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Unexpected rise of atmospheric secondary aerosols from biomass burning during the COVID-19 lockdown period in Hangzhou, China

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HIGHLIGHTS

- The number of Fe-rich and elemental carbon particles decreased by 93.2% and 48.2% during the lockdown.
- The number of biomass burning particles increased by 155.2% during the lockdown.
- Motor vehicle exhaust and industrial emissions were significantly reduced during the lockdown.
- Enhanced fugitive combustion contributed to the particles accumulation.

ABSTRACT

After the global outbreak of COVID-19, the Chinese government took many measures to control the spread of the virus. The measures led to a reduction in anthropogenic emissions nationwide. Data from a single particle aerosol mass spectrometer in an eastern Chinese megacity (Hangzhou) before, during, and after the COVID-19 lockdown (5 January to February 29, 2020) was used to understand the effect lockdown had on atmospheric particles. The collected single particle mass spectra were clustered into eight categories. Before the lockdown, the proportions of particles ranked in order of: EC (57.9%) < K-SN (13.6%) < Fe-rich (10.2%) < ECOC (6.7%) < K–Na (6.6%) < OC (3.4%) < K–Pb (1.0%) < K–Al (0.7%). During the lockdown period, the EC and Fe-rich particles decreased by 42.8% and 93.2% compared to before lockdown due to reduced vehicle exhaust and industrial activity. By contrast, the K-SN and K–Na particles containing biomass burning tracers increased by 155.2% and 45.2% during the same time, respectively. During the lockdown, the proportions of particles ranked in order of: K-SN (39.7%) < EC (38.1%) < K–Na (11.0%) < ECOC (7.7%) < OC (1.2%) < K–Pb (0.9%) < Fe-rich (0.8%) < K–Al (0.6%). Back trajectory analysis indicated that both inland (Anhui and Shandong provinces) and marine transported air masses may have contributed to the increase in K-SN and K–Na particles during the lockdown, and that increased number of fugitive combustion points (i.e., household fuel, biomass combustion) was a contributing factor. Therefore, the results imply that regional synergistic control measures on fugitive combustion emissions are needed to ensure good air quality.

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1. Introduction

After the outbreak of coronavirus disease-2019 (COVID-19) in December 2019, the virus’s (SARS-CoV-2) high infectivity rate led to its rapid spread worldwide (Wu et al., 2020). As of March 17, 2021, there have been 120,383,919 confirmed cases of COVID-19, including 2,664,386 deaths (https://covid19.who.int/). During this time, the Chinese government adopted many measures to control the spread of the virus. For example, the government implemented traffic control and entertainment venue shutdowns in January 2020 (Tian et al., 2020). Strict regulatory measures resulted in relatively low emissions from anthropogenic sources such as vehicle exhaust and industrial emissions, decreasing air pollutants nationwide (Cui et al., 2020; Shi and Brasseur, 2020). The Copernicus Atmosphere Monitoring Service (CAMS) observed a 20.0–30.0% reduction in the PM$_{2.5}$ concentrations in China (Yang et al., 2020). Additionally, the concentrations of PM$_{2.5}$, PM$_{10}$, CO, NO$_x$, and SO$_2$ in the Yangtze River Delta (YRD) region decreased by 12.3%, 19.6%, 7.8%, 18.5%, and 29.3%, respectively, during the lockdown compared with pre-epidemic levels in 2019 (Li et al., 2020).

Despite the sharp decline of particle matter and gaseous pollutants, unexpected haze episodes were observed nationwide during the COVID-19 lockdown. The average O$_3$ concentrations increased by 112.0% and 73.0% in northern and central China, respectively (Liu et al., 2021). Elevated Ox (NO$_2$+O$_3$) and radicals promoted the production of secondary aerosols nationwide (Meng et al., 2021; Tian et al., 2021). The mass concentration of fine particles in Shanghai during the 2020 New Year Holiday was two times higher than in 2019 (Chang et al., 2020). During the lockdown, sulfate and oxygenated organic aerosols contributed to two haze episodes with PM$_{2.5}$ concentrations exceeding 100 μg/m$^3$ in Shanghai (Chen et al., 2020). Increased PM$_{2.5}$ secondary inorganic aerosols were observed in Wuhan due to fireworks burning during the lockdown (Zheng et al., 2020). The concentration of organic nitrate markedly increased from pre-lockdown (0.5 ± 0.6 μg/m$^3$) to lockdown (5.3 ± 3.1 μg/m$^3$) in the northwest region where pollution was present (Duan et al., 2021). Although changes of chemical compositions and sources in atmospheric particles during the lockdown period have been studied, the internal mixing state and particulate reaction paths of organic and inorganic components have rarely been reported.

