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A chemical cocktail during the COVID-19 outbreak in Beijing, China: Insights from six-year aerosol particle composition measurements during the Chinese New Year holiday

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HIGHLIGHTS
• Different responses of primary and secondary species to the COVID-19 outbreak
• 30–50% decreases in primary aerosol species during the Chinese New Year holiday
• Much smaller changes in secondary species compared with primary aerosol species
• Large increases in sulfur and nitrogen oxidation capacity during the last decade

GRAPHICAL ABSTRACT

ABSTRACT

The rapidly spread coronavirus disease (COVID-19) has limited people’s outdoor activities and hence caused substantial reductions in anthropogenic emissions around the world. However, the air quality in some megacities has not been improved as expected due to the complex responses of aerosol chemistry to the changes in precursors and meteorology. Here we demonstrate the responses of primary and secondary aerosol species to the changes in anthropogenic emissions during the COVID-19 outbreak in Beijing, China along with the Chinese New Year (CNY) holiday effects on air pollution by using six-year aerosol particle composition measurements. Our results showed large reductions in primary aerosol species associated with traffic, cooking and coal combustion emissions by 30–50% on average during the CNY, while the decreases in secondary aerosol species were much small (5–12%). These results point towards a future challenge in mitigating secondary air pollution because the reduced gaseous precursors may not suppress secondary aerosol formation efficiently under stagnant meteorological conditions. By analyzing the long-term measurements from 2012 to 2020, we found considerable increases in the ratios of nitrate to sulfate, secondary to primary OA, and sulfur and nitrogen oxidation capacity despite the overall decreasing trends in mass concentrations of most aerosol species, suggesting that the decreases in anthropogenic emissions have facilitated secondary formation processes during the last decade.

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1. Introduction

The coronavirus, SARS-CoV-2 that was discovered in 2019 spreads rapidly around the globe (Wang et al., 2020a; Zhu et al., 2020), and the coronavirus disease (COVID-19) has caused an infection of more than 10 million and a death of more than 500,000 people until 1 July 2020 (https://covid19.who.int/). To contain the COVID-19 outbreak, a number of countries and cities implemented lockdown measures to reduce human outdoor activities, which provides a unique opportunity to investigate the response of air pollution to the changes in anthropogenic emissions. For example, many studies have reported large reductions in NOx due to the significantly reduced traffic emissions during the COVID-19 outbreak (Bauwens et al., 2020; Fan et al., 2020; Zhang et al., 2020) despite the increases in O3. However, several studies also found that the reduced anthropogenic emissions did not eliminate the occurrence of severe haze events in China (Chang et al., 2020; Huang et al., 2020; Wang et al., 2020b) due to the nonlinear relationships between particulate matter (PM) and their precursors, unfavorable meteorology and enhanced secondary production. Indeed, the average PM2.5 (particulate matter with aerodynamic diameter less than 2.5 μm) concentration during the first season in Beijing in 2020 was the same as that in 2019 (52 μg m−3) according to the report of Beijing Municipal Ecology and Environment Bureau. Considering that most studies above were limited by analyzing the COVID-19 impacts alone in 2020 which can be influenced by the meteorology substantially, our understanding on the chemical responses of gaseous and PM species to the changes in anthropogenic emissions is far from complete.

The COVID-19 lockdown in China started from 23 January 2020, a day before the Chinese New Year (CNY) holiday. In general, anthropogenic emissions have significant changes during the CNY because of the migration of people from the city to their rural hometown. Jiang et al. (2015) and Zhang et al. (2016b) found the most significant reductions in primary emissions including cooking organic aerosol (COA) and NOx during CNY in Beijing, consistent with the decreases in local cooking and traffic emissions. However, the changes in secondary inorganic aerosol (SIA) and secondary OA (SOA) were comparably small and even had slight increases, pointing towards the limited effects of local emission controls alone on mitigation of severe haze events. One reason is that the large reductions in primary species were compensated by the enhanced secondary production under unfavorable meteorological conditions. This is also consistent with a recent study by Ma et al. (2020) showing that the emergency response measures during severe haze episodes only reduced the PM levels by 7% in Beijing.

