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Impact of COVID-19 lockdown on carbonaceous aerosols in a polluted city: Composition characterization, source apportionment, influence factors of secondary formation

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HIGHLIGHTS:

• O3 increased by 127% while SOC decreased by 21% during lockdown period.
• SOC generation was more influenced by NO2 than by O3.
• Positive effect of RH on SOC became negative when RH was >80%, 60% in two periods.
• SOC concentrations were obtained by two methods and the results were comparable.

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ABSTRACT

Carbonaceous fractions throughout the normal period and lockdown period (LP) before and during COVID-19 outbreak were analyzed in a polluted city, Zhengzhou, China. During LP, fine particulate matters, elemental carbon (EC), and secondary organic aerosol (SOC) concentrations fell significantly (29%, 32% and 21%), whereas organic carbon (OC) only decreased by 4%. Furthermore, the mean OC/EC ratio increased (from 3.8 to 5.4) and the EC fractions declined dramatically, indicating a reduction in vehicle emission contribution. The fact that OC1–3, EC, and EC1 had good correlations suggested that OC1–3 emanated from primary emissions. OC4 was partly from secondary generation, and increased correlations of OC4 with OC1–3 during LP indicated a decrease in the share of SOC. SOC was more impacted by NO2 throughout the research phase, thereby the concentrations were lower during LP when NO2 levels were lower. SOC and relative humidity (RH) were found to be positively associated only when RH was below 80% and 60% during the normal period (NP) and LP, respectively. SOC, Coal combustion, gasoline vehicles, biomass burning, diesel vehicles were identified as major sources by the Positive Matrix Factorization (PMF) model. Contribution of SOC apportioned by PMF was 3.4 and 3.0 μg/m³, comparable to the calculated findings (3.8 and 3.0 μg/m³) during the two periods. During LP, contributions from gasoline vehicles dropped the most, from 47% to 37% and from 7.1 to 4.3 μg/m³, contribution of biomass burning and diesel vehicles fell by 3% (0.6 μg/m³) and 1% (0.4 μg/m³), and coal combustion concentrations remained nearly constant. The findings of this study highlight the immense importance of
1. Introduction

Various air pollution concerns have emerged in China as the process of urbanization and industrialization has accelerated in the last three decades, and air quality has deteriorated dramatically and expanded to the region centered on cities (Chen and Yao, 2008). In recent years, in the urban agglomeration areas where they take the lead in the development of the economy, the traditional soot-type pollution problems characterized by sulfur dioxide (SO\(_2\)), nitrogen oxides (NOx), and inhalable particulate matter (PM\(_{10}\)) are still serious and have not yet been fundamentally resolved, secondary pollution such as ozone (O\(_3\)) and fine particulate matter (PM\(_{2.5}\)) has been severe and more harmful (Ren et al., 2017; Wang et al., 2021; Zhang et al., 2020; Zhao et al., 2020). Although PM\(_{2.5}\) presents seasonal variations, its annual concentration is relatively high in many urban areas, which will affect environmental quality, atmospheric visibility, climate change, and endanger human health (Lall et al., 2004; Pope and Dockery, 2006; Pui et al., 2014). The composition of PM\(_{2.5}\) is complex, mainly including carbonaceous components, water-soluble ions, and elements components (He et al., 2001; Zhang et al., 2014). Carbonaceous components as important components of atmospheric PM\(_{2.5}\) have received special attention because they play a critical role in global climate change, atmospheric visibility degradation, and regional air quality deterioration, as well as have a significant impact on human health (Horvath, 1993; Seinfeld and Pandis, 1998; Bergstrom et al., 2002; Menon et al., 2002; Poschl, 2005; Ji et al., 2019). Carbonaceous components include organic carbon (OC) and elemental carbon (EC) (Schwarz et al., 2008; Zhu et al., 2014). Primary organic carbon (POC) emitted directly by primary sources (such as fossil fuel combustion, biomass combustion, plant debris, and so on) is included in OC, as well as secondary organic carbon (SOC) formed by photochemical reactions and secondary condensation of gaseous organic hydrocarbons in the atmosphere (Turpin and Huntzicker, 1995; Schwarz et al., 2008; Zhu et al., 2014). EC mainly comes from the incomplete combustion of fuels (coal, fossil fuels, biomass, etc.) (Roelmann et al., 2006; Schwarz et al., 2008; Bish et al., 2015). The chemical properties of EC are rather stable, and no further chemical changes will occur after being discharged from the pollution source, so it’s commonly used as a primary emission indicator (Ho et al., 2006; Han et al., 2010). OC has a scattering effect on light, and EC has a strong ability to absorb light (Horvath, 1993; Seinfeld and Pandis, 1998; Bergstrom et al., 2002; Menon et al., 2002; Ji et al., 2019). Both of them will have a crucial impact on atmospheric visibility and regional climate change, and can also enter the alveoli and putting humans at risk (Seinfeld and Pandis, 1998; Poschl, 2005). Therefore, much work has been done on carbonaceous aerosols. For example, Christiansen et al. (2020) investigated decadal changes in OC over the United States; Santos et al. (2016) conducted an in-depth analysis of OC and EC at various sampling sites in São Paulo, Brazil; Tiwari et al. (2013) investigated the temporal characteristics and sources of carbonaceous aerosol over Delhi in the Indo-Gangetic Basin, and Tham et al. (2019) studied the effect of peat-forest smoke on urban PM\(_{2.5}\) in Singapore’s Maritime Continent during 2012–2015 based on carbonaceous aerosol fractions. Chinese academicians have also performed research on carbonaceous aerosols. Zhu et al. (2014) compared and evaluated carbon fractions in various environments; Liu et al. (2016) investigated the characteristics of carbonaceous aerosol during the Chinese Spring Festival in Tianjin; Ji et al. (2019) investigated carbonaceous aerosol levels in the Beijing-Tianjin-Hebei region. The behavior of carbonaceous fractions under thermal-optical examination and the mechanism of SOC generation, on the other hand, are exceedingly complex and have not been thoroughly investigated. In-depth analyses of the various fractions of carbonaceous aerosols and the factors that influence SOC formation in polluted cities, particularly in areas with severe secondary pollution, are urgently needed.