Single-particle aerosol mass spectrometry (SPAMS) is utilized to identify the sources and chemical reaction processes of atmospheric aerosols. (Silva et al., 1999; Dall’osto and Harrison, 2006; Moffet et al., 2008; Pratt and Prather, 2009). Many studies of single particle have been carried out by SPAMS in the YRD region (Yang et al., 2009) measured oxalic acid using single particle aerosol time-of-flight mass spectrometry (ATOFMS) and found biomass combustion was the main source of particles containing oxalic acid in Shanghai. (Zhang et al., 2009) analyzed lead (Pb) in individual aerosol, identifying sources such as coal combustion, waste incineration, and phosphate industry in Shanghai (Hu et al., 2018) and (Wang et al., 2021) used SPAMS to investigate the seasonal variations of atmospheric particles and identified dominant components of PM$_{2.5}$ at severe polluted episodes in Nanjing. (Cai et al., 2020) found that the aging process of single particle during the winter sandstorm in Ningbo was mainly through the surface heterogeneous reaction, rather than the collision of particles. Although many studies related to the characteristics of atmospheric single particle were carried out, comprehensive real-time measurements of single particle during a specific stage such as the COVID-19 lockdown period have been rarely reported.

A SPAMS was deployed in an eastern Chinese megacity (Hangzhou) before the COVID-19 lockdown period from 5 January to February 29, 2020 after the lockdown was lifted. The diurnal cycles, particle proportions, and size distributions were investigated by comparing the particles detected during the three periods, and a backward trajectories model was applied to analyze the pollution patterns. When anthropogenic emissions were low, secondary particulate sources and reaction paths were elucidated by studying single-particle accumulation characteristics and changes in their chemical composition.

2. Methods

2.1. Sample collection

According to official government documents, Zhejiang province launched the first-level response to a major public health emergency on January 23, 2020. The earliest date for enterprises in Hangzhou to resume work was February 9, 2020 (Yuan et al., 2021). Therefore, the measurements were carried out from 5 January to February 29, 2020. The measuring period was divided into three periods: before the lockdown (BL, 2020/1/5–2020/1/22), during the lockdown (DL, 2020/1/23–2020/2/9), after the lockdown (AL, 2020/2/10–2020/2/29). The sampling inlet was placed approximately 3 m above the roof of an eight-floor building (Binjiang district government building, 120.2°E, 30.2°N, Zhejiang province). The sampling site was surrounded by main roads, commercial and residential buildings.

Data of meteorological parameters and atmospheric pollutants including CO, SO$_2$, NO$_x$, O$_3$, PM$_{10}$ and PM$_{2.5}$ measured at Binjiang station (120.2°E, 30.2°N) were provided by Hangzhou Ecological and Environmental Monitoring Center. The meteorological parameters included air temperature (T), relative humidity (RH), wind speed (WS), wind direction (WD) and visibility.

2.2. Instrument and data analysis

2.2.1. Single particle measurements and analysis

Atmospheric particles in the 0.2–2.0 μm diameter range were collected by the SPAMS-0515 (developed by Hexin Analytical Instrument Co., Ltd., China) at 1-h resolution. The aerosol stream at a flow rate of 75 ml/min was dried by a homemade silica gel diffusion dryer to remove liquid water from the air. After the acceleration and concentration process in the aerodynamic lens, aerosol particles in the atmosphere were sized by two 532 nm solid-state continuous lasers. Then particles were ionized by a 266 nm pulsed laser and the mass spectra of particles were analyzed by a dual polarity time-of-flight mass spectrometer. The hit rate of SPAMS is defined as the ratio of the number of particles ionized to the number of particles sized. During the sampling period, the average hit rate of SPAMS was 31.6% within the recommended range (Li et al., 2011).

The single particle analysis software toolkit YAADA 2.0 () based on adaptive resonance neural network classification method (ART-2a) was used to cluster particles into different categories based on their similarities of mass spectra (Song et al., 1999). The iteration times and calculation speed of ART-2a can be determined by adjusting algorithm parameters (Phares et al., 2001). For this work, the ART-2a parameters included a learning rate of 0.05, a vigilance factor of 0.85, and 19 iterations.