Compared to the CNY with decreased local emissions, regional emission controls in Beijing and surrounding regions were implemented during several specific events, e.g., Asia – Pacific Economic Conference (APEC) in 2014 and Victory Day Parade in 2015. Results showed that the joint emission controls over a regional scale were effective in reducing gaseous precursors, and hence suppressed the secondary formation and growth (Chen et al., 2015; Sun et al., 2016b; Xu et al., 2015; Zhao et al., 2017). As a result, air quality was substantially improved during these events, and well known as “APEC blue” and “Parade blue”. However, many studies also pointed out the importance of meteorology which can contributed more than 50% to the reduction in PM2.5 (Ansari et al., 2019; Zhang et al., 2016a). These results highlight the complex effects of anthropogenic emissions and meteorology, leading to large uncertainties in quantifying their contributions to improvement of air quality. In addition to the relatively short periods of control experiments above, the anthropogenic emissions have been changing over the time since the implementation of “Atmospheric Pollution Prevention and Control Action Plan” in 2013 (Zhang et al., 2019). As a response, the physical and chemical properties of aerosol particles are also changing (Song et al., 2019). Zhou et al. (2019) found that the changes in different aerosol species from 2011–2012 to 2017–2018 were different. In particular, the changes in nitrate were relatively small and even showed some increases compared with the ubiquitous reductions in organics and other aerosol species. By comparing winter aerosol chemistry between 2014 and 2016, Xu et al. (2019) found that not only aerosol composition, but the size distributions, oxidation properties of OA, and the sources of OA can also have substantial changes due to the influences of emission changes and meteorology.

Despite these efforts, the COVID-19 outbreak provides the longest “controlled experiment” to investigate the responses of gaseous species, primary and secondary aerosol species, and hence air pollution to the large reductions in anthropogenic activities. In particular, two severe haze episodes occurred in northern China during the COVID-19 lockdown period when the emissions were expected to be the lowest compared with the same periods in previous years. Although many studies have demonstrated the changes in major air pollutants, e.g., NOx, PM2.5, O3, CO, and SO2 in China during the COVID-19 lockdown (Bauwens et al., 2020; Shi and Brasseur, 2020), few studies have addressed the changes in aerosol composition, sources, and evolution processes (Chang et al., 2020; Huang et al., 2020), and also the differences compared with previous years. In this work, we demonstrate the changes in primary and secondary aerosol species as responses to the emission reductions during the COVID-19 outbreak by using three-month aerosol particle composition measurements and receptor models. In particular, we analyze additional five-year data (2012, 2013, 2015, 2018, and 2019) during the same period of COVID-19 to better illustrate the CNY holiday effects on aerosol chemistry in megacities under different meteorology and emission environments. In addition, the evolution of aerosol chemistry after CNY with consistently low local emissions in 2020 is elucidated and then compared with previous years when anthropogenic emissions return to normal levels.

2. Experimental methods

2.1. Sampling site and measurements

Aerosol particle composition was measured at the tower branch of Institute of Atmospheric Physics, an urban site located between the north 3rd and 4th ring road in Beijing (Sun et al., 2012). A quadrupole aerosol chemical speciation monitor (Q-ACSM, Ng et al., 2011) was used to measure non-refractory submicron aerosol (NR-PM1) species, i.e., organics (Org), sulfate (SO4), nitrate (NO3), ammonium (NH4), and chloride (Cl), during January–March in 2012, 2013, 2015, and 2018, while a time-of-flight ACSM (ToF-ACSM, Fröhlich et al., 2013) that is equipped with a PM2.5 aerodynamic lens and a capture vaporizer (Xu et al., 2017) was used to measure NR-PM2.5 aerosol species in 2019 and 2020. The detailed descriptions of the sampling site, the operation, and calibration of the ACSMs have been given in our previous studies (Lei et al., 2020; Sun et al., 2012; Sun et al., 2015). By comparing the total NR-PM1 and NR-PM2.5 measured at our sampling site with the PM2.5 at the Olympic Center, we found that the ratio of NR-PM1 and NR-PM2.5 was approximately 0.65 on average, consistent with our early study in Beijing (Sun et al., 2012). Therefore, all NR-PM1 aerosol
species were scaled to NR-PM$_{2.5}$ in this study by using the correction factor of 0.65 for better comparisons of aerosol chemistry in different years. It should be noted that such correction may introduce some uncertainties due to the chemical differences of PM$_1$ and PM$_{2.5}$ particularly under high relative humidity levels (Sun et al., 2020).