Zhengzhou is in the south of the North China Plain, on the Yellow River’s lower reaches, and is close to the Beijing-Tianjin-Hebei region. It is the focal city of the Central Plains City Cluster and the center of China’s economic expansion from east to west. It is a major transportation hub and the capital of Henan Province, which is mostly an agricultural province with extensive agricultural, industrial, and domestic trade development. As a result, high pollutant emissions and severe atmospheric pollution have resulted. According to Bai et al. (2020), the yearly emissions of OC and EC in PM\(_{2.5}\) in Henan province were 161.2 and 83.1 Gg in 2016, respectively, and the role of Zhengzhou’s emissions cannot be overlooked. According to Liu et al. (2019), the yearly average concentrations of OC and EC in PM\(_{2.5}\) in Zhengzhou in 2017 were 10.5 ± 8.4 and 4.4 ± 2.5 μg/m\(^3\), respectively, with more severe pollution in the autumn and winter. As a typical city with severe carbonaceous aerosol pollution, Zhengzhou is an excellent candidate for this research.

The Coronavirus disease (COVID-19) emerged and spread swiftly in China during the winter of 2019 (late January 2020), prompting the Chinese authorities to respond with a complete city lockdown. This also presents a unique opportunity to investigate variations in carbonaceous fractions when anthropogenic activities are drastically reduced.

This study sets out to analyze the characteristics of carbonaceous aerosol fractions in the polluted city Zhengzhou before and during lockdown of the COVID-19 outbreak based on the continuous high temporal resolution measurements, estimates the concentration of SOC in both periods, and explores the influencing factors of SOC formations by combining the variations of meteorological factors and atmospheric oxidizing pollutants. In addition, the sources of carbonaceous aerosols were investigated using the Positive Matrix Factorization (PMF) model. The present study reveals the pollution characteristics, source distributions of carbonaceous fractions, and affected factors of SOC generation in the polluted city and exploits the hitherto unprecedented opportunity of anthropogenic source reduction in carbonaceous component variations and SOC generation, and provide significant insight into the temporal variations and sources of carbonaceous fractions in polluted cities.
Safety and Health) protocol (details in Text S1). The carbon fractions detected after the specific temperatures (an initially stepped temperature ramp of 310, 475, 615, and 870 °C, and a second temperature ramp of 550, 625, 700, 775, 850, and 870 °C) were coded as OC1, OC2, OC3, OC4, EC1, EC2, EC3, EC4, EC5, and EC6. The relative standard deviation was calculated to be 4% by repeated measurements of the standard solution of sucrose injected on the blank quartz filter.

The concentrations with a resolution of 1 h of particulates and trace gases, including PM$_{2.5}$, PM$_{10}$, SO$_2$, nitrogen dioxide (NO$_2$), carbon monoxide (CO), and O$_3$ were obtained by TE Model 1400a, TE Model 1405, and online observation instruments TE 43i, 42i, 48i, and 49i (Thermo Electron, USA). The meteorological conditions, including atmospheric pressure (P), temperature (T), relative humidity (RH), wind direction (WD), and wind speed (WS) were recorded by an automatic weather station Model QXZ 1.0 (Yigu Technologies, China) close to the sampling site with the accuracies of ±0.3 hPa, ±0.3 °C, ±3%, ±3′, ±(0.3 ± 0.3) m/s.

The EC-tracer method was utilized to estimate SOC concentrations, where the minimum OC/EC ratio was applied for the indicative of the primary OC to EC (Castro et al., 1999; Day et al., 2015). The calculation formulas for POC and SOC are as follows (Li et al., 2015):

$$\text{POC} = EC \times \frac{OC}{EC_{\text{max}}}$$

$$\text{SOC} = OC - POC,$$

where the minimum ratios of OC to EC are 2.0 and 3.5 for NP and LP, respectively.