2.2.2. Regional transport analysis

The backward trajectories and a potential source contribution function (PSCF) models were applied to study the impact of regional atmospheric transport on different types of particles. In the HYSPLIT-based backward trajectories model, 500 m was chosen as the arriving height to reduce the impact of ground friction according to former studies (Polissar et al., 2001). The PSCF model was used to clarify the pollution contribution of each transport mode, and the polluted trajectories were filtered out in combination with the pollution setting (Zeng and Hopke, 1989). The higher the weighted PCSF (WPSF) value the more likely the pollution source (Aubin et al., 1985). Moreover, the parameters were set as follows, the grid cell solution was 1° × 1°, and the criterion was set to the 75% quantile of particle counts.
3. Results and discussion

3.1. Overview of meteorological parameters and air pollutants

A time series of meteorological parameters, including the mass concentrations of CO, SO\(_2\), NO\(_2\), O\(_3\), PM\(_{10}\), PM\(_{2.5}\), and SPAMS-detected particles in all periods are shown in Fig. 1. The changes in mean mass concentrations of pollutants and particle counts of each particle category are summarized in Fig. 2. The meteorological characteristics were low temperature, high humidity, and low wind speed during the measurement period (Table 1). The mean concentration of SO\(_2\) only dropped slightly from 6.4 \(\mu\)g/m\(^3\) to 6.2 \(\mu\)g/m\(^3\), probably due to the continuous use of coal for electricity during the lockdown (Chang et al., 2020). After the COVID-19 outbreak, the ratio of SO\(_2\)/NO\(_2\) increased sharply because of reduced vehicle exhaust and stable emissions from fixed sources for continuous electricity supply. The concentration of NO\(_2\) decreased by 69.5% from 46.7 \(\mu\)g/m\(^3\) to 14.3 \(\mu\)g/m\(^3\) during the lockdown and increased to 17.3 \(\mu\)g/m\(^3\) after the lockdown. The average decline rate of NO\(_2\) in the YRD region was measured to be 39.0% which was much lower than the sharp decrease rate in Hangzhou (Fan et al., 2021). The dramatic reduction in nitrogen oxides brought a chain reaction, one of which was the increase in O\(_3\) concentration. The studies showed that although decreased volatile organic compounds (VOCs) lowered O\(_3\) production, it did not eliminate the weak nighttime NO titration reaction on O\(_3\) production due to a dramatic drop in NO concentrations over a short period (Seinfeld and Pandis, 2016; Zhu et al., 2021). The mean O\(_3\) concentration increased by 165.7% from 26.2 \(\mu\)g/m\(^3\) to 69.6 \(\mu\)g/m\(^3\) during the lockdown in Hangzhou, far exceeding the 52% increase in average O\(_3\) concentration in the YRD region (Fan et al., 2021). After the lockdown, the mean concentration of O\(_3\) dropped from 69.6 \(\mu\)g/m\(^3\) to 54.7 \(\mu\)g/m\(^3\), resulting from enhanced nighttime O\(_3\) depletion by elevated NO concentrations (Wang et al., 2021). The average mass concentration of PM\(_{2.5}\) decreased by 28.6% from 40.4 \(\mu\)g/m\(^3\) to 28.8 \(\mu\)g/m\(^3\) during the lockdown. After the lockdown, the mean concentration of PM\(_{2.5}\) decreased by 12.1% compared to during the lockdown. The reduction of PM\(_{2.5}\) in Hangzhou is smaller than the average declining rate of the Yangtze River Delta region which was measured to be 36.0% by (Yao et al., 2021), suggesting that particulate matter generation in Hangzhou was still high during the epidemic despite the restricted human activities.