Equivalent black carbon (BC) was measured by an Aethalometer (model AE22, Magee Scientific) in 2013, and AE33 during the other four years. The gaseous species of CO, O$_3$, SO$_2$, NO$_2$, and PM$_{2.5}$ were measured at the sampling site by a suite of gas analyzers, and a Tapered Element Oscillating Microbalance (TEOM) in 2012 and 2013 (Sun et al., 2020), while the measurements at the environmental monitoring station of the Olympic Center were used after 2013. The meteorological parameters such as relative humidity (RH), temperature ($T$), wind speed (WS), and wind direction (WD) were measured at 103 m on the Beijing 325 m meteorological tower to avoid the influences of urban canopy.

2.2. Data analysis

Both Q-ACSM and ToF-ACSM data were analyzed following the standard protocols. The mass concentrations of aerosol species were quantified using a composition dependent collection efficiency (CE) for Q-ACSM (Middlebrook et al., 2012), while a constant value of 1 for ToF-ACSM because the newly developed capture vaporizer has a fairly constant CE of 1 (Hu et al., 2017). In general, the default relative ionization efficiencies (RIEs) were applied for organics, nitrate and chloride, while those of ammonium and sulfate were from the calibrations of pure ammonium nitrate and ammonium sulfate. The mass quantifications have been fully evaluated by comparing with PM$_{2.5}$ and offline filter analysis of water-soluble aerosol species in previous studies (Jiang et al., 2015; Qiu et al., 2020).

Primary and secondary OA were determined using positive matrix factorization (PMF) or multilinear engine (ME-2) (Paatero, 1999; Paatero and Tapper, 1994; Ulbrich et al., 2009). Five OA factors including fossil fuel-related OA (FFOA), biomass burning OA (BBOA), cooking OA (COA), less oxidized oxygenated OA (LO-OOA), more oxidized OOA (MO-OOA) were resolved by ME-2 during 2012–2013 (Sun et al., 2018), and three OA factors, i.e., FFOA, COA, and OOA were identified by PMF in 2015 and 2018 (Zhang et al., 2016b; Zhou et al., 2019). Comparatively, FFOA, COA, LO-OOA and MO-OOA were identified by PMF analysis of OA from ToF-ACSM measurements. The detailed evaluations of PMF factors were given in previous publications (Sun et al., 2018; Zhang et al., 2016b; Zhou et al., 2019). Note that the COA resolved from the CV-ToF-ACSM tends to be lower than that determined from AMS by 40–60% (Zheng et al., 2020). The reasons are not very clear yet, but could be due to the large uncertainties in RIE and CE of COA (Xu et al., 2018). To better investigate the changes in OA factors in different years, the OA factors were grouped into three categories, i.e., COA, non-cooking POA (nc-POA) including FFOA and BBOA, SOA (OOA or LO-OOA + MO-OOA).

According to the different emission scenarios, we classified each study into four different periods including before Chinese New Year (BCNY), CNY holiday, after CNY (ACNY), and non-heating period (NHP) (Table S1). BCNY represents the regular heating season from January to the day of CNY. CNY is the 7-day spring festival holiday except the 10-day holiday in 2020. ACNY refers to the period after CNY to 15 March when the heating season stops, and NHP is the period of 16–31 March. Although the central heating was extended to 31 March in 2020, NHP was still defined mainly because of higher $T$ than the other three periods, and lower emissions for residential heating. The COVID-19 lockdown starting from 23 January covered CNY, ACNY, and NHP in 2020.

3. Results and discussion

3.1. Changes in aerosol species before and during the COVID-19 outbreak

Fig. 1 presents the time series of meteorological parameters, aerosol species, and OA factors from 1 January to 31 March in 2020. Although many studies have reported large reductions in gaseous precursors, e.g., NO$_2$ during the COVID-19 outbreak (Fan et al., 2020; Shi and
Brasseur, 2020; Zhao et al., 2020), most aerosol species showed unexpected increases. For instance, the average mass concentrations of PM$_{2.5}$ (NR-PM$_{2.5}$ + BC) were 70.5 and 55.3 μg m$^{-3}$ during CNY and ACNY, which were increased by 54% and 96%, respectively, compared with that before CNY (35.9 μg m$^{-3}$). Such increases were mainly caused by the two severe haze episodes during 24–28 January and 6–13 February with the highest PM$_{2.5}$ concentration reaching approximately 250 μg m$^{-3}$. Back trajectory and potential source contribution function analysis suggested that the occurrences of the two severe haze episodes were mainly associated with air masses from the east and the south (Figs. S1 and S2). These results clearly indicate that the current emission reductions fail to meet the requirements to eliminate severe haze episodes over a regional scale especially under stagnant meteorological conditions.

