Characterization of the aerosol chemical composition during the COVID-19 lockdown period in Suzhou in the Yangtze River Delta, China

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\textbf{ABSTRACT}

To control the spread of COVID-19, rigorous restrictions have been implemented in China, resulting in a great reduction in pollutant emissions. In this study, we evaluated the air quality in the Yangtze River Delta during the COVID-19 lockdown period using satellite and ground-based data, including particle matter (PM), trace gases, water-soluble ions (WSIs) and black carbon (BC). We found that the impacts of lockdown policy on air quality cannot be accurately assessed using MODIS aerosol optical depth (AOD) data, whereas the tropospheric nitrogen dioxide (NO\textsubscript{2}) vertical column density can well reflect the influences of these restrictions on human activities. Compared to the pre-COVID period, the PM\textsubscript{2.5}, PM\textsubscript{10}, NO\textsubscript{2}, carbon monoxide (CO), BC and WSIs during the lockdown in Suzhou were observed to decrease by 37.2%, 38.3%, 64.5%, 26.1%, 53.3% and 58.6%, respectively, while the sulfur dioxide (SO\textsubscript{2}) and ozone (O\textsubscript{3}) increased by 1.5% and 104.7%. The WSIs ranked in the order of NO\textsubscript{3}\textsuperscript{-} > NH\textsubscript{4}\textsuperscript{+} > SO\textsubscript{2}\textsubscript{2-} > Cl\textsuperscript{-} > Ca\textsuperscript{2+} > K\textsuperscript{+} > Mg\textsuperscript{2+} > Na\textsuperscript{+} during the lockdown period. By comparisons with the ion concentrations during the pre-COVID period, we found that the ions NO\textsubscript{3}\textsuperscript{-}, NH\textsubscript{4}\textsuperscript{+}, SO\textsubscript{2}\textsubscript{2-}, Cl\textsuperscript{-}, Ca\textsuperscript{2+}, K\textsuperscript{+} and Na\textsuperscript{+} decreased by 66.3%, 48.8%, 52.9%, 56.9%, 57.9% and 76.3%, respectively, during the lockdown, in contrast to Mg\textsuperscript{2+}, which increased by 30.2%. The lockdown policy was found to have great impacts on the diurnal variations of Cl\textsuperscript{-}, SO\textsubscript{2}\textsubscript{2-}, Na\textsuperscript{+} and Ca\textsuperscript{2+}.

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\textbf{Introduction}

As the symbol of modern civilization and social progress, cities are the major centers of population, economic and social development. Compared to rural areas, the problem of compound air pollution in urban regions has received increasing attention in recent decades due to the numerous emission sources and focused intensity of pollutants (Li et al., 2019b, 2019c; Song et al., 2017; Wang et al., 2014b, 2020d). As one of the countries with the fastest economic development in the world, the urbanization in China is rapidly developing, result-
ing in groups of megacities with permanent residents exceeding 10 million, around which urban agglomeration has evolved in areas such as the North China Plain (NCP), Yangtze River Delta (YRD), and Pearl River Delta (PRD). As such, these regions feature the worst air pollution in China (An et al., 2019; Chan and Yao, 2008; Ding et al., 2016; Ge et al., 2018; Guo et al., 2020; Huang et al., 2014). The compound air pollution in urban agglomeration has received much attention since the large scale explosion of regional haze events in Central and Eastern China (CEC) in January 2013 (An et al., 2019; Cheng et al., 2016; Ding et al., 2016; Huang et al., 2014; Wang et al., 2014b; Zhang et al., 2014). In September 2013, the State Council issued the Action Plan for Prevention and Control of Air Pollution, demanding that PM$_{10}$ concentrations decrease by more than 10% in 2017 compared to the level in 2012 in cities at the prefectural level and above; additionally, a target number of excellent and good days with an air quality index (AQI) less than 100 was required, following the China Environmental Protection Standard ‘HJ 633-2012’ (http://www.gov.cn/zhengce/content/2013-09/13/content_4561.htm). Noticeably, these regulatory measures have resulted in significant reduction in primary PM emissions, but the secondary pollutant ozone (O$_3$) remains prominent (Huang et al., 2021; Li et al., 2019b; Wang et al., 2020d; Zeng et al., 2019). Numerous studies have indicated that compound air pollution has resulted from the primary pollutants emitted by industry, power plants, traffic and heating processes and from the secondary pollutants generated by complex physical, chemical and biological processes (An et al., 2019; Fenger, 2009; Guo et al., 2020; Li et al., 2019c; Zhang et al., 2020; Zhu et al., 2011). These pollutants may quickly accumulate at high concentrations under static meteorological conditions and then undergo cross border transport processes, leading to complicated effects on human health and the environment (Huang et al., 2014; Luo et al., 2020; Wang et al., 2014b; Xu et al., 2013; Zhang et al., 2020). Additionally, air pollution also has complex interactions with large scale weather and climate (Cai et al., 2017; Lou et al., 2019; Quinn and Bates, 2003).