In the atmospheric aging process, H\(_2\)SO\(_4\) from gaseous oxidation of SO\(_2\) can be oxidized by O\(_3\), HONO and NO\(_2\) to form H\(_2\)SO\(_4\) in the aqueous phase as reported by (Wang et al., 2020). The formation pathway of HNO\(_3\) has been suggested via the aqueous disproportionation reaction of NO\(_2\) in an alkaline environment (Green et al., 2019). As important atmospheric oxidants, Ox (O\(_3\)+NO\(_2\)) concentration increased from 72.9 \(\mu\)g/m\(^3\) to 83.9 \(\mu\)g/m\(^3\) during the lockdown in Hangzhou, which implied increased atmospheric oxidation capacity. It has been observed that enhanced atmospheric oxidation levels promoted the formation of secondary particles during the lockdown nationwide (Meng et al., 2021; Tian et al., 2021). Due to the reduction of O\(_3\) concentration, the average concentration of Ox decreased by 15.2% after the lockdown. The PM\(_{2.5}/\text{CO}\) ratio is an indicator used to weigh the impact of primary emissions and meteorological factors on the fine particles (Zhang and Cao, 2015; L. Li et al., 2020). The increased PM\(_{2.5}/\text{CO}\) ratio in Hangzhou showed that secondary aerosols took up a higher proportion of atmospheric particles during the lockdown than usual. After the lockdown, the PM\(_{2.5}/\text{CO}\) dropped by 12.2%, indicating the reduction of atmospheric oxidation capacity. The increased proportion of secondary particles in Hangzhou during the lockdown can be preliminarily inferred to be due to the enhanced oxidization capacity of the atmosphere.

3.2. Characteristics of single particles during each period

A total of 930941, 879286 and 896258 particles with positive and negative mass spectra were collected and analyzed before, during and after the lockdown. The data are summarized in Table 1. The particle types were split into eight groups, the average mass spectra of each type are shown in Fig. S1, and their mixing state is shown in Fig. S4. Time series and correlation of the mass concentration of PM\(_{2.5}\) and the number concentration of particles measured by SPAMS are summarized in Fig. S2 and Fig. S3. The total particle counts displayed a strong correlation with PM\(_{2.5}\) concentrations (R\(^2\) = 0.85, Fig. S3), reflecting the reliability and stability of data obtained by SPAMS. To analyze the dominant components in each period by comparing the particle composition of PM\(_{2.5}\) in the most polluted episodes, the particle proportions in different levels of PM\(_{2.5}\) (based on hourly data) are summarized in Fig. 3 (b) and the mass spectrometry data of all periods when the PM\(_{2.5}\) hourly mass concentration was higher than 75 \(\mu\)g/m\(^3\) was compiled into average spectra in Fig. S5.

3.2.1. EC

EC particles were identified as containing a dual polarity carbon cluster, such as 12[C]\(^+\), 24[C\(_2\)]\(^+\), and 36[C\(_3\)]\(^+\), with no obvious OC...
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High relative peak area of 97\[HSO_4\]^- played a vital role in the formation of EC particles, illustrated by a marker ions (Toner et al., 2006). Previous studies showed that sulfuric acid dominated the polluting process and accounted for 60.5% at the most polluted interval (GPMD$_{2.5}$≥76 µg/m$^3$), while this proportion dropped to 40.7% during the lockdown. During the lockdown, the relative peak area of 36[C$_3$]$^+$ and 62[NO$_3$]$^-\$ at polluted episodes decreased by 26.3% and 26.2%, respectively. The proportion of EC particles increased to 61.4% at the most polluted interval and the relative peak area of 36[C$_3$]$^+$ and 62[NO$_3$]$^-$ increased by 39.1% and 48.9% after the lockdown. (Xu et al., 2020) has reported that the traffic flow decrease ratio was 84.0% in the urban area of Hangzhou, leading the black carbon concentration to drop by 44.0% from 2.3 to 1.3 µg/m$^3$ during the COVID-19 lockdown period. Therefore, the decline of EC particles can be attributed to the decrease of on-road-vehicle numbers resulting from travelling restrictions during the lockdown.

3.2.2. K-SN

The K-SN particles were characterized by 39[K]$^+$ as well as sulfate at m/z = 97[HSO$_4$]$^-$ and nitrate at m/z = 46[NO$_3$]$^-$ and 62[NO$_3$]$^-$ in the negative spectra. K and Cl were considered products of biomass burning (Dall Osto and Harrison, 2006). However, studies showed that K remained in the particle phase in the subsequent evolution process, while Cl was distributed into the gas phase (Liu et al., 2021). 90.4% of particles resulting from biomass burning were observed to undergo a secondary mixing of K$^+$ with HSO$_4^-$ and NO$_3^-$ (Bi et al., 2011). In eastern China, household fuel like stored straw and firewood used for residential heating and cooking are the main sources of particles resulting from biomass burning (Silva et al., 1999).