Aerosol composition changed substantially before and during the COVID-19 outbreak. As shown in Fig. 1, organics and nitrate were two major species in PM$_{2.5}$ during all periods in this study. In particular, the nitrate contributions increased gradually from 24% before CNY to 26% during CNY, and then exceeded organics after CNY and NHP becoming the dominant species in PM$_{2.5}$ (31% and 37%, respectively). Although NO$_2$ decreased by ~40% during the COVID-19 period, the formation of nitrate appeared not to be affected simultaneously. This is consistent with a winter study in the US showing a negligible change in nitrate with a reduction of 35% in NO$_x$ emissions (Shah et al., 2018) due to the increased particle acidity (pH) shifting more gaseous HNO$_3$ to the particulate nitrate although the total nitrate (HNO$_3$ + NO$_3^-$) decreased linearly with NO$_x$ emissions. In fact, the particle pH was found to increase by approximately 0.3–0.4 unit in winter in Beijing during the past five years due to the decrease in sulfate and the increase in ammonia (Song et al., 2019), which would facilitate the transformation of more HNO$_3$ to nitrate particles. The increased O$_3$ and NO$_3^-$ radical oxidation associated with enhanced nocturnal nitrate formation could be another reason (Huang et al., 2020). The major change in sulfate during the COVID-19 outbreak was the decrease in sulfate contribution from 17% before CNY to 9% during NHP, consistent with the large reduction in SO$_2$ by 40%. However, the sulfate concentration after CNY was 65% higher than that before CNY despite a 52% reduction in SO$_2$, mainly due to enhanced sulfate formation under higher RH levels (53% vs. 37%, respectively). Although NO$_2$ decreased by ~40% during the COVID-19 period, the formation of nitrate appeared not to be affected simultaneously. This is consistent with a winter study in the US showing a negligible change in nitrate with a reduction of 35% in NO$_x$ emissions (Shah et al., 2018) due to the increased particle acidity (pH) shifting more gaseous HNO$_3$ to the particulate nitrate although the total nitrate (HNO$_3$ + NO$_3^-$) decreased linearly with NO$_x$ emissions. In fact, the particle pH was found to increase by approximately 0.3–0.4 unit in winter in Beijing during the past five years due to the decrease in sulfate and the increase in ammonia (Song et al., 2019), which would facilitate the transformation of more HNO$_3$ to nitrate particles. The increased O$_3$ and NO$_3^-$ radical oxidation associated with enhanced nocturnal nitrate formation could be another reason (Huang et al., 2020). The major change in sulfate during the COVID-19 outbreak was the decrease in sulfate contribution from 17% before CNY to 9% during NHP, consistent with the large reduction in SO$_2$ by 40%. However, the sulfate concentration after CNY was 65% higher than that before CNY despite a 52% reduction in SO$_2$, mainly due to enhanced sulfate formation under higher RH levels (53% vs. 42% as indicated by the higher sulfur oxidation ratio (SOR, molar fraction of sulfate in total sulfur, i.e., sulfate + SO$_2$) (0.64 vs. 0.34). Different from sulfate and nitrate, the BC contribution to PM$_{2.5}$ was decreased by more than a factor of 2 from 7% before CNY to 3% during the early period of the COVID-19 (CNY and ACNY), and the mass concentration was decreased by up to 22%, supporting the considerable reductions in primary emissions despite the influences of the two severe haze episodes. The BC contribution was gradually back to normal level (5%) during NHP because of the recovery of work and production.