PMF model (5.0, US EPA) was utilized for the source identification of carbonaceous aerosols. The principle is specified in EPA’s PMF Fundamentals and User Guide (Norris et al., 2014) and previous studies (Liu et al., 2018; Soleimanian et al., 2019). In this study, the uncertainty for the concentration of species above and below the method detection limit (MDL) was calculated as (0.1 × concentration + MDL/3), and (0.2 × concentration + MDL/3), where the concentration below the MDL was replaced by 0.5 times MDL (Farnham et al., 2002; Tauler et al., 2009). When the data were missed, the median of the species was applied to the gap-fill, and the uncertainty was four times the uncertainty calculated by the above method. And the uncertainty of species set for "weak" variables was trebled.

3. Results and discussion

3.1. Total and differential carbonaceous aerosol fractions

The temporal variations of the meteorological parameters, PM$_{2.5}$, OC and EC over the sampling periods are depicted in Fig. 1. During LP, the WS had increased significantly, especially from the entire southerly direction, which could also be observed in the rose diagram of wind speed and wind frequency (Fig. S2). The average WS was 0.8 ± 0.9 and 1.7 ± 1.0 m/s in NP and LP. And the average atmospheric pressure during NP was 1009 ± 7 hPa, the RH was 57 ± 23%, and the temperature was 7.3 ± 5.2 °C, while in the LP, they all exhibited slightly higher value, with the average atmospheric pressure was 1013 ± 6 hPa, the RH was 62 ± 20%, and temperature 7.5 ± 4.5 °C. PM$_{2.5}$ concentration showed a significant decrease (29%) during the LP, from 95 ± 63 to 67 ± 35 μg/m$^3$, which was broadly consistent with the results in the study conducted in California of USA (38%), Wuhan (37%), and Shijiazhuang (15%) in China (Lian et al., 2020; Liu et al., 2021; Feng et al., 2022).

Notably, as shown in Fig. 1, OC variations were closely related to the variation in PM$_{2.5}$ with a correlation coefficient of 0.86 (P < 0.01) between them, and it was obvious that the reduction of OC during LP was less than that of PM$_{2.5}$ with the correlation coefficient fell to 0.77 (P < 0.01). Average concentrations of carbonaceous aerosols, and average ratios of SOC/OC, and OC/EC during NP and LP are shown in Fig. 2. Compared to NP, OC mean concentration slightly decreased from 10.0 to 9.6 μg/m$^3$ (P < 0.05). Among OC fractions (OC$_3$), average concentrations of OC1, and OC4 increased (P < 0.01) during lockdown compared to NP, OC2 hardly changed, whereas OC3 decreased significantly (presented in Fig. S3 and discussed in Text S2). While the anthropogenic emissions were greatly reduced, OC concentration did not decrease significantly but increased as a percentage in PM$_{2.5}$ (from 11 to 14%). However, an obvious decrease was found in the mean concentration of EC, from 2.8 to 1.9 μg/m$^3$ (P < 0.001). All the EC fractions (EC$_3$) decreased during lockdown (Fig. S3 and Text S2). In addition, the correlation coefficients between PM$_{2.5}$ and EC during NP and LP were 0.81 and 0.83 (P < 0.01), respectively, revealing the strong correlations between them. Compared to other studies, the mean total carbon (TC) level (12.8 and 12.5 μg/m$^3$ in the two periods) in Zhengzhou was higher than that in Guangzhou of China from December 24, 2019 to January 7, 2020 (10.9 μg/m$^3$), while lower than that in Shijiazhuang, China (16.5 and 21.0 μg/m$^3$ in NP and LP) and Delhi of India in 2019 and 2020 with the mean TC

![Fig. 1. Temporal variations of the meteorological parameters, PM$_{2.5}$, OC, and EC.](image-url)
concentrations of 22.8 and 20.4 \( \mu g/m^3 \) (Huang et al., 2022; Feng et al., 2022; Sharma et al., 2022).