Table 1

Summary of average meteorological parameters, pollutants mass concentration and particle counts before, during and after the lockdown.

| Pollutants (µg/m$^3$) | BL   | DL   | AL   |
|-----------------------|------|------|------|
| SO$_2$                | 6.2  | 6.2  | 6.5  |
| NO$_2$                | 14.3 | 14.3 | 17.3 |
| O$_3$                 | 69.6 | 69.6 | 54.7 |
| CO                    | 657.3| 657.3| 658.0|
| PM$_{10}$             | 42.7 | 42.7 | 42.7 |
| PM$_{2.5}$            | 25.3 | 25.3 | 25.3 |

particle counts and proportions

| EC                  | 334 579 (38.1%) | 380 896 (42.8%) |
| K-SN                | 349 431 (39.7%) | 223 323 (24.9%) |
| Fe-rich             | 6597 (0.8%)     | 4723 (0.5%)     |
| K-Na                | 7099 (8.7%)     | 7099 (8.7%)     |
| ECOC                | 68 064 (7.7%)   | 124 497 (13.9%) |
| OC                  | 94 503 (10.2%)  | 97 090 (11.0%)  |
| K-Pb                | 7498 (0.9%)     | 2433 (0.3%)     |
| K-Al                | 61 602 (6.6%)   | 97 090 (11.0%)  |
| Total               | 879 286         | 879 286         |

Fig. 2. (a) Changes in SO$_2$, NO$_2$, O$_3$, CO, PM$_{10}$, PM$_{2.5}$, Ox (O$_3$+NO$_2$) average concentrations and SO$_2$/NO$_2$, PM$_{2.5}$/PM$_{10}$ ratios before, during and after the lockdown; (b) Changes in average particle counts of each particle category before, during and after the lockdown (abbreviated as BL, DL and AL).
proportion of $\text{SO}_4^{2-}$ in $\text{PM}_{2.5}$ increased by 13.6%, while the proportion of $\text{NO}_3^-$ decreased by 11.5% during COVID-19 lockdown in Hangzhou. During the lockdown, the relative peak area of $39\text{[K]}^+$ and $97\text{[HSO}_4^-]$ at polluted episodes increased by 51.9% and 55.0%, respectively. After the lockdown, the number of K-SN particles decreased by 40.2%. The proportion of K-SN particles dropped from 40.0% to 14.2% and the relative peak area of $39\text{[K]}^+$ and $97\text{[HSO}_4^-]$ decreased by 19.0% and 35.5% at the most polluted episodes after the lockdown.

Before the Chinese 2020 Spring Festival, 130 million people migrated from cities to the countryside, and nearly 82.0% of them had to stay in the countryside after the holiday because of the COVID-19 outbreak, causing a 9.0% increase in the rural population (Shen et al., 2021). Recent research found that the average concentration of particulate contaminants from residential biomass burning in rural areas was twice as much as in urban areas during the lockdown in Hangzhou (Xu et al., 2020). The same thing happened in northern China, the source contribution of biomass burning to $\text{PM}_{2.5}$ increased from 11.0% to 20.0% during the lockdown in Tangshan (Li et al., 2021). It can be speculated that the explosive growth of K-SN particles was related to the increased biomass burning emissions during the lockdown.

3.2.3. Fe-rich

Fe-rich particles exhibited a high relative area of $56\text{[Fe]}^+$, and originated from dust, coal combustion, and the steel industry (Cui et al., 2020; Lu et al., 2017). Fe-rich particles occupied 10.2%, 0.8% and 4.6% of the total particle counts in three periods, respectively. During the lockdown, the Fe-rich particle counts decreased by 93.2% and its proportion at polluted episodes also decreased from 9.3% to less than 2%. During the same period, the relative peak area of $56\text{[Fe]}^+$ decreased by 59.7%. After the lockdown, the number of Fe-rich particles increased.
sharp by 456.3% and occupied 10.1% at the most polluted episodes. This result is consistent with the 78.0% decline of the concentration of Fe in PM$_{2.5}$ measured by (Liu et al., 2021) during the lockdown in Hangzhou. As a significant emission from the metal industry and road dust, the decrease in Fe-rich particles can be considered as a result of shutdowns and travelling control during the lockdown.