The contributions of distinct emission sources should first be clarified when implementing the joint prevention and control of regional air pollution. Therefore, the key step is to distinguish the precursors and their sources that contribute the most to the pollution when studying its formation mechanisms and impact factors (An et al., 2019; Cheng et al., 2016; Li et al., 2019a; Zhang et al., 2020). For now, the impacts of emission reduction measurements on air quality have been discussed for several important activity periods (Beijing Olympics, APEC, G20 Summit) (Cai and Xie, 2011; Li et al., 2017a; Shen et al., 2017; Wang et al., 2016, 2018; Xu et al., 2016; Zhang et al., 2016).

However, previous emission reductions were mostly aimed at a certain region with a relatively low reduction extent and accordingly cannot eliminate the impacts of regional pollutant transport processes (Li et al., 2017b, 2019a; Shen et al., 2017; Wang et al., 2010). To control the spread of COVID-19, China launched a level-I response to this public health emergency in 31 provinces, autonomous regions and municipalities as early as January 27, 2020, when it was the first country to shut down commercial activities, restrict travel, and require its people to stay home (Tian et al., 2020; Wang et al., 2020a, 2020b, 2020c, 2020e). COVID-19 was declared a global pandemic by the World Health Organization (WHO) on March 11, 2020; subsequently, public health regulations, including travel restrictions, curfews, and quarantines, have been implemented in many countries around the world. The lockdown policy is believed to have yielded great reductions in air pollutants, especially in China, and thus it provides a favorable opportunity to assess the impacts of anthropogenic sources on air quality in urban agglomerations. Many studies have revealed that air pollutants including aerosol optical depth (AOD), particle matter (PM), nitrogen dioxide (NO$_2$) and carbon monoxide (CO) decreased significantly during the global lockdown, while the secondary pollutant O$_3$ increased (Filonchyk et al., 2020; Kerimray et al., 2020; Nakada and Urban, 2020; Wang et al., 2020c). These related studies were more directed at satellite and ground-based routine data, and observations of aerosol chemical compositions have rarely been investigated to date. In this study, we evaluated the change in air quality during the COVID-19 lockdown period using satellite and ground-based data; the temporal evolution of PM, trace gases, water-soluble ions (WSIs) and BC were analyzed in detail before, during and after the lockdown in Suzhou.

1. Materials and methods

1.1. Sample sites

The observation site was located at the Suzhou South Gate Station (31.29°N, 120.63°E), which is a national control point of the China Environmental Monitoring Station. Situated in the Gusu District of Suzhou, the site is surrounded by residential areas and is 100 m away from the South West Road of Suzhou to the south, making it a mixed region of commercial and residential areas. The observation time period was from December 1, 2019 to March 31, 2020.

1.2. Satellite data

The MODIS is a detector mounted on the Terra and Aqua satellites of the EOS. In this study, Terra MODIS C6.1 Level 3 aerosol products (MOD08_M3) at $1°$ × $1°$ were used, and data were downloaded from the NASA Level 1 and Atmosphere Archive and Distribution System (https://ladsweb.nascom.nasa.gov/data/search.html). The dark target and deep blue merged AOD data at 550 nm (hereafter referred to as AOD) were principally used. We also used tropospheric NO$_2$ vertical column density (VCD) data from the GOME-2 (METOP-B) (http://www.temis.nl/index.php) with a resolution of 0.25° × 0.25°, and the observations were averaged on a monthly basis. Detailed information about the GOME-2 can be found in the related literature (Georgoulas et al., 2019).

1.3. Ground-based observation data

WSIs in PM$_{2.5}$ were detected by using the Ambient Ion Monitor-Ion Chromatograph (AIM-IC, URG-9000D, Thermo Scientific™), which can continuously measure the mass concentration of ions including Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_3^-$.
and SO$_2^{2-}$. The instrument configuration includes a sample collection unit (URG-9000D) for collecting water-soluble particles into solution and a sample detection unit (IC, Dionex ICS-5000) for analyzing ions (Malaguti et al., 2015). For quality control and assurance of the anion and cation particles in the system, collection efficiency, flow calibration and air tightness tests were performed each month. The accuracy of the IC analysis is verified by an internal check standard of lithium bromide that is injected with each sample. In the external calibration method, ICS were calibrated by measuring varying concentrations of the standard agent (Merck, Germany) (Tang et al., 2020). The detection limits of Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Cl$^-$, NO$_3^-$ and SO$_2^{2-}$ were 0.02, 0.02, 0.02, 0.02, 0.02, 0.02, 0.03 and 0.05 μg/m$^3$, respectively. BC mass concentrations were observed with a Model AE-31 aethalometer (Magee Scientific, USA) that uses two-point measurement technology and dynamic zero-point calibration to provide continuous observations at fixed points at seven wavelengths (370, 470, 520, 590, 660, 880, and 950 nm). Instrument principles can be found in Hansen and Schnell (2005). Although the measurements were made every 5-min, the data were averaged at a resolution of 1 h to reduce the uncertainties derived from instrumental noise, flow rate, filter spot area and detector response (Corrigan et al., 2006). The silica gel in the drier was routinely changed according to the monitored relative humidity (RH), in order to ensure the RH of the sample air below 40%. The air in the container was sent to the surrounding area of the drier to reduce the temperature difference between the inside of the container and the drier. The temperature inside the container was maintained around 25°C. PM$_{2.5}$ and PM$_{10}$ were measured by the Synchronized Hybrid Ambient Real-time Particulate Monitor (SHARP Model 5030i, Thermo Scientific™), and the trace gases NO$_2$, sulfur dioxide (SO$_2$), CO and O$_3$ were monitored by a series of monitors (42i, 43i, 48i, and 49i, Thermo Scientific™). Ding et al. (2013) provides a more detailed introduction to this instrumentation. Additionally, meteorological factors (temperature, RH, wind speed, wind direction, visibility and precipitation) were observed by the CSI-CR1000 automatic weather station. The time resolution is 1 hour.