The average OC/EC ratio increased during LP, from 3.8 to 5.4, both lower than that in eastern Himalaya, India (4.2 and 5.7 during NP and LP), whereas, higher than the ratio of OC to EC in Guangzhou (2.8 in the winter of 2019–2020) and Delhi (2.3 and 2.3 in 2019 and 2020) (Chatterjee et al., 2021; Huang et al., 2022; Sharma et al., 2022). The differences in OC/EC ratios between these regions might arise from the differences in source emissions. OC/EC provides a preliminary determination of the carbonaceous component’s emission source, with greater OC/EC ratios typically representing biomass combustion as the dominant source, while lower ratios indicating a dominant contribution from fossil fuel combustion (Watson et al., 2001; Na et al., 2004; Ram et al., 2008; Saarikoski et al., 2008). Watson et al. (2001) reported that the ratios of OC to EC were 4.2, and 14.5 for residential wood burning and forest fires, respectively, and Saarikoski et al. (2008) also listed that the OC/EC ratio for biomass combustion was 6.6. The OC/EC ratios of 2.2 and 0.8 were reported for gasoline vehicles and heavy-duty diesel vehicles (Na et al., 2004), and a similar result of 0.71 was reported for the OC/EC from traffic emission (Saarikoski et al., 2008). And OC/EC for coal combustion was reported as 2.7 in the study by Watson et al. (2001). Therefore, the results in this study showed the carbonaceous aerosols were contributed by the mixture emissions of biomass burning, vehicle emissions, and coal combustion. During LP, markets, gatherings, theater performances, and other crowd gathering activities were suspended, and most work and industry was stopped, a lot of business was closed, and all classes were suspended according to the national first-level response to epidemic prevention and control of China government which meant that the pollutant emissions of mobile and stationary sources were significantly reduced. The increase in the average OC/EC ratio represented a decrease in the share of vehicle emissions, which coincided with the dominant reduction of anthropogenic activities during lockdown, and the same upward trend during the two periods was also observed in eastern Himalaya, India (from 4.2 to 5.7) (Chatterjee et al., 2021). In addition, OC/EC can be used to determine the presence of SOC, and OC/EC > 2 means the presence of SOC (Gray et al., 1986; Turpin and Huintzicker, 1991; Chow et al., 1996; Lim and Turpin, 2002). The OC/EC ratios in this study were 2.0–14.5 and 3.5 to 10.5 in NP and LP, respectively, suggesting the generation of SOC in both periods.

Compared to NP, the POC concentration increased slightly during the LP, from 6.2 to 6.6 \( \mu g/m^3 \) (\( P < 0.005 \)), and the SOC concentration decreased from 3.8 to 3.0 \( \mu g/m^3 \) (\( P < 0.001 \)). Also, the ratio of SOC to OC was found to decrease during lockdown, due to the small variation in OC and the significant decrease in SOC. These differences should be related to the difference in emissions from the pollution source of OC, and possibly the differences in meteorological parameters. The lower atmospheric pressure, WS, and temperature during LP were more likely to lead to more accumulation and less dispersion of pollutants, and more occurrence of secondary generations, resulting in lower POC concentrations and higher SOC concentrations. The influence factors of SOC generation would be discussed in detail in section 3.3.

### 3.2. Diurnal variations of carbonaceous aerosol fractions

The diurnal variations of OC, EC, POC, and SOC during NP and LP are illustrated in Fig. 3. EC and SOC showed higher hourly mean concentrations in NP than in LP, POC was found to be higher in LP and OC concentrations were extremely close in the two periods. The maximum concentration of OC was at midnight, the minimum concentration was in the afternoon, at 14:00 in NP, and at 15:00 in LP. Over multiple periods (1:00–7:00, 14:00–17:00, and 22:00–23:00), the hourly mean concentration of OC during the two periods fluctuated in opposite directions, and POC variations were found to be remarkably similar to OC variations, suggesting that OC variations were responsive to POC variations. As can be seen from Fig. 3, POC variations also showed almost the same trend as EC variations. POC and EC concentrations were lower during the daytime than during the nighttime in NP, while there was little fluctuation in them for the diurnal variation during lockdown. This indicated POC and EC as primary source markers were in more stable concentrations throughout the day due to reduced anthropogenic activities. The highest SOC concentrations were found at 0:00 (4.3 and 4.0 \( \mu g/m^3 \)) in both periods, in addition, the SOC variation in NP showed two peak concentrations at 12:00 and 19:00 (4.3 and 4.3 \( \mu g/m^3 \)), respectively. Due to the enormous number of photochemical reactions that were generated by the noticeably heightened precursor emissions in the morning, as well as the elevated temperature and solar radiation, the peak in SOC concentration occurred at noon. As the temperature rose in the afternoon (Fig. S4), the mixing height of the boundary layer rose, the wind speed increased as well (Fig. S4), facilitating in the dispersion of pollutants and resulting in a fall in SOC concentration (Huang et al., 2022). In the evening, on the one hand, pollutants accumulated up in the evening due to the deteriorating meteorological conditions and the decreased atmospheric boundary layer height; on the other hand, pollutant emissions substantially increased during rush hour, leading to further secondary conversions, and consequently, there was a recurrence of the SOC concentration peak. However, during LP, the hourly concentrations in the afternoon were all relatively low and the lowest SOC concentration was found at 14:00 (2.6 \( \mu g/m^3 \)), and there were no moments when the concentrations were particularly high, indicating that without the large amount of precursor emissions in the rush hour of morning and evening when anthropogenic activities were reduced, the SOC concentrations were lower and there was no longer a significant increase in SOC throughout the day. Although there was no peak at 19:00 during the lockdown period, there was also a slow upward trend resulting from the pollutants accumulation as a result of the poor meteorological conditions (Fig. S4) and the decreased atmospheric boundary layer height (Miyaizaki et al., 2009). These findings demonstrated that the peak of SOC concentration at this time in the normal period was more related to the increase of anthropogenic sources of precursors, while the changes during lockdown might be more affected by changes in the natural atmospheric environment.