Organic aerosol composition also changed substantially during the COVID-19 outbreak. In particular, the contribution of SOA (=LO-OOA + MO-OOA) to OA showed large increases from 75% to 90–91% during the early period of COVID-19 (CNY and ACNY), while the COA was decreased by a factor of more than 2 from 15% to 4–5% for COA, and from 11% to 4–5% for FFOA. Such results are consistent with the fact that anthropogenic activities associated with traffic, cooking and coal combustion emissions were reduced significantly during the COVID-19 lockdown period. Similar reductions in POM were also observed during the CNY holiday in previous years (Jiang et al., 2015; Zhang et al., 2016b). However, the difference is that the COA and FFOA were rapidly back to normal levels after CNY in previous years (Zhang et al., 2016b), while they remained consistently low until NHP when the COA contribution (10%) was recovered to ~70% of that during pre-COVID-19 period. Not only the emissions were reduced, but the living styles of people were changed during the COVID-19 outbreak. Because most restaurants were not open, people were used to cooking by themselves at home, leading to large changes in diurnal patterns of COA. As indicated in Fig. S3g, the unique noontime peak of COA disappeared, and the dinnertime peak was also largely reduced by a factor of more than 2 compared with that before CNY. Fig. 1 also shows a significant change in SOA composition before and during the COVID-19 outbreak. Although LO-OOA dominated SOA during all periods, the increase in MO-OOA was more significant from 16% during pre-COVID to 27–28% during COVID-19. These results suggest that the changes in precursors of NO$_x$ and VOCs because of reduced anthropogenic emissions have also affected the formation of different SOA factors.

### 3.2. Changes in aerosol species before, during and after CNY from 2012 to 2020

Fig. 2 presents a comparison of aerosol composition during four periods, i.e., BCNY, CNY, ACNY, and NHP among six years. Although the mass concentrations of PM and aerosol species showed large variations among different periods in different years, overall decreasing trends from 2013 to 2020 were observed, consistent with the effectiveness of clean air actions in improving air quality in recent years (Zhang et al., 2019). We found that aerosol composition showed the most significant changes after 2018, which was characterized by a large increase in nitrate and decreases in organics and chloride. For instance, the nitrate contribution in PM was increased by 8–10% from 2013–2015 to 2018–2020, while the contributions of organics and chloride were decreased by 6–15% and 4–6%, respectively. Such changes in aerosol composition were likely due to the use of clean fuel in winter heating season, and the small decreases in nitrate precursors of NO$_x$ (Zhang et al., 2019; Zheng et al., 2018; Zou et al., 2019). The changes in OA composition from 2012 to 2020 were also substantial. The mass concentrations of non-cooking POA showed the most significant decrease by 72–84% during 2018–2020 compared with that before 2015. Comparably, the decreases in SOA concentrations were smaller by 38–71%, while those of COA were more prominent in 2019–2020. As a result, the SOA contribution showed a clear increase during 2019–2020 associated with a corresponding decrease in POA. For example, SOA on average contributed 74% to the total OA before CNY, and the contribution was increased to 90–91% during the early two periods of COVID-19. Although previous study showed that the ACSM with CV tended to report higher SOA than the AMS with SS (Zheng et al., 2020), the comparisons between 2019 and 2020 with the same ToF-ACSM also confirmed the elevated SOA contributions during the COVID-19 period (90–91% vs. 70–84%). One possible explanation is the consistently low POA concentrations due to the reduced anthropogenic activities.

Fig. 2 also shows that the holiday effects on aerosol chemistry varied significantly in different years. Although the anthropogenic emissions were reduced substantially during CNY, we did not observe the expected decreases in PM for each year. For example, the PM$_{2.5}$ was even increased by 130% and 96% in 2018 and 2020, respectively although it was decreased by 16–46% for the rest four years. These results indicate that the PM pollution in Beijing is complex because of the synergistic effects of local emissions and regional transport, and the influences of different meteorological environments. We found that secondary aerosol (SIA + SOA) accounted for >70% during all four different periods, and the contribution was up to 90–93%. Therefore, reducing local emissions alone would not improve air quality significantly considering that the contributions of primary emissions were generally less than 30%. This is also consistent with the result from a recent study that the emergency response measures during the “orange alert” or “red alert” such as reducing vehicles on the road, stopping construction activities, and shutting down some factories only reduced the surface PM$_{2.5}$ by 7% during severe haze episodes (Ma et al., 2020).