2. Results and discussion

2.1. Overview of the AOD and tropospheric NO$_2$ VCD

The regional distribution of AOD values is significant in the CEC as shown in Fig. S1, and high AOD values were observed in the NCP, YRD and Twain-Hu Basin (THB), where megacities such as Shanghai, Shijiazhuang, Tianjing and Wuhan dominated. Notable AOD boundaries in these megacities were noticed when the pollution was relatively weak (Fig. S1a) and disappeared under heavy pollution periods (Fig. S1b), revealing a regional transport process of aerosols.

Fig. S1c exhibits an obvious reduction in AOD values in the CEC due to the COVID-19 lockdown policy, while high AOD value centers were still found in the YRD, NCP and THB, mostly due to heavy industrial emissions, such as fuel-burning power generation and iron, steel, and coking processes. Although almost all medium and small industries except power plants and large-scale enterprises were closed during the lockdown, the manufacturing sector did not actually show major slowdown: according to the industrial production data published by the bureau of statistics in the provinces of the YRD, the production of iron and other non-ferrous materials, medical and pharmaceutical remained roughly constant. The impact of the COVID-19 epidemic on industrial production can be seen in the sharp decline of 29% and 32% in industrial electricity consumption in January-February 2020 in Anhui and Zhejiang provinces. Industry (32.2%-61.1%) and residential emissions (2.1%-28.5%) were the major sources of PM$_{2.5}$ in YRD during the lockdown (Li et al. 2020). People started back to work in March while the AOD values were relatively low (Fig. S1d). Conditions in the atmospheric boundary layer (convection and mixing layer height), pollutant lifetime and properties, source regions and transport patterns, and wet scavenging all could result in differences between satellite and surface pollutant observations (Qu et al., 2016; Shen et al., 2020; Yang et al., 2019). As satellite inversion data, AOD is related to surface particles as well as other factors, for example, moisture content in the air (Shen et al., 2020), and as such, the AOD values cannot well reflect the changes in surface particles. Therefore, the impacts of the lockdown policy on air quality cannot be accurately assessed using MODIS AOD data.

The distribution of tropospheric NO$_2$ VCD can well reflect the impacts of the lockdown policy on human activities, as shown in Fig. 1. Before the lockdown and the Chinese Spring Festival (SF), high NO$_2$ values had a regional distribution in the CEC (Fig. 1a), which is in accordance with the economy, population and vehicle ownership. In January 2020, high NO$_2$ values were still observed in Shandong, Hebei, Henan, Shanxi and Anhui, where an inflow of populations usually occurs during the SF without a ban on fireworks. With an outflow of population and no fireworks, the YRD had a remarkable reduction in NO$_2$ values. Moreover, a continuous and strong precipitation process south of the Yellow River during January-February was also responsible for this notable reduction (Jiang et al., 2020).

The restrictions on traffic sources are believed to be the main drivers of the decreased NO$_2$ during the lockdown. In February, the latitudinal circulations dominated in the middle and high latitudes of Europe and Asia, accompanied by low East Asian winter monsoonal winds and weak East Asian trough, such synoptic condition resulted in fewer cold air fronts than previous years with weaker intensity, which was favorable to pollutant accumulation (Cao et al., 2020). Meanwhile, the YRD region was controlled by a uniform pressure field with low wind speeds in the range of 2-4 m/sec, high RH exceeding 70% was also observed even over 90% in several time segments. As such, the tropospheric NO$_2$ VCD was still high despite the rigorous restrictions in February. Meanwhile, the traffic emissions increased again when people started back to work, leading to the high NO$_2$ values in the NCP and YRD in March (Fig. 1d); a similar pattern is observed for the surface NO$_2$ change in Suzhou (Fig. 2), which had a sharp reduction on January 25 that began to rise on February 24.