OC3 of LP was significantly lower throughout the day, which was closely related to vehicle emissions (Qi et al., 2018; Kočak et al., 2021). OC1, OC2, and OC3 all showed daily variation characteristics of lower daytime concentrations than nighttime concentrations during the two periods, which might be due to the more accumulation and less
dispersion of the pollutants at the night. However, OC4 reached its highest value at noon during the two periods, possibly attributed to the secondary generation of OC. During NP, the OC4 also gradually increased at nightfall (19:00), which was consistent with the trend of SOC variation, once again proving that there was the obvious contribution of secondary generation of OC in OC4. The increase in OC4 and SOC concentration was partly due to not only the accumulation of pollutants arisen from the deteriorating meteorological conditions and the decreased atmospheric boundary layer height but also the increase in precursor emissions at nightfall, including during the off-duty rush hour. In addition, the OC4 diurnal variation was different from the SOC diurnal variation in LP, which demonstrated that the variation of OC4 concentration was also partially attributed to the variation of primary emissions, and as the results discussed in the previous section, OC4 was more strongly correlated with the carbonaceous fraction of primary source emissions during LP compared to NP. In short, the phenomenon that the concentration of OC4 was higher during the daytime indicated the existence of SOC generated by secondary reactions in OC4, while the different diurnal trends in the two periods might be due to the different dispersion conditions, different primary emissions, and different reaction mechanisms caused by the differences in oxidation conditions, oxidation rate, precursor classes, and precursor concentrations. For example, the reduction of NO\textsubscript{2} concentration and rise in O\textsubscript{3} concentration in LP might play a dominant role in the reduction of SOC concentration, and the details are to be discussed in section 3.3.

Almost all the EC\textsubscript{x} had higher concentrations during NP than during LP, with the largest difference for EC3, followed by EC4, EC2, and EC1, with little difference for EC5 and EC6. Combined with the source emission changes during LP, it was assumed that the reduction in EC\textsubscript{x} was mainly caused by the reduction in anthropogenic primary source emissions, such as vehicle emission and industry (Chatterjee et al., 2021; Koçak et al., 2021). Detailed discussions are in Text S3.

3.3. Influence factors of SOC

The daily variations of PM\textsubscript{2.5}, PM\textsubscript{10}, SO\textsubscript{2}, NO\textsubscript{2}, CO, and O\textsubscript{3} during NP and LP are shown in Fig. 5. Except for O\textsubscript{3}, the other five parameters showed a significant decrease during LP, especially NO\textsubscript{2} (decreased by 64% with the average concentration decreasing by 37 \(\mu g/m^3\)), and similar results were also found in Wuhan, China (Liu et al., 2021). The daily variation trends were slightly different between the two periods, which might be influenced by the changes in source emissions. The daily trends of O\textsubscript{3} were consistent for both periods with the valleys at 8:00 and peaks in the afternoon (15:00 in NP and 16:00 in LP), but O\textsubscript{3} concentrations were much higher during LP than during NP, with an increase of 127%. The elevated O\textsubscript{3} during the COVID-19 lockdown compared with the period before the lockdown was also observed with the different degrees of increase rates in other regions, such as California in the USA (14% increase), São Paulo in Brazil (11% increase), Wuhan in China (117% increase), Ispra in Italy with an increase of 21%, and Beijing and Shijiazhuang in China with the increase of 241% and 176% (Lian et al., 2020; Nakada and Urban, 2020; Liu et al., 2021; Putaud et al., 2021;
Feng et al., 2022). This was since the weakened scavenging effect on NO and HO$_2$ due to lower PM$_{2.5}$ concentration led to an increase in O$_3$ concentration, and important oxidants (e.g., OH radicals) and NO$_x$ competed for VOCs, and with the abatement effect, VOCs were more inclined to react with OH and increase HO$_2$, which also led to a significant increase in O$_3$ (Chatterjee et al., 2021; Huang et al., 2021). The diurnal variations of O$_3$ and NO$_2$ demonstrated an obvious chemical coupling effect. The concentration of NO$_2$ peaked at 8:00 in the morning due to the emission during rush hour, as well as the reaction between NO and O$_3$, which was also caused lowest concentration of O$_3$ at this time (Leighton, 1961). Subsequently, NO$_2$ progressively decreased as a result of its photolysis, which produced O$_3$ and caused O$_2$ to gradually rise (Tiwari et al., 2015). At 14:00, NO$_2$ reached its hourly minimum concentration, whereas O$_3$ reached its hourly maximum at 15:00. Following that, NO$_2$ increased and O$_3$ concentration decreased. The SOC concentrations decreased during LP as mentioned before, which might be related to the decrease in NO$_2$. NO$_2$ concentration reached the valleys at 14:00 in the two periods, and SOC concentration was also low at this time (Fig. 4a). In NP, the SOC variation was similar to the NO$_2$ variation and there was a delay effect on the variation of SOC concentration compared to the NO$_2$, while O$_3$ variations were almost the opposite. During LP, their variation trends were almost consistent with NP, and the pattern was more pronounced, that was, the variations of NO$_2$ and O$_3$ were completely opposite, while the trends of SOC and NO$_2$ were consistent, also with a short time delay.