3.2.4. K–Na

Intense ions at 23[Na]$^+$ and 39[K]$^+$ were markers of K–Na particles. According to Figs. S4 and 23[Al]$^+$ had a high mixing degree for this particle type. K–Na particles partly came from mixing marine aerosols with airborne soil during long-distance atmospheric transport (Mofet et al., 2008; Vu et al., 2015). The same particle composition was also observed in some biomass combustion particles in coastal areas (Zhang et al., 2013). The proportion of K–Na in three periods was 6.6%, 11.0% and 8.7%, respectively. During the lockdown, the number of K–Na particles increased by 45.2% and its proportion at the most polluted episodes also increased from 6.0% to 12.2%. After the lockdown, K–Na particle counts decreased by 24.9%. It can be speculated that the increase of K–Na particles was caused by the mixing of oceanic airflow and biomass burning emissions, but this conclusion needs to be further verified by atmospheric regional transport models.

3.2.5. ECOC and OC

The general feature of ECOC particles was that the particle spectra had peaks indicative of EC(12[C]$_3^+$), 24[C]$_{24}^+$, and 36[C]$_{36}^+$ and OC. The OC particles were identified by 39[K]$^+$ and OC marker ions such as 27[C]$_{27}H$_2$H^+$ and 43[C]$_{43}H$_4$O^+$. ECOC particles occupied 6.7%, 7.7% and 13.9% in three periods, respectively. The number of ECOC particles experienced a slight increase of 9.7% during the lockdown and a substantial increase of 69.6% after the lockdown. But the proportion of ECOC particles at the most polluted episode decreased from 7.0% to 4.2% during the lockdown and remained the same level after the lockdown despite the dramatic increase of the ECOC particle counts. The proportion of OC particles in three periods was less than 5.0%, but it also experienced a similarly dramatic increase as ECOC after the lockdown. The changes in the number of ECOC and OC particles are in accordance with findings reported by (Feng et al., 2022) in which the concentration of secondary organic carbon displayed a significant increase due to enhanced atmospheric oxidation capacity in North China Plain region. During the lockdown, the concentration of Ox increased by 18.6% which enhanced atmospheric oxidation capacity in North China Plain region.

3.2.6. K–Pb and K–Al

The K–Pb particles contained 39[K]$^+$ and had signals at m/z = 206, 207, and 208. The K–Al particles exhibited an intense signal of 39[K]$^+$ and 23[Al]$^+$. Former investigations have found that K–Pb particles are mainly from the deposition of airborne lead, while street dust is the important source of K–Al particles (Tanner et al., 2008; Hu et al., 2014). The proportion of K–Pb and K–Al particles in the total number of particles is less than 2.0% and changed very little in all three periods. This result suggests that the number of soil dust particles was relatively stable throughout the measurement period.

3.3. Diurnal variation and size distribution of particles

The diurnal cycles of each particle category before, during, and after the lockdown are presented in Fig. 3 (a). The relative peak area of NO$_3^-$ and HSO$_4^-$ was high in the negative spectra of all types of particles as shown in Fig. S1, and the particles containing these two components had bimodal distribution. Before the lockdown, the diurnal profile of K–SN particles presented an approximate bimodal distribution with two peaks appearing at 12:00–14:00 and 22:00–23:00. During and after the lockdown, K–SN diurnal cycle peaks were at 08:00–10:00 and 20:00–23:00. As the number of particles increased, the daytime peak of K–SN particles was more pronounced than that before the lockdown. It has been reported that the high Ox concentrations enhanced the photo-oxidation in the daytime, which promoted the formation of secondary particles and resulted in changes in diurnal variation (Cheng et al., 2021). EC and Fe-rich particles showed more stable diurnal variations than K–SN particles. Throughout the whole monitoring period, EC diurnal cycle peaks appeared at 06:00–10:00 and 20:00–23:00, and the diurnal cycles of the Fe-rich particles were similar to EC, but the first peak appeared slightly earlier at 04:00–06:00. (Pal et al., 2014) suggested that the anthropogenic emissions during the day and the nighttime low-temperature inversion led to the bimodal distribution of particles. However, the K–Na, ECOC, and OC particles with low emissions or affected by regional atmospheric transport had different diurnal distributions.

