et al., 2017). The unscaled size distribution of C$_2$ particles mainly exists in the range of 0.4 to 1.5 μm with similar size distribution during the day and night especially in the larger size of 0.8 μm in the whole sampling period, but exhibited different peak modes before and during the lockdown (Fig. 5a). The number fraction of C$_2$ particles peaked at ~0.3 μm with a range of 0.4 to 1.3 μm before the lockdown. However, C$_2$ particles presented broader size mode from 0.4 to 1.5 μm and peaked at the larger size of ~0.8 μm during the lockdown than that before the lockdown, possibly attributed...
to the condensation and coagulation of $C_2$ particles while aging during the lockdown (Zhang et al., 2017). In addition, the higher percentage contribution of $C_2$ particles to the total detected particles was another important explanation for the larger size of $C_2$ particles during the lockdown (Huang et al., 2019). Therefore, the particles during the lockdown can be considered to be more aged than those before the lockdown. The increase in the temperature was favorable for the formation of $C_2$ particles and its precursors (Meng et al., 2018). However, the higher temperature could increase the volatilization of oxalic acid, resulting in the decrease of oxalic acid in the particulate phase (Bilde et al., 2015). Therefore, there was no any correlation ($R^2 < 0.2$) between $C_2$ particles and temperature before and during the lockdown, respectively.

Fig. 3. The average positive and negative ion mass spectra of oxalic acid ($C_2$) containing particles (a) before the lockdown, (b) during the lockdown. Color bars represent each peak area corresponding to a specific fraction in individual particles.

Fig. 4. (a) Hourly variations in total particle counts, PM$_{2.5}$ mass, oxalic acid ($C_2$) containing particles and the ratio of $C_2$ particles/total particles; (b) temporal variations in the fractions of five kinds of $C_2$ particles; (c) average percentages of five kinds of $C_2$ particles in the whole period.
suggesting that the temperature was a minor contributor to the formation of $C_2$ particles in this study.

3.3. Aqueous phase production of oxalic acid particles before the lockdown

Primary emissions from BB contribute only a negligible fraction to atmospheric $C_2$ particles (Meng et al., 2013; Yang et al., 2009). There is a growing consensus on the significance of $C_2$ particles from biomass burning particles through aqueous-phase oxidation according to field measurements (Cheng et al., 2017; Wang et al., 2020b; Xu et al., 2020a; Zhu et al., 2018). The positive mass spectrum of $C_2$ particles was characterized by a strong intensity of BB markers (e.g., $115K_2Cl^+$), as well as carbonaceous species such as $27C_2H_3$.

The positive mass spectrum of $C_2$ particles displayed strong correlation with sulfate particles ($R^2 = 0.75$, Fig. 6) and both particles exhibited similar diurnal patterns of variations with RH and ALWC, with a smaller peak at 4:00 and a larger peak at 9:00, suggesting that the enhanced production was significantly determined by RH and ALWC. However, such similar variations were not obtained in the organic precursors such as Gly, mGly and $C_3$-$C_5$ diacids, which exhibited different variations with RH and ALWC (Fig. 7a). The ratio of relative peak area of $C_2$ particles to precursors in the same particles was used to assess the conversion of precursors to $C_2$ particles (Lin et al., 2020; Zhang et al., 2019). The ratios of $C_2$/Gly and $C_2$/mGly correlated well with RH and ALWC ($R^2 > 0.5$, Fig. 6), suggesting that the conversion of dicarbonyls to $C_2$ particles was influenced significantly by RH and ALWC.

The enhanced production of $C_2$ particles was not only associated with high RH and ALWC, but also closely related to the strong acidic environment (Jang et al., 2002; Lim et al., 2010; Meng et al., 2018). The SPAMS cannot provide aerosol acidity similar to the bulk mass technology because of transmission efficiencies, hit efficiency and matrix effect on data gathering (Lin et al., 2020). To better understand the impact of acid condition on the formation of $C_2$ particles, relative aerosol acidity ($R_{ra}$) was defined as the ratio of total peak areas of sulfate and nitrate to that of ammonium (Denkenberger et al., 2007). $R_{ra}$ is correlated strongly with pH$_{a}$ calculated by the ISORROPIA-II model before ($R^2 = 0.62$, Fig. S3a) and during the lockdown ($R^2 = 0.62$, Fig. S3b), respectively, confirming the validity of $R_{ra}$ estimated by the SPAMS. The higher $R_{ra}$ ($77.0 ± 20.1$) of particles before the lockdown than during the lockdown ($61.6 ± 16.0$) implied that the aerosol particles before the lockdown was more acidic. The hourly variations of $R_{ra}$ exhibited a similar pattern as the peak area of Gly and mGly (Fig. 7a), suggesting that the production of precursors of $C_2$ particles was closely associated with the enhanced $R_{ra}$. Laboratory experiment demonstrated that the uptake and formation of Gly and mGly could be promoted in acidic conditions.
However, the increased C2 particles were not obtained with the enhanced Rra (Fig. 7a), which was consistent with the measurements in the rural area of Pearl River Delta (Cheng et al., 2017) and Nanling background station (Lin et al., 2020) of China. The ratios of C2/Gly ($R^2 > 0.6$, Fig. 6) and C2/mGly ($R^2 > 0.5$, Fig. 6) are highly correlated with Rra and pHm, suggesting that the enhancement of aerosol acidity can promote the conversion of precursors to C2 particles in the aqueous phase despite no correlation between C2 particles and Rra or pHm ($R^2 < 0.25$, Fig. 6).