The diurnal variations in the difference ratios of NO$_2$ and SOC during the lockdown period compared to the normal period were also calculated and shown in Fig. 4b. It can be observed that the fluctuations in their difference ratios were extremely similar, and when the NO$_2$ difference ratio rose, so did the SOC difference ratio. The NO$_2$ difference ratios at 3:00, 7:00, and 18:00 had increased. Correspondingly, the difference ratios of SOC were higher at 4:00, 8:00, and 19:00, the rise was an hour later than the increase in NO$_2$ difference ratios. Furthermore, the SOC difference ratio had an obvious peak at 12:00, and although NO$_2$ had no obvious peak during this time, the difference ratio of NO$_2$ at 11:00 was higher than the prior hour. More SOC growth at this time might be more susceptible to NO$_2$ growth, and should be jointly promoted by other factors. Therefore, it was tentatively inferred that the generation of SOC was closely related to the NO$_2$ concentration.

Fig. 5 shows the variations of O$_3$ concentration with NO$_2$ as a function of SOC concentrations in the normal and lockdown periods. O$_3$ concentration decreased with the increase of NO$_2$ concentration during NP and lockdown period, and it was more obvious in NP. Negative correlations were found between them, and the correlation in NP ($r = -0.53, P < 0.01$) was higher than in LP ($r = -0.48, P < 0.01$). The higher SOC ($>6$ μg/m$^3$) in NP was more densely distributed in the flat area of the curve where the O$_3$ concentrations leveled off ($<30$ μg/m$^3$) and NO$_2$ concentration was higher ($>50$ μg/m$^3$). The relatively high SOC ($>4$ μg/m$^3$) during LP was also found in the NO$_2$ concentration range of 10–20 μg/m$^3$, where the O$_3$ concentration range was wide. When NO$_2$ and O$_3$ concentrations were at moderate levels, there was also a certain high concentration distribution ($>4$ μg/m$^3$) of SOC, the corresponding points are located in the right circle in Fig. 5. Overall, during NP, the correlation between O$_3$ and NO$_2$ was better, high concentrations of SOC were more likely to exist when NO$_2$ was high and O$_3$ concentration was low; during LP, the correlation between O$_3$ and NO$_2$ was slightly lower than NP, slightly higher SOC was associated with lower NO$_2$ concentrations, while less affected by the concentration of O$_3$, and both NO$_2$ and O$_3$ concentrations at moderate levels. Therefore, SOC concentration might be more influenced by NO$_2$, which explained why SOC concentrations during LP were lower than during NP. In addition, during LP, SOC concentrations in the daytime were lower than at nighttime, which was probably due to that there were mainly more nocturnal heterogeneous reaction processes, and that was why the nighttime trends were consistent for both normal and lockdown periods (Zhang et al., 2018).

SOC production was also influenced by RH, they were positively correlated on the whole ($r = 0.35$ and $0.43$ during the normal and lockdown periods), however, different correlation results were found under different RH ranges (Fig. 5d). During NP, when RH was lower than 80%, a positive correlation was observed between SOC and RH ($r = 0.29, P < 0.01$), and the $r$ values for RH below 60% and between 60% and 80% were 0.24 and 0.22 ($P < 0.01$). However, there was no correlation between SOC and RH when RH was $>80$, and the slope of the fitting line became negative. During the lockdown event, a positive correlation ($r = 0.49, P < 0.01$) was found between SOC and RH when RH was below 60%, whereas when RH was $>60$, the slope of the fitting line became negative. There was no correlation between SOC and RH when RH was between 60% and 80%, and they became negatively correlated ($r = -0.32, P < 0.01$) when RH was above 80%. It should be the reason for the decrease in SOC concentration during LP. With the increase of RH (RH $>80$% during NP and RH $>60$% during LP), the water absorption of aerosol would increase, which would reduce the acidity of aerosol droplet, thus slowing down the promotion of acidity on SOC generation (Gaston et al., 2014; Liang et al., 2019). Another essential point to make was, the increase in RH would change the surface properties of the aerosols, thereby affecting the absorption rate of SOA reaction, and weakening the photochemical reaction, which was the most predominant pathway for the generation of SOA (Liang et al., 2019). The RH critical values on the inflection point during the two periods were different, which was attributed to the complexity of the secondary organic generation mechanism and the multiplicity of affected factors. In addition to the RH effects, SOC yields and SOC concentrations were also affected by other factors, such as reaction rates, temperature, WS, and other photochemical reaction conditions.

![Fig. 4.](image-url) a. Diurnal variations of NO$_2$, O$_3$, and SOC during the two periods; b. Diurnal variations of difference ratios of NO$_2$ and SOC during the lockdown compared to the normal periods.
and dispersion conditions. The more intuitive factor, WS, during LP was significantly higher than NP, with the increasing frequency of high WS and the more scattered WD (Fig. S2), which was conducive to the pollutant dispersion, and might be also a reason for the lower SOC concentration during LP.