Air pollutants decreased noticeably during the lockdown in Suzhou (Fig. 2). Concentrations of WSIs and PM$_{2.5}$ were lower than those before and after the lockdown. However, the ions/PM$_{2.5}$ ratio peaked during February 11-17. In contrast to the change in SO$_2$, NO$_2$ and CO, with a remarkable reduction
during the lockdown, $O_3$ was substantially enhanced, resulting from the sharp decrease in NOx during the COVID-19 lockdown, which had weaker NO-titration effects on $O_3$. As an atmospheric oxidant, increased $O_3$ concentration will enhance the formation of secondary inorganic and organic particulate matter. Huang et al. (2020) also reported large decreases in NOx emissions from transportation increased ozone and nighttime NOx radical formation during the lockdown, and these increases in atmospheric oxidizing capacity in turn facilitated the formation of secondary particulate matter.

Additionally, the temperature and RH changed slightly before, during and after the lockdown, as the temperature began to rise in March (Fig. 2). The temperature was the lowest in January with an average of 6.5°C and the highest in March with an average of 12.6°C and the maximum of 25°C (Fig. S2). The RH has shown a contrary variation to that of temperature, with averages of 81% and 68% in January and March. Besides, high RH exceeding 60% was normally observed with obvious diurnal variations during the whole period (Fig. 2), which was ascribed to several precipitation processes (Fig. S2). The fluc-

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Fig. 1 – Spatial distributions of tropospheric NO2 vertical column density. note: TJ: Tianjin, SJZ: Shijiazhuang, JN: Ji’nan, ZH: Zhengzhou, WH: Wuhan, HF: Hefei, NJ: Nanjing, SZ: Suzhou, SH: Shanghai.
tuation of pressure was usually accompanied with these rainfall events. The wind speeds changed slightly during the observation period, which had lower (higher) speed in December (March) with an average of 3.1 m/sec (3.7 m/sec). Low and high visibility were noticed in January and March with averages of 7.2 km and 17.6 km, respectively. As shown in Fig. S2, the lockdown policy exerted great improvement of the visibility after January 26.

The aforementioned discussion revealed that the meteorological conditions were relatively stable during the observation period in Suzhou, especially for the wind speeds and RH that can exert great impacts on air pollutants. As such, the pollutant variations in Suzhou might be caused by the changes of emission sources. However, the RH exerted great impacts on the sulfate as shown in Fig. 2, with higher RH corresponding to higher sulfate. Although it was reported that aerosol pollution has shifted from sulfate-dominated to nitrate-dominated in many eastern Chinese cities due to the more rapid decrease in SO2 emissions than NOx in recent years (Chu et al., 2021; Wen et al., 2018). He et al. (2014) discovered that the co-existing of mineral particles and high NOx concentrations in the air can promote the transformation of SO2 to sulfate during the haze process. Such phenomenon revealed that the sulfate may be generated sharply under the compound pollution conditions with high RH and air pollutant concentrations. Hence, we divided the observation period into five stages: the pre-COVID (December 1, 2019-January 22, 2020), SF (January 23-26, 2020), lockdown (January 27-February 24, 2020), secondary response (February 25-March 27, 2020), and tertiary response (March 28-31, 2020).

2.2. Changes in PM and trace gases during different periods

The SF and lockdown policy were found to have had large impacts on the PM and trace gases, as shown in Fig. 3. The pollutants PM2.5, PM10, SO2, NO2 and CO had low concentrations during the SF, with values that were 42.1%, 53.2%, 75.7%, 17.7% and 53.0% of the pre-COVID values, respectively. On the one hand, emissions sources had great reductions due to the closed factories and enterprises and outflow of the population from Suzhou; on the other hand, a continuous and strong precipitation process occurred January 21-27, leading to a significant scavenging effect on air pollutants. During the SF, the diurnal variations in PM2.5, PM10 and CO were noticeably higher in the early morning than in the daytime (Fig. 4), which was mainly caused by the fireworks; in particular, the PM10 concentration at 00:00 during the SF (68.3 μg/m3) was even higher than that during the pre-COVID period, resulting in a low visibility of 5.8 km at 00:00 (Fig. 5).

The concentrations of PM2.5 and PM10 during the lockdown were 35.9 and 36.5 μg/m2, which were 37.2% and 38.3%
lower than the pre-COVID values, while the diurnal variation in PM during the lockdown was consistent with that pre-COVID, except that the concentrations significantly decreased (Fig. 4). Compared to the pre-COVID period, SO₂ increased by only 1.5%, with an average of 5.2 µg/m³ during the lockdown. Meanwhile, the diurnal variations in SO₂ during the pre-COVID and lockdown periods were consistent (Fig. 4), indicating a small impact of the lockdown policy on the SO₂ concentrations.

Fig. 3 shows small discrepancy of SO₂ concentrations in different stages. SO₂ is normally from the industrial processes including the thermal power, iron and steel and coking (Kharol et al., 2020), which were little affected by the SF and lockdown as a result. Lower SO₂ concentrations in the SF and the tertiary response stage were attributed to the rainfall processes with accumulation precipitation of 35.7 mm and 36.5 mm, respectively.