### 3.4. $O_3$-dominated formation pathways of oxalic acid during the lockdown

$O_3$ (Yu et al., 2019) and solar radiation (Deshmukh et al., 2018) have been proposed as reliable indicators of photochemical oxidation in gaseous phase. The $O_3$-dominated photochemical pathways are also proposed to be closely involved in the formation of C2 particles from field observations (Meng et al., 2020; Mochizuki et al., 2017). Although the primary sources including biomass burning and coal combustion declined sharply, the higher number and percentage of C2 particles were observed during the lockdown than before the lockdown (Fig. 2). Considering the remarkable enhancement of $O_3$ concentration and solar radiation during the lockdown discussed in Section 3.1, Figs. 1 and S2, the photochemical pathways could play significant roles in the formation of C2 particles. In contrast to the diurnal variations before the lockdown, C2 particles and C2/total presented larger values in the day than those in the night (Fig. S2). The relatively higher $O_3$ concentration and the stronger solar radiation conditions in the daytime can promote the photochemical formation of $\alpha$-dicarbonyls and other precursors from VOCs (Cheng et al., 2017; Myriokefalitakis et al., 2011), which further accelerated the formation of C2 particles. As shown in Fig. S2, the number and percentage of C2 particles exhibited similar pattern of variation with $O_3$ concentration. Moreover, it is interesting to note that the number of C2 particles ($R^2 = 0.78$), C2/total ($R^2 = 0.65$) and C2/C4 ratios ($R^2 = 0.52$) are correlated strongly with $O_3$ concentration and solar radiation (only from 9:00 to 18:00) ($R^2 > 0.65$) during the lockdown, which could be concluded that the $O_3$-dominated photochemical processing under the stronger solar radiation contributed substantially to the C2 formation during the lockdown.

To investigate the photochemical pathways of C2 particles and influencing factors during the lockdown, the hourly variations of C2 through acidic-catalyzed heterogeneous reaction (Jang et al., 2002). However, the increased C2 particles were not obtained with the enhanced Rra (Fig. 7a), which was consistent with the measurements in the rural area of Pearl River Delta (Cheng et al., 2017) and Nanling background station (Lin et al., 2020) of China. The ratios of C2/Gly ($R^2 > 0.6$, Fig. 6) and C2/mGly ($R^2 > 0.5$, Fig. 6) are highly correlated with Rra and pHm, suggesting that the enhancement of aerosol acidity can promote the conversion of precursors to C2 particles in the aqueous phase despite no correlation between C2 particles and Rra or pHm ($R^2 < 0.25$, Fig. 6).
particles, the precursors (e.g., Gly, mGly, Pyr, oC2 and C2-C5 dicarboxylic acids), O3, and physical parameters (ALWC and pH_{a}) averaged from 9 to 13 February during the lockdown were presented in Fig. 7b along with meteorological parameters (e.g., RH and solar radiation). The date from 9 to 13 February was characterized by higher concentration of O3 and stronger solar radiation (Fig. 1). The O3 concentration and solar radiation increased from 9:00 and showed a peak at 16:00, while C2 particles and C2/total ratio began to increase at 9:00 and reached a smaller peak at 15:00 and a bigger peak at 20:00 (Fig. 7b). The RH was relatively lower from 9:00 to 20:00 than that in other time (Fig. 7b), indicating a negligible impact of aerosol acidity on the photochemical formation of C2 particles. If the ratios of C2/C4, C3/C4, and C2/total detected diacids (sum of C2-C5 diacids) (C2/TDAs) are correlated significantly with O3, C2 should be produced from the photochemical degradation of longer chain diacids (Kawamura and Ikushima, 1993; Zhao et al., 2020). Strong correlations were obtained between the ratios of C2/C4, C3/C4, and C2/total detected diacids and O3 (R^2 > 0.65, Fig. 8) from 9:00 to 16:00 than those (0.50 < R^2 < 0.56, Fig. 7) from 16:00 to 20:00. In addition, higher correlations (R^2 > 0.88, Table 2) were also found between C2 and longer chain diacids including C3-C5 diacids from 9:00 to 16:00 than those (0.48 < R^2 < 0.56, Table 2) from 16:00 to 20:00. The consumption rates of longer-chain diacids for producing C2 has proven to be slower than their supply rates (Zhao et al., 2020). These findings implied that the photodegradation of longer chain diacids contributed more to the formation of C2 particles from 9:00 to 16:00. As shown in Fig. 7b, RH and ALWC began to increase at 16:00 when C2 particles and C2/total ratio exhibited similar variations with RH and ALWC during the lockdown.