3.4. Source identification of carbonaceous aerosol fractions

To better identify pollution sources of carbonaceous aerosols via the PMF model, OC and EC fractions, NO$_2$, SO$_2$, and CO were introduced to the model. EC2 and EC5 were determined as weak variables for the samples from NP and SO$_2$ and NO$_2$ were determined as weak variables for the samples from LP. In trying the different solutions with 3–7 factors, error estimation for the factor solutions was implemented and the

**Correlation is significant at the 0.01 level (2-tailed).**
In Factor 1, high loadings of OC4 (97% and 90% in the normal and lockdown periods), OC3 (32% and 68% in the two periods), and a little contribution of OC2 (5% and 4%) were observed. OC3 and OC4 related to 475–870 °C were dominated by organic matter with lower vapor pressures and had already been reported to be the tracers of secondary organic aerosols (Schauer et al., 1996; Kroll and Seinfeld, 2008; Li et al., 2018; Soleimanian et al., 2019). In addition, OC$_{300-450}$ °C was also identified as aged organic aerosol by Vodialka et al. (2015), which proved that OC2 (310–475 °C) in this research was partly associated with SOC. Therefore, this factor was identified as the SOC source. The contribution of factor 1 to carbonaceous aerosols was 22% and 26% in the normal and lockdown periods, with the contributed concentrations being 3.4 and 3.0 μg/m$^3$ (Fig. 7). SOC concentrations were also estimated in section 3.1 (3.8 and 3.0 μg/m$^3$). The results of SOC contributions from these two methods were directly observed to be close, and the characteristics of less concentration during LP are consistent, which also corroborated the reliability and accuracy of the results.

Factor 2 was interpreted as coal combustion with high contribution of OC1, OC2, EC1, SO$_2$, and CO. Previous study has reported that OC2 (140–280 °C) is mainly derived from coal combustion (Li et al., 2018), which is likely related to the OC1 fraction (0–310 °C) in this research. Liu et al. (2006) also researched that OC (120 °C) and OC (250 °C) were partially associated with coal combustion. In addition, Koçak et al. (2021) attributed OC2 (310–475 °C) partially to coal combustion, and SO$_2$ and CO were evident tracers from coal combustion (Vodialka et al., 2015). There was also some EC1 loading (17% and 60%) in this factor, which also accorded with the previous study conducted in Haikou, China (Li et al., 2018). From Fig. 7, Factor 2 was the second contributor to the carbonaceous aerosols and the contributions in the normal and lockdown periods were 19% and 28%, respectively, with concentrations of 3.0 and 3.2 μg/m$^3$. Although the percentage of coal combustion in TC increased a lot, the concentration change was negligible. This result might be related to the increase in activities such as domestic heating due to increased home time offsetting the reduction in coal combustion that had stopped in lots of industrial sectors. To control coal combustion emissions, a lot of efforts had made in Zhengzhou, such as reducing the total coal consumption of coal-fired power plants, strengthening the control of bulk coal combustion, strictly controlling coal consumption, and strictly implementing the substitution of equivalent or reduced coal consumption, further expanding the scope of elimination of small coal-fired boilers, and so on (http://public.zhengzhou.gov.cn/interpret depart/245402.jhtml, http://www.zhengzhou.gov.cn/news1/61477.jhtml). Based on this, the slight change in the concentrations of coal combustion before and during the lockdown suggested that it was difficult to further reduce the contribution of coal combustion to carbonaceous aerosols, which was a challenge to the subsequent control of carbonaceous aerosol pollution.

The chemical profile of factor 3 was defined by NO$_2$ (the loadings of 80% and 70% during the normal and lockdown periods), EC1 (the loadings of 76% and 40%), OC2 (the loadings of 54% and 52%), and OC3 (the loadings of 60% and 32%), mainly derived from gasoline vehicles (Chow et al., 2004; Cao et al., 2005; Mcdonald et al., 2013; Li et al., 2018; Köçak et al., 2021). Thus, factor 3 was identified as the emissions of gasoline vehicles, and this factor was the major contributor to OC (44% and 37%) and TC (47% and 37%) across all the research periods. As can be seen in Fig. 7, the contribution of this factor was the most in both percentages and concentrations during both two periods. As of the end of 2019, the number of civil motor vehicles in Zhengzhou had reached 3.856 million, an increase of 10.9% over the previous year (http://tjj.zhengzhou.gov.cn/tjgb/3112732.jhtml). The large number of motor vehicles and the large increase rate brought about the result that the motor vehicle emission source was more and more dominant in pollution sources, which was the reason that the contribution of gasoline vehicle emissions in NP in this study reached 47%. During LP, anthropogenic activities were greatly reduced, which meant a substantial reduction in motor vehicle emissions, however, remained the largest contributor among all these sources. On the one hand, the necessary industrial production had not completely stopped during LP, and some enterprises in Henan province gradually resumed work and production in the middle of February. On the other hand, there had been an increase in the flow of vehicles carrying the necessary commodities, medical supplies, and medical equipment due to the COVID-19 pandemic, and the sampling site was close to the main roads. As such, the gasoline vehicles still contributed a lot, nevertheless, the concentration of that decreased significantly, from 7.3 to 4.1 μg/m$^3$. The forced reduction of anthropogenic activities due to the epidemic lockdown is a rare and special scenario for passive emission reduction. In such a case, the significant contribution of gasoline vehicle emissions to carbonaceous aerosols in Zhengzhou is more obvious, also providing strong evidence that vehicle emission reduction has made a great contribution to carbonaceous aerosol emission reduction.