NO₂ and CO had average concentrations of 18.4 µg/m³ and 0.7 mg/m³ during the lockdown, respectively, which were 64.5% and 26.1% lower than those pre-COVID. The reduction in traffic emissions was responsible for the decreases in NO₂. Hence, the diurnal variation in NO₂ during the lockdown differed from the other periods with the disappearance of peak values during rush hours (Fig. 4d). Apart from vehicle exhaust, CO is mostly from industrial emissions, thus leading to a lower extent of reduction. Diurnal variations in CO during the lockdown were consistent with those of the other periods; with the exception of a noticeable decrease in concentrations as well (Fig. 4c). The temperature, wind speed and RH were observed to have coincident diurnal variations during the lockdown, pre-COVID and secondary response periods (Fig. 5); therefore, the reduction in emissions sources was the main driver of the changes in air pollutants during the lockdown. Li et al. (2020) found that human activities were lowered significantly during the COVID-19 period in YRD: industrial operations, vehicle kilometers travelled, constructions in operation, etc. were significantly reduced, leading to lowered SO₂, NOₓ, PM₂.₅ and VOCs emissions by approximately 16%-26%, 29%-47%, 27%-46% and 37%-57% during the lockdown and secondary response periods respectively. These revealed the great impacts of lockdown policy on the decrease in emission sources of air pollutants. Chu et al. (2021) reported that the emission from stationary sources, such as coal-fired power plants, iron and steel production, didn’t decreased as much as traffic during the COVID-19, which resulted the marked decreases in NO₂ and PM₂.₅ yet much smaller decreases in SO₂ and CO over China.

Air pollutants began to gradually increase in March. During the secondary response, concentrations of PM₂.₅, PM₁₀, SO₂ and NO₂ increased by 2.4%, 36.0%, 27.3% and 89.5%, respec-
tively, compared to the lockdown period, while CO decreased by 10.2%. The YRD region was controlled by low temperatures and high RH and was affected by a cold front during the tertiary response, resulting in several precipitation processes. As such, during the tertiary response, the pollutants PM$_{2.5}$, PM$_{10}$ and SO$_2$ decreased by 43.2%, 25.9% and 58.8%, respectively, compared to the secondary response; in contrast, the trace gases NO$_2$ and CO increased by 18.4% and 19.4%, respectively.

As an important secondary pollutant, O$_3$ was influenced by its precursors, temperature and solar radiation. The O$_3$ concentrations were high and changed slightly during the SF, lockdown and secondary response periods. Compared to the pre-COVID period, higher O$_3$ concentrations were found during the lockdown and secondary response periods with similar diurnal variations (Fig. 4f). The increases of ozone concentrations, as opposed to decrease to other pollutants, are mainly explained by an unprecedented reduction in NOx emissions leading to a lower O$_3$ titration by NO (Sicard et al., 2020).

Fig. 3 presents that the NO$_2$ had great decreases during the SF, lockdown and secondary response periods, especially in the SF and lockdown stages, which resulted in weaker O$_3$ titration by NO and the following higher O$_3$ concentrations despite the large amounts of rainfall and pollutant emissions. The increase in O$_3$ during the lockdown in YRD has been discussed in detail elsewhere (Huang et al., 2020). A discrepancy in the diurnal variation of O$_3$ was also observed during the SF and tertiary response, resulting from high RH throughout the day due to the continuous precipitation process (Fig. 5).

2.3. Changes in BC and WSIs during different periods

The highest and lowest BC concentrations were found during the pre-COVID and SF periods, with averages of 3,153 and 1,112 ng/m$^3$, respectively (Fig. 6a). During the lockdown, the BC concentration was 1,473 ng/m$^3$, which was 53.3% lower than pre-COVID. Hereafter, BC changed slightly, increasing only by 12.2% during the secondary response. As the primary pollutant in the air, the diurnal variations in BC were observed to be similar during the pre-COVID, lockdown, secondary and tertiary response periods (Fig. 6b). The BC concentrations in the pre-COVID stage were all day higher than the other stages. Meanwhile, the BC concentrations had few discrepancies among the lockdown, secondary and tertiary response periods, revealing a major source of BC from the industrial processes in Suzhou. Lower BC concentrations in the SF and tertiary response stages were due to the continuous precipitation process (Fig. 6). Although BC concentrations in the secondary response stage was higher than the lockdown, it accounted for 52.4% of the value in the pre-COVID stage, which revealed that the production intensity was still weaker than the pre-COVID when people back to work.
Fig. 5 – Diurnal variations of (a) T, (b) wind speed, (c) RH and (d) visibility during different periods.