We further evaluated the holiday effects on different gaseous and aerosol species across different PM and RH levels (Fig. 3). The reason is that the clean and haze episodes associated with different RH and PM levels alternated frequently in Beijing (Fig. 1) depending on the sources of air masses (Jiang et al., 2015; Sun et al., 2016a; Sun et al., 2013). As shown in Fig. 3, the changes in primary and secondary species
due to the holiday effects varied largely among different years. For example, the average mass concentrations of BC, COA, and nC-POA were reduced by 32–38% during low PM levels (<35 μg m⁻³), while by 41–53% during high PM levels (>75 μg m⁻³). However, the reductions in gaseous species varied more differently. NO₂ showed the largest reduction by up to 51% during moderate PM levels (35–75 μg m⁻³), while the reductions in CO and SO₂ were comparably small by up to 35% and 36%, respectively. In contrast, the reductions in the three gaseous species were the smallest during low PM levels (<35 μg m⁻³). Our results illustrate the direct responses of primary aerosol and gaseous species to the changes in anthropogenic emissions during CNY, which were characterized by ubiquitous reductions across different PM levels, and the average reductions were overall more significant during highly polluted periods than clean days.

Comparatively, the changes in secondary aerosol species, including SIA and SOA during CNY were much smaller than those of primary aerosol species, and some of them even showed increases, highlighting very different chemical responses of secondary aerosol to emission changes. We noticed that the reductions in SIA and SOA were most significant during low PM levels (<35 μg m⁻³), which were 17.6% and 16.5% for sulfate and nitrate, and 5.5% for SOA, while those during high PM periods were much smaller and even showed a 6.4% increase for nitrate. These results suggest that the large reductions of gaseous precursors did not result in the corresponding decreases in secondary aerosol species during highly polluted periods despite their comparable reductions during low PM periods. One of the major reasons was due to the enhanced secondary aerosol formation during polluted conditions which was also supported by higher SOR and nitrogen oxidation ratio (NOR, molar fraction of nitrate in total nitrogen, i.e., nitrate + NO₂). In fact, recent studies found similarly high OH concentration during winter haze events as that during non-haze events despite a 50% decrease in photolysis rate \( j(O^1 D) \) further supporting the presence of strong gas-phase oxidation during highly polluted periods (Lu et al., 2019; Slater et al., 2020). Although \( O_3 \) showed large increases during CNY due to the reductions in NO₂ and VOCs, we found that \( O_3 (=O_3 + NO₂) \), a more conserved tracer for photochemical processing (Herndon et al., 2008), was decreased by 0.9–25.6% across the different PM levels, suggesting that the atmospheric oxidation capacity in winter using \( O_3 \) as a tracer may have uncertainties due to the much higher NO₂ than \( O_3 \).

The changes under three different RH levels further supported much larger reductions in primary aerosol and gaseous species than secondary species during CNY. However, we found that the reductions in primary aerosol species were the most significant during low RH levels (<40%), e.g., 55–61% for BC, COA and nC-POA, and 32–46% for CO, NO₂, and SO₂, while much smaller reductions, i.e., 8–30% and 17–35%, respectively during moderate RH levels (40–60%). Similarly, secondary aerosol species showed the largest reductions by 17–35% under RH < 40%, while overall increases by 1.4–9.2% when RH was between 40% and 60%. Our results demonstrate that the chemical responses of primary and secondary species to the reduced anthropogenic emissions can be RH dependent. The reason for the smaller reductions during RH = 40–60% was likely due to the dominant photochemical processing (Xu et al., 2019) and the transitional stage from clean period to severe haze episode associated with strong regional transport (Zhu et al., 2016).

### 3.3. Chemical insights into the changes from 2012 to 2020

Fig. 4 shows the changes of the average ratios for different aerosol species, SOR, and NOR during four periods from 2012 to 2020. We observed considerable increases in NO₂/SO₄ ratios after 2018, and the ratios of NO₂/SO₄ were all above 1.5. In particular, the ratios of NO₂/SO₄ during NHP ranged from 2.5 to 4.2 during the year of 2018–2020, which were much higher than that (1.3–1.8) before 2015. These results highlight the increasing role of nitrate in PM pollution in recent years (Li et al., 2018a; Xie et al., 2020; Xu et al., 2019; Zhou et al., 2019), and the roles were more significant after the heating season ended. We noticed that the ratios of NO₂/SO₄ during CNY were generally comparable to those before CNY during all years, indicating the more reduced traffic NOₓ than SO₂ did not result in the corresponding decrease in NO₂/SO₄ ratio. This is consistent with a recent study showing that ~32% reduction of NOₓ only decreased nitrate by 0.2% due to the increased \( O_3 \) and OH, and the subsequent higher oxidation of NOₓ to HNO₃ (Fu et al., 2020).
In fact, higher NOR during CNY than before and after CNY was observed during all years (Fig. 4f), supporting the increased nitrogen oxidation during periods with low traffic emissions. In addition, the NOR showed an overall increasing trend during the last eight years, except the period of BCNY when the changes in NOR were relatively small. For example, the NOR was increased from 0.13–0.21 in 2012–2015 to 0.20–0.30 in 2018–2020 during CNY, and from 0.12–0.19 to 0.19–0.29 after CNY. These results indicate that the increased O3 and atmospheric oxidation capacity in recent years (Li et al., 2018b) have caused more efficient nitrate formation. SOR also showed an overall increasing trend during all periods except NHP, and the increase during ACNY was the most significant, for instance, from 0.20 in 2012–2015 to 0.64 in 2020. Most importantly, we found the highest NOR and SOR during the early two periods of COVID-19 in 2020 than the other five years. Although the precursor concentrations were reduced substantially, the increased oxidation capacity during the COVID-19 compensated for the decreases in sulfate and nitrate concentrations.