The variation of trend in particle size is shown in Fig. 4 and Fig. S6. The average particle size was 0.5–0.6 μm. Ambient particles in the size range of 0.5–1.0 μm are confirmed to be formed from the nanoparticles by volume-phase reactions in clouds and wet aerosols (Wu et al., 2018; Ervens et al., 2011). It can be inferred that the majority of particles sampled during the monitoring period have undergone the atmospheric aging process. Submicron particles accounted for 92.3% of the particles before the lockdown, 94.1% during the lockdown, and 96.9% after the lockdown. The distribution ratio of particles in the diameter range of 0.2–0.5 μm was 10.1% before the lockdown, 15.0% during the lockdown, and 19.6% after the lockdown. (Tang et al., 2021) observed an increased number of particles (100 nm < Da < 698 nm) during the lockdown and proposed that the enhanced intensity of the atmospheric oxidation process promoted secondary particles formation. Other atmospheric studies during the lockdown also observed increased secondary aerosols production due to the high Ox concentrations during the lockdown (Yadav et al., 2021; Hong et al., 2021; Huang et al., 2021). Therefore, the high proportion of submicron particles during the lockdown might originate from enhanced atmospheric oxidation capacity in Hangzhou.

The EC and K–SN particles accounted for 70.0–80.0% of submicron particles. While the number of EC particles dropped sharply during the lockdown, the proportion of sub-micron particles slightly increased. On the one hand, the proportion of submicron K–SN particles increased from 13.8% to 40.1%. On the other hand, the proportion of K–SN particles with the size of 0.2–0.5 μm during the lockdown remained unchanged, mainly due to the heterogeneous reaction and the moisture absorption process of particles born from biomass burning with an initial particle size of 100–200 nm (Vu et al., 2015). The number of K–Na particles increased by nearly 60.0% during the lockdown, but the enhanced K–Na particles were primarily distributed in the 1.0–2.0 μm range, different from the increasing K–SN pattern. The majority of aerosols collected in the marine boundary layer were of submicron diameter (Covert et al., 1996). These particles underwent the ageing process and mixed with large particles such as airborne soil and biomass burning particles during long-distance atmospheric transport, resulting in particle diameter growth.

3.4. Potential geographical origins of particles

The backward trajectories and potential source contribution function (PSCF) models were applied to analyze the pollution patterns during each period. Combined with the wind direction and speed, the source distribution of particles is shown in Figs. S7 and a preliminary judgment was made on the changes in the number of different particles within the wind field. Before the lockdown, the high EC and Fe-rich particle counts and the low wind speed correlated more than other periods. New particle generation is more likely to occur in environments with low wind speeds (<2 m/s) and the local accumulation of aged particles are also highly related to low wind speed (Bao et al., 2019; Jones et al., 2010;
Before the lockdown, the high EC and Fe-rich particle counts and the low wind speed correlated more than other periods, which reflected that local emissions were the main sources of EC and Fe-rich particles at that time. During the lockdown, the increased K–SN and K–Na particle counts were from the medium wind speed area, illustrating the impact of regional atmospheric transport. The Fe-rich and ECOC particles rebounded significantly after the lockdown, and the corresponding wind speed was higher than before the lockdown, indicating a synergistic effect of atmospheric transport and increased local anthropogenic emissions.

The 48 h backward trajectories from 5 Jan to 29 Feb were grouped into four clusters. The results of the cluster-mean trajectories and the proportion of particles in each period are shown in Fig. S8. The air parcels of Cluster 1 came from southern Jiangsu province and were transported to the sampling site through some cities in northern Hangzhou. Cluster 1 accounted for 35.9% of the trajectories and had the highest proportion (51.6%) before the lockdown. The air parcels from Cluster 2 originated from the marine area. These air parcels passed over the Bohai Sea and the Yellow Sea and finally arrived in Hangzhou via the coastal areas of Jiangsu and Shanghai. Cluster 2 accounted for 47.2% during the lockdown and had the highest proportion in the three periods. The air parcels from Cluster 3 departed from the northern part of Hunan Province, passing through Jiangxi Province from the northwest to the southeast, and reached Hangzhou through the western Zhejiang region. After the lockdown, Cluster 3 played an important role in regional atmospheric transport, but it accounted for less than 10.0% of the trajectories before and during the lockdown. The air parcels from Cluster 4 originated from the Beijing–Tianjin–Hebei area and passed through Shandong and Anhui to Hangzhou. Cluster 4 had the highest proportion (21.5%) after the lockdown.

Before the lockdown, the EC and K–SN particles dominated all of the clusters. The EC particles accounted for more than 40%, while the K–SN particles accounted for only 15.0%. The proportion of K–SN and K–Na particles increased approximately 25.0% in Clusters 1, 2, and 4 during the lockdown, attributing the accumulation of the K–SN and K–Na particles to regional atmospheric transport. After the lockdown, the EC and Fe-rich particle proportions rebounded, and the ECOC particles occupied a more significant proportion than other periods. Before and after the lockdown, vehicle exhaust and work activities resulted in the rise of carbon-containing particles nationwide, altering the dominating particle composition.