Fig. 6 – (a) Concentrations and (b) diurnal variations of BC during different periods.
Concentrations of WSIs were observed to be the lowest during the lockdown with an average of 9.8 μg/m³ (Fig. 7a), which decreased by 58.6% compared to the pre-COVID period. Furthermore, the ion/PM$_2.5$ ratio had the lowest values, 27.4%, during the lockdown and ranged from 41.6% to 49.9% during the other periods. Such a difference illustrated the great changes in the chemical components in PM$_2.5$ during the lockdown. Zheng et al. (2020) reported that primary emission reduced while secondary formation enhanced since lockdown in Wuhan, the lockdown measures not only reduced the mass concentrations of air pollutants and associated chemical compositions, but also modified the diurnal variation patterns of PM$_2.5$ sources. Although traffic emissions are believed to have been greatly reduced during the lockdown, the NO$_3^-$/SO$_4^{2-}$ ratio was found to be the lowest during the SF, probably due to the occurrence of the lowest proportion of NO$_3^-$ (31.9%), ascribed to the decreased traffic emissions, and the highest SO$_4^{2-}$ fraction (36.1%), caused by fireworks. Meanwhile, the ion concentrations of K$^+$ and Mg$^{2+}$ also had increased proportions of 2.7% and 1.9%. Fig. 8 shows that the ion concentrations of K$^+$, Mg$^{2+}$ and Cl$^-$ were higher at night than during the daytime during the SF, which is in accordance with the previous result (Wang et al., 2014a). Sun et al. (2020) considered that the lockdown overall caused ubiquitous reductions in gaseous species (NO$_2$, CO, and SO$_2$) and primary aerosol species (FFOA, COA, and BC) by 25-46% and 30-50%, respectively, during the Spring Festival in Beijing. 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%).

During the lockdown, the ion concentrations were ranked in the order of NO$_3^-$ > NH$_4^+$ > S O$_4^{2-}$ > Cl$^-$ > Ca$^{2+}$ > K$^+$ > Mg$^{2+}$ > Na$^+$; they reordered to NO$_3^-$ > SO$_4^{2-}$ > NH$_4^+$ > Cl$^-$ > Ca$^{2+}$ > K$^+$ > Na$^+$ > Mg$^{2+}$ during the pre-COVID period and SO$_4^{2-}$ > NO$_3^-$ > NH$_4^+$ > Cl$^-$ > K$^+$ > Mg$^{2+}$ > Ca$^{2+}$ > Na$^+$ during the SF. By comparisons with the pre-COVID ion concentrations, we found that ions NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, Cl$^-$, Ca$^{2+}$, K$^+$ and Na$^+$ decreased by 66.3%, 48.8%, 52.9%, 56.9%, 57.9% and 76.3%, respectively, during the lockdown; the exception was Mg$^{2+}$, with a 30.2% increase.

We calculated that the NO$_3^-$/SO$_4^{2-}$ ratio was 1.5 during the lockdown, which was much lower than pre-COVID (2.1). With the resumption of work and production, the NO$_3^-$/SO$_4^{2-}$ ratio increased rapidly to a value of 3.0 during the secondary response; the proportion of NO$_3^-$ to the total WSIs also rebounded to values comparable to those pre-COVID. The sulfur oxidation ratio (SOR) during the lockdown decreased noticeably to 59.0% of the pre-COVID values. In contrast, the nitrogen oxidation ratio (NOR) during the lockdown was calculated to be 1.7 times higher than the pre-COVID values. However, we found that the proportions of NO$_3^-$ and SO$_4^{2-}$ were 37.6% and 25.5%, respectively, during the lockdown and changed to 46.1% and 22.4% during the pre-COVID period. A great reduction in NO$_2$ concentrations during the lockdown was respon-
sible for the low NO$_3^-$ fraction, although the NOR was high. Chen et al. (2020) observed that fast chemical transformation of gaseous pollutants to secondary aerosols could lead to air pollution even if anthropogenic activities were suppressed to a great extent during the lockdown in Shanghai.

By comparison of Figs. 3 and 7, contrary variations of SO$_2$ and SO$_4^{2-}$ were found in the SF, lockdown and secondary response stages. SO$_2$ exhibited an increasing trend with the values in the secondary response stage 1.7 times higher than the SF. The proportions of SO$_4^{2-}$ shown a decreasing trend with values of 25.5% and 15.1% in the lockdown and secondary response stage despite the slight variation of its concentrations (2.5 and 2.4 µg/m$^3$). Meanwhile, the SOR was 0.4 in the SF stage, which were 1.6 and 2.0 times higher than the lockdown and secondary response stages. Higher RH up to 91.1% in the SF favored the SO$_4^{2-}$ formation by liquid reactions of SO$_2$ except the firework contribution. Low SOR and RH (71.1% and 67.7%) in the lockdown and secondary response stages revealed the weak generation of SO$_4^{2-}$ through SO$_2$. The sharp increase in NO$_3^-$ up to 7.4 µg/m$^3$ in the secondary response stage was mainly due to the work resumption, which were 2.2 and 2.0 times larger than the SF and lockdown. Such increase in NO$_3^-$ also decreased the fraction of SO$_4^{2-}$.