The changes in SOA/SIA during the past eight years were also observed (Fig. 4b). While the ratios of SOA/SIA were fairly comparable before 2015, mostly between 0.5 and 0.7, they decreased to ~0.3–0.5 for most of the time after 2018, suggesting that the changes in precursors (VOCs, NOx, and SO2) have more impacts on the formation of SOA than SIA. Also, we found that the decreases in POA were much more significant during the last two years, leading to much lower POA/SAO ratios in 2019–2020 (~0.1–0.4) than those before 2019 (~0.4–0.8 except ~1.35 before CNY in 2015 and 2018). This result suggests different chemical responses of POA and SOA to the emission changes with POA being more efficiently reduced. We noticed that POA/SAO ratios during the COVID-19 (CNY and ACNY) were the lowest (0.10 and 0.11, respectively), and even more than twice lower than those during the same period in 2012 (Fig. 4c), which agreed well with the consistently low anthropogenic emissions during the COVID-19 period. In fact, we also observed the decreases in BC/CO ratios during the COVID-19 period (Fig. 4d), suggesting the reductions in different primary emissions were different, e.g., coal combustion, traffic emissions, and biomass burning. Further support is the large increase in BC/CO during NHP when the coal combustion emissions for residential heating were almost eliminated.

### Investigation of the chemical evolution of aerosol species in different years

Fig. 5 shows a comparison of the evolution of mass fractions of major aerosol species before, during, and after CNY in different years. The changes in OA contributions were overall similar among different years which were characterized by decreasing trends from BCNY to ACNY. This is generally consistent with the decreasing coal combustion emissions due to the gradual rise of ambient temperature after CNY (Fig. S4). However, the changes in OA contributions during CNY varied significantly in different years because of the different changes in POA and SOA. We noticed that the OA contributions in PM after 2018 were ubiquitously lower than those before 2015 (Fig. 5a). For example, the OA contributions were decreased from ~50–60% in 2012 to ~30–40% in 2020, suggesting a large decrease in OA emissions during the past
eight years. One of the major reasons is the continuous promotion of the clean fuels in both urban and rural areas in Beijing (Zhang et al., 2019). However, the OA contributions were relatively comparable in different years after approximately 30 days since CNY further supporting that the changes in OA emissions were more significant during heating period.

The mass fractions of nitrate in PM showed opposite trends as those of OA (Fig. 5c). While the nitrate contributions were fairly stable before CNY which were ~10–15% before 2015 and ~20% after 2018, they showed gradual increases from ~20% to 30% in 30 days after CNY during 2018–2020, and such increases agreed well with the changes in temperature from ~−5 °C to ~10 °C (Fig. S4). These results clearly indicate the increased photochemical production of nitrate in a month after CNY when the temperature was not high enough to cause significant evaporative loss yet. However, although the NO3/PM also increased as a function of time after CNY before 2015, the increases were relatively small, ~5%, further supporting the increased role of nitrate in recent years.

Note that the nitrate contributions became relatively stable after 30 days from CNY, which were ~30% during 2018–2019 and ~20% during 2012–2015, however, they showed continuous increases during the COVID-19 period until ~40% by the end of March 2020 although NO2 remained consistently low. Compared with nitrate, we did not observe clear trends in SO4/PM before and after CNY during all years (Fig. 5b) although SO2 was decreased by 78% from 12.7 (±3.3) ppb in 2012 to 2.8 (±0.9) ppb in 2019, and sulfate was decreased by 58% from 16.0 (±6.7) μg m⁻³ to 6.1 (±1.6) μg m⁻³. In fact, the SO4/PM varied similarly between 10% and 20% during the last eight years indicating that sulfate consistently played an important role in PM pollution in Beijing although nitrate exceeded sulfate for most of the time.