### Table 2

| Compound | C2 (9:00–16:00) | C2 (16:00–20:00) |
|----------|----------------|-----------------|
| C2       | 0.92           | 0.53            |
| C4       | 0.93           | 0.55            |
| C3       | 0.89           | 0.49            |
| Gly      | 0.45           | 0.89            |
| mGly     | 0.38           | 0.65            |
| oC2      | 0.41           | 0.82            |
| Pyr      | 0.36           | 0.56            |

The oxidation rate of mGly (1.1 × 10^9 M s^{-1}) with OH radicals in the aqueous phase is lower than Gly (3 × 10^{10} M s^{-1}) (Carlton et al., 2007). Furthermore, the C2/Gly ratio is correlated strongly with RH, ALWC and O3 (0.58 < R^2 < 0.65, Fig. 8), while C2/mGly ratio is correlated moderately with RH, ALWC and O3 (0.34 < R^2 < 0.46, Fig. 8). These findings suggested that the accelerated secondary formation of C2 was dominantly from the aqueous photoperoxidation of Gly from 16:00 to 20:00 in which high RH and ALWC were key favorable factors. The above results may explain the smaller peak at 15:00 and the bigger peak at 20:00. After the culmination, C2 particles and C2/total began to decrease from 21:00 (Fig. 7b), suggesting that the formation of C2 particles was overwhelmed by a removal via dry deposition or transport out of the sampling region (Kawamura and Yasui, 2005).

Modeling studies and field observations reported that the photochemical decomposition of Fe-oxalate complexes is regarded as a substantial sink of C2 (Cheng et al., 2017; Weller et al., 2014; Zhang et al., 2019). Based on the highly abundant ion peaks of Fe in the positive spectrum of C2 particles, the photolysis of Fe-oxalate complexes was expected to be a significant sink of C2 particles. The mass concentration of C2 and Fe (III) cannot be measured in this study by SPAMS, the diurnal variations in the peak areas of Fe and C2 particles were employed to understand the role of Fe in the formation process of C2 particles in the HM particles (Fig. 9). It is interesting to note that the variation patterns of peak area of C2 particles were opposite to the peak area of iron from 9:00 to 20:00 (Fig. 9). Such a phenomenon was also observed in the rural area of Pearl River Delta of China, where an opposite pattern of variations of C2 particles and iron occurred from 5:00 to 19:00 (Cheng et al., 2017). In addition, the peak area of Fe started to increase with a minimum at 2:00 while the peak area of C2 particles started to decrease with a maximum at 2:00 accordingly (Fig. 9), which was in accordance with the diurnal variation arising from the nighttime production of Fe-oxalate complexes and subsequent photochemical decomposition.

![Fig. 8](https://example.com/fig8.png)

**Fig. 8.** Correlation coefficients (R^2) of the ratios of C2/mGly, C2/Gly, C2/total numbers of C2 to C5 diacids (TDAs), C3/C4 and C2/C4 with O3 concentration, the relative humidity (RH) and aerosol liquid water content (ALWC) from 9:00 to 16:00 and from 16:00 to 20:00 during the lockdown.

![Fig. 9](https://example.com/fig9.png)

**Fig. 9.** Hourly variations in the peak area of Fe and oxalic acid (C2) containing particles.
under solar radiation during the day. These results implied that the loss of C2 particles via the photolysis of Fe-oxalate complexes was expected to be an efficient sink.

4. Summary and conclusions

Human activities decreased significantly during the COVID-19 lockdown, leading to significant reductions of the air pollutants including PM2.5, PM10, SO2, NO2, and CO. However, O3 increased by 63.9% synchronously which in turn enhanced the atmospheric oxidizing capacity. The numbers and number fractions of C2 particles and its precursors were higher during the lockdown compared to those before the lockdown, which suggested the enhanced formation of secondary organic species during the lockdown. Moreover, the higher ratios of C2/total, C2/Gly, C2/mGly, C2/oC2 and C2/Pyr as well as the more intense signals of secondary inorganic species (ammonium, nitrate, and sulfate) were observed during the lockdown than those before the lockdown, indicating that the aerosols during the lockdown were more aged. As high as 38.3% of C2 particles contained biomass burning markers before the lockdown but dropped to only 9.3% during the lockdown due to the shut-down of power plants using biomass as fuel. Before the lockdown, the higher number and fractions of C2 particles at night, the diurnal characteristic of C2 particles as well as the strong correlations of C2 par-

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at [https://doi.org/10.1016/j.scitotenv.2020.143709](https://doi.org/10.1016/j.scitotenv.2020.143709).