Fig. 8 illustrates that different WSIs during the lockdown had distinct diurnal variations. The ions Cl$^-$, K$^+$, Mg$^{2+}$ and Na$^+$ had inconspicuous variations due to their low concentrations. Ca$^{2+}$ had a unimodal distribution with high concentrations in the daytime and low values at night. The aforementioned ions were much affected by the local emissions and meteorological factors due to their low content in the air, which we have not discussed in detail.

The diurnal variation of NO$_3^-$ during the lockdown was similar to that during the pre-COVID and secondary response periods, with high values at night and low values in the daytime. As shown in Fig. 5, similar diurnal variations were observed for temperature, RH and wind speed during the pre-COVID, lockdown and secondary response periods. High RH at night was conducive to nitrate formation. During the lockdown, SO$_4^{2-}$ had a unimodal distribution peaking at 12:00-14:00, which also corresponded to the period of peak values for SO$_2$ and O$_3$ (Fig. 4) and high temperature and visibility (Fig. 5), revealing strong photochemical reactions generating sulfate in the air. The SO$_4^{2-}$ showed a valley value in the midday and peak values in the rush hours during the pre-COVID and SF periods, which highlighted its sources from direct emissions of air pollutants and heterogeneous reaction processes instead of the photochemical reactions. The concentration of NH$_4^+$ during the lockdown was also observed to be high in the daytime and low at night, which was similar to those of the pre-COVID and secondary response periods, except with lower concentrations.
3. Conclusions

In this study, we evaluate the air quality in the Yangtze River Delta during the COVID-19 lockdown period using satellite and ground-based data including PM, trace gases, water-soluble ions (WSIs) and BC. We found that the impacts of lockdown policy on air quality cannot be accurately assessed using MODIS AOD data, whereas the tropospheric NO2 VCD can well reflect the influences of these restrictions on human activities. Compared to the pre-COVID period, the PM2.5, PM10, NO2, CO, BC and WSIs during the lockdown in Suzhou were observed to have decreased by 37.2%, 38.3%, 64.5%, 26.1%, 53.3% and 58.6%, respectively, while the SO2 and O3 increased by 1.5% and 104.7%, respectively. The ion/PM2.5 ratio had its lowest value of 27.4% during the lockdown and ranged from 41.6% to 49.9% during the other periods. The WSIs were ranked in the order of NO3− > NH4+ > SO42− > Cl− > Ca2+ > K+ > Mg2+ > Na+ during the lockdown and reordered to NO3− > SO42− > NH4+ > Cl− > Ca2+ > K+ > Na+ > Mg2+ during the pre-COVID period and SO42− > NO3− > NH4+ > Cl− > K+ > Mg2+ > Ca2+ > Na+ during the SF. By comparisons with ion concentrations during the pre-COVID period, we found that ions of NO3−, NH4+, SO42−, Cl−, Ca2+, K+ and Na+ during the lockdown decreased by 66.3%, 48.8%, 52.9%, 56.9%, 75.9% and 76.3%, respectively, in contrast to Mg2+, which had an increase of 30.2%. The lockdown policy was found to have great impacts on the diurnal variations of Cl−, SO42−, Na+ and Ca2+ and small impacts on the diurnal variations of BC, K+, Mg2+, NH4+ and NO3−.

Appendix A

Acknowledgments

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Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.09.019.

REFERENCES

An, Z., Huang, R., Zhang, R., Tie, X., Li, G., Cao, J., et al., 2019. Severe haze in Northern China: a synergy of anthropogenic emissions and atmospheric processes. Proc. Natl. Acad. Sci. U.S.A. 116 (18), 8657–8666.

Cai, H., Xie, S., 2011. Traffic-related air pollution modeling during the 2008 Beijing Olympic Games: the effects of an odd-even day traffic restriction scheme. Sci. Total Environ. 409 (10), 1935–1948.

Cai, W., Li, K., Liao, H., Wang, H., Wu, L., 2017. Weather conditions conducive to Beijing severe haze more frequent under climate change. Nat. Clim. Change 7 (4), 257–262.

Cao, S., He, L., Shen, X., Hu, N., 2020. Analysis of the February 2020 atmospheric circulation and weather. Meteor. Mon. 46 (5), 725–732.

Chan, C., Yao, X., 2008. Air pollution in mega cities in China. Atmos. Environ. 42 (1), 1–42.

Chen, H., Huo, J., Fu, Q., Duan, Y., Xiao, H., Chen, J., 2020. Impact of quarantine measures on chemical compositions of PM2.5 during the COVID-19 epidemic in Shanghai. China. Sci. Total Environ., 140758.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., et al., 2016. Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. Sci. Adv. 2 (12), e1601530.

Chu, B., Zhang, S., Liu, J., Ma, Q., He, H., 2021. Significant concurrent decrease in PM2.5 and NO2 concentrations in China during COVID-19 epidemic. J. Environ. Sci. 99, 346–353.

Corrigan, C., Ramanathan, V., Schauer, J., 2006. Impact of monsoon transitions on the physical and optical properties of aerosols. J. Geophys. Res. 111, 1–15.