Factor 4 had some loadings of OC1, OC2, and EC$_n$, which were reported to be associated with biomass burning by previous studies (Cao et al., 2005; Liu et al., 2018; Soleimanian et al., 2019), so Factor 4 was identified as a biomass burning source. The contributions of this factor were 8% and 5% in the two periods, with concentrations of 1.2 and 0.6
μg/m³. In recent years, Zhengzhou has gradually upgraded the management and control of crop straw burning. It was strictly forbidden to burn crop wastes such as crop straws, garbage, weeds, and fallen leaves in the open air, and the comprehensive utilization of crop straws was encouraged (www.zhengzhou.gov.cn). Consequently, the contribution of biomass burning accounted for only a small fraction of carbonaceous aerosols. Besides this, the relatively low contribution during LP indicated the presence of fewer biomass burning-related activities.

The main carbonaceous fractions defining factor 5 were EC2, EC3, and EC4, which were closely related to diesel vehicle emissions (Lv et al., 2018; Qi et al., 2018; Koçak et al., 2021). Also, the partial apportionment of NO₂ in this factor suggested the emission of diesel vehicles. Therefore, factor 5 was identified as the emission source of diesel vehicles. Factor 5 had the smallest contribution among all these factors, contributing 5% and 4% to TC in the normal and lockdown periods, respectively. This result was inseparable from the implementation of government management policies. Since November 2018, Zhengzhou Municipal Government has comprehensively restricted heavy-duty diesel vehicle emissions below the National IV standard, from driving on urban roads (http://public.zhengzhou.gov.cn/?d=29). The concentrations of diesel vehicle emissions were 0.8 and 0.4 μg/m³ during the two periods, also indicating a reduction in the emissions of diesel vehicles during LP.

4. Conclusions
Carbonaceous fractions including OC1, OC2, OC3, OC4, EC1, EC2, EC3, EC4, EC5, and EC6 during NP before COVID-19 and LP of the COVID-19 outbreak were analyzed in a typical polluted city Zhengzhou, the core city of the Central Plains City Cluster of China. During LP, PM₂.5, OC, EC, and SOC concentrations all fell, with the exception of OC, which only decreased by 4%. The mean ratio of OC to EC increased, indicating that the carbonaceous aerosols were less affected by vehicle emissions during LP. The significant decrease in the concentrations of ECₜ, which were mostly markers of vehicle emissions, also indicated a reduction in the contribution of vehicle emissions. OC4 was partly from secondary generation, and the increase in correlation of OC4 with other OCₜ during lockdown indicated a decrease in the share of SOA and an increase in the share of primary emissions. OC, EC, and SOC showed higher hourly mean concentrations during NP with OC levels fluctuating less. During NP, SOC reached two peak values (4.3 and 4.3 μg/m³) at 12:00 and 19:00, respectively, however during lockdown, SOC did not rise appreciably throughout the day. SOC concentrations were more influenced by NO₂ as result, SOC concentrations were lower during LP when NO₂ concentrations were lower. SOC and RH were only positively associated when RH was below 80% during NP and below 60% during lockdown. Additionally, during LP, SOC concentrations were lower during the day than at night, which was probably due to the presence of more nocturnal heterogeneous reaction pathways, which also explained why overnight trends were constant for both NP and LP. The contribution of SOC apportioned by PMF was 3.4 and 3.0 μg/m³ during the two periods, which was comparable to the SOC results (3.8 and 3.0 μg/m³) estimated by the method of OC/EC minimum ratios. During lockdown, the contributions from gasoline vehicles decreased the most with the percentage from 47% to 37% and the concentration from 7.1 to 4.3 μg/m³. The contribution of biomass burning and diesel vehicles fell by 3% (0.6 μg/m³) and 1% (0.4 μg/m³). And coal combustion concentrations remained roughly constant, possibly due to increasing residential heating balancing the drop in coal combustion that had ceased in many industrial sectors. This research investigates changes in gas pollutants and carbonaceous fractions under situations of substantial reduction in anthropogenic activities, as well as the impact on SOC formation and carbonaceous aerosol sources. The findings of this work could provide fresh insight into the evolution of carbonaceous aerosols a hitherto unprecedented condition for atmospheric pollution control.

CRediT author statement
Zhe Dong: Conceptualization, Methodology, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization. Shenbo Wang: Investigation, Data Curation. Jiaxin Sun: Investigation. Luqi Shang: Investigation. Zihan Li: Investigation. Ruiqin Zhang: Conceptualization, Methodology, Resources, Data Curation, Writing - Review & Editing, Supervision, Funding acquisition.

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability
Data will be made available on request.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.136028.

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