Fig. 5 shows that the WPSCF values of the EC and Fe-rich particles were over 0.7 at the junction of northern Jiangsu province and Anhui province and the junction of western Fujian province and Guangzhou province before the lockdown. The pollution sources of K–SN were distributed in bands, mainly in the Fujian and Anhui provinces and parts of the Zhejiang province before the lockdown. During the lockdown, southern Jiangsu province and northern Anhui province were likely to be EC particle sources according to the spatial distribution of their WPSCF values. The WPSCF values of the K–SN particles rose to 0.8–1.0 in the Anhui province, central Shandong province, and the junction of Hebei and the Anhui province. As shown in Fig. S9, fugitive combustion sources in this area increased significantly during the lockdown. According to the data from the National Aeronautics and Space Administration (NASA), the number of fugitive combustion sources increased by 24.1% in Zhejiang province during the lockdown in China (https://firms.modaps.eosdis.nasa.gov/). It was speculated that the atmospheric transport of increased household fuel emissions from the surrounding area resulted in the accumulation of K–SN particles during the lockdown. The distribution of K–Na particle pollution sources was similar to K–SN due to secondary mixing with sea salt particles and combustion products in the coastal areas. After the lockdown, the high WPSCF values of the EC and K–SN particles were transferred to South China.

4. Conclusion

During the COVID-19 outbreak, the Hangzhou Municipal Government’s restrictions on human activities caused the overall mass concentration of fine particulate matter in the atmosphere to decrease, but
unexpected air pollution episodes still existed. Before the lockdown, the proportion of particles ranked in order of: EC (57.9%) < K-SN (13.6%) < Fe-rich (10.2%) < ECOC (6.7%) < K-Na (6.6%) < OC (3.4%) < K–Pb (1.0%) < K–Al (0.7%). During the lockdown period, the EC and Fe-rich particles decreased by 42.8% and 93.2% compared to before lockdown due to reduced vehicle exhaust and industrial activity. By contrast, the K-SN and K-Na particles containing biomass burning tracers increased by 155.2% and 45.2% during the same time, respectively. During the lockdown, the proportion of particles ranked in order of: K-SN (39.7%) < EC (38.1%) < K–Na (11.0%) < ECOC (7.7%) < OC (1.2%) < K–Pb (0.9%) < Fe-rich (0.8%) < K–Al (0.6%). After the lockdown, the number of EC, Fe-rich, ECOC and OC particles increased by 6.7%, 456.3%, 69.6% and 266.7% respectively. But the number of K-SN and K–Na particles decreased by 40.2% and 24.9% due to the changes in atmospheric transport characteristics and reduction of atmospheric oxidation capacity. After the lockdown, the proportion of particles ranked in order of: EC (42.9%) < K-SN (24.9%) < ECOC (13.9%) < K–Na (8.7%) < OC (4.7%) < Fe-rich (4.6%) < K-Pb (0.5%) < K–Al (0.3%) 

EC and Fe-rich particles showed more stable bimodal distributions than K-SN particles throughout the whole monitoring period, while the high Ox concentrations enhanced the atmospheric oxidation and resulted in changes in the daytime peak of K-SN particles. Moreover, increased Ox (O3 + NO2) led to enhanced atmospheric secondary aerosol production and a slightly increased proportion of submicron particles from 92.3% to 94.1%. The backward trajectories model results illustrated that inland (Anhui and Shandong provinces) and marine transported air masses may have contributed to the increased K–SN and K–Na particle concentrations, respectively, and the fugitive combustion emissions from the inland air mass could be an essential factor. The results highlight that although vehicle exhaust and industrial activities were significantly reduced during the lockdown period, the increasing fugitive combustion sources led to fine particles accumulation.

CRediT authorship contribution statement

Huifeng Xu: Writing – original draft, Writing – review & editing. Linghong Chen: Methodology, Resources. Jiansong Chen: Data curation, Resources. Zhihr Bao: Conceptualization, Writing – review & editing. Chenxi Wang: Software. Xiang Gao: Data curation. Kefa Cen: 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.

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Appendix A. Supplementary data

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