Fig. 5 also shows significant changes in OA composition before and during CNY. On average, SOA contributed ~40–60% to OA before CNY, and the contributions varied differently in different years with the lowest contribution in 2015 and 2018 (Fig. 5e). The contributions of SOA then showed considerable increases, generally ~10% during CNY associated with corresponding decreases in POA. Such variations were mainly due to the changes in anthropogenic emissions during the CNY holiday. Although the POA contributions in several years showed temporal increases after CNY due to the rebound of anthropogenic activities, they generally remained low until the end of March, which were ~40% before 2018 and ~20% during 2019–2020. As a result, OA was dominated by SOA after CNY on average accounting for ~60% of the total SOA, and even up to ~90% during 2019–2020. The trends of BC/PM as a function of time were similar to those of POA (Fig. 5d), consistent with the good correlations of BC with nc-POA, one of the major components of POA (Fig. 1). We noticed that the contributions of POA and BC were decreased substantially during all periods in 2019 and 2020. For instance, the BC contributions in PM were decreased from ~8–10% in 2015 and 2018 to ~5% in 2020, and those of POA were decreased from ~40% to ~20% in 2020. In particular, POA and BC showed ubiquitous decreases in 2020 compared with the same measurements in 2019. These results indicate that the measures of clean air action since 2013 have reduced primary emissions efficiently. Note that the contributions of POA and BC showed some increases in 45 days after COVID-19 lockdown, suggesting the resumption of work and production because the COVID-19 has been relatively well controlled already.

4. Conclusions

We have investigated the responses of aerosol species to the emission reductions during the COVID-19 outbreak in 2020 in Beijing. While gaseous NOx and cooking OA were decreased by 38–39% and 40–55%, respectively, during the early two periods of COVID-19 lockdown (CNY
and ACNY), secondary inorganic aerosol and SOA showed unexpectedly significant increases by 60–110% and 52–175%, respectively due to enhanced secondary formation and regional transport from the south and the east. Our results demonstrate that the effect of reducing local emissions, e.g., traffic and cooking on air quality improvement can be significantly suppressed under stagnant meteorological conditions. By analyzing five more years’ data, we found that the CNY holiday effects on PM pollution varied largely among different years, but overall caused ubiquitous reductions in gaseous species (NO2, CO, and SO2) and primary aerosol species (FFOA, COA, and BC) by 25–46% and 30–50%, respectively. In contrast, the CNY holiday impacts on the changes in secondary aerosol species were relatively small by only decreasing 5–12%, and even caused a slight increase for sulfate (3%). Compared with the relatively short period of emission reductions during CNY, we found that most aerosol species except nitrate showed considerable decreases as responses to the clean air action in 2013. As a consequence, nitrate exceeded sulfate for most of the time and became the most important SIA species, and SOA also showed largely elevated contributions in OA by accounting for 70%. We also found that the reductions in anthropogenic emissions during the last decade have increased secondary aerosol formation as suggested by the increasing sulfur and nitrogen oxidation capacities. Our results highlight the complex responses of primary and secondary aerosol species to the emission changes in particular under stagnant meteorological conditions, pointing towards a great challenge for future mitigation of secondary aerosol in PM pollution, and an urgent need for a better understanding of the chemical interactions between gaseous precursors and secondary aerosol under complex meteorological environments.

CRediT authorship contribution statement

Yele Sun: Conceptualization, Methodology, Formal analysis, Writing - original draft, Funding acquisition. Lu Lei: Validation, Formal analysis, Investigation. Wei Zhou: Validation, Formal analysis, Investigation. Chun Chen: Validation, Formal analysis, Investigation. Yao He: Validation, Investigation. Jiaxing Sun: Validation, Investigation. Qingqing Wang: Validation, Investigation. Dongsheng Ji: Validation, Investigation. Weiqi Xu: Validation, Investigation. Zifa Wang: Writing - review & editing.

Declaration of competing interest

The authors declare no competing financial interest.
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Data availability

The data in this study are available upon request from the corresponding author (sunyle@milai.ac.cn).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.140739.

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