Ding, A., Fu, C., Yang, X., Sun, J., Zheng, L., Xie, Y., et al., 2013. Ozone and fine particle in the western Yangtze River Delta: an overview of 1 yr data at the SORPES station. Atmos. Chem. Phys. 13 (11), 5813–5830.

Ding, A., Huang, X., Nie, W., Sun, J., Kerminen, V., Petäjä, T., et al., 2016. Enhanced haze pollution by black carbon in megacities in China. Geophys. Res. Lett. 43 (6), 2873–2879.

Fenger, J., 2009. Air pollution in the last 50 years-From local to global. Atmos. Environ. 43 (1), 13–22.

Filoncyk, M., Hurynovich, V., Yan, H., Gusev, A., Shpilevskaya, N., 2020. Impact Assessment of COVID-19 on Variations of SO2, NO2, CO and AOD over East China. Aerosol Air Qual. Res. https://doi.org/10.4209/aaqr.2020.05.0226.

Ge, B., Wang, Z., Lin, W., Xu, X., Li, J., Ji, D., et al., 2018. Air pollution over the North China Plain and its implication of regional transport: a new sight from the observed evidences. Environ. Pollut. 234, 29–38.

Georgoulas, A.K., van der A, R.J., Stammes, P., Boersma, K.F., Eskes, H.J., 2019. Trends and trend reversal detection in 2 decades of tropospheric NO2 satellite observations. Atmos. Chem. Phys. 19, 6299–6294.

Guo, S., Hu, M., Peng, J., Wu, Z., Zamora, M.L., Shang, D., et al., 2020. Remarkable nucleation and growth of ultrafine particles from vehicular exhaust. Proc. Natl. Acad. Sci. U.S.A. 117 (7), 3427–3432.

Hansen, A.D.A., Schnell, R.C., 2005. The Aethalometer. Magee Scientific Company, Berkeley, California, USA, pp. 1–209.

He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., et al., 2014. Mineral dust and NOx promote the conversion of SO2 to sulfate in heavy pollution days. Sci. Rep. 4, 04172.

Huang, R., Zhang, Y., Bozzetti, C., Ho, K., Cao, J., Han, Y., et al., 2014. High secondary aerosol contribution to particulate pollution during haze events in China. Nature 514 (7521), 218–222.

Huang, X., Ding, A., Gao, J., Zheng, B., Zhou, D., Qi, X., et al., 2020. Enhanced secondary pollution offset reduction of primary emissions during COVID-19 lockdown in China. Natl. Sci. Rev. nwa133 https://doi.org/10.1093/nsr/nwa133.

Huang, X., Tang, G., Zhang, J., Liu, B., Liu, C., Zhang, J., et al., 2021. Characteristics of PM2.5 pollution in Beijing after the improvement of air quality. J. Environ. Sci. 100, 1–10.

Jiang, Q., Gui, H., Xu, R., 2020. Analysis of January 2020 atmospheric circulation and weather. Meteor. Mon. 46 (4), 575–580.

Kerimray, A., Baimatova, N., Ibragimova, O.P., Bukenov, B., Kenessov, B., Plotitsyn, P., et al., 2020. Assessing air quality changes in large cities during COVID-19 lockdowns: The impacts of traffic-free urban conditions in Almaty, Kazakhstan. Sci. Total Environ., 139179.

Kharol, S.K., Fioletov, V., McLinden, C.A., Shephard, M.W.,
Li, H., Wang, D., Cui, L., Gao, Y., Hoo, J., Wang, X., et al., 2019a. Characteristics of atmospheric PM$_{2.5}$ composition during the implementation of stringent pollution control measures in shanghai for the 2016 G20 summit. Sci. Total Environ. 648, 1121–1129.

Li, K., Jacob, D.J., Liao, H., Shen, L., Zhang, Q., Bates, K.H., 2019b. Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China. Proc. Natl. Acad. Sci. U.S.A. 116 (2), 422–427.

Li, K., Jacob, D.J., Liao, H., Zhu, J., Shah, V., Shen, L., et al., 2019c. A two-pollutant strategy for improving ozone and particulate air quality in China. Nat. Geosci. 12 (11), 906–910.

Li, L., Li, Q., Huang, L., Wang, Q., Zhu, A., Xu, J., et al., 2020. Air quality changes during the COVID-19 lockdown over the Yangtze River Delta Region: An insight into the impact of human activity pattern changes on air pollution variation. Sci. Total Environ., 139282.

Li, X., Qiao, Y., Zhu, J., Shi, L., Wang, Y., 2017a. The “APEC blue” endeavor: Causal effects of air pollution regulation on air quality in China. J. Clean. Prod. 168, 1381–1388.

Li, Z., Guo, J., Ding, A., Liao, H., Liu, J., Sun, Y., et al., 2017b. Aerosol and boundary-layer interactions and impact on air quality. Natl. Sci. Rev. 4 (6), 810–833.

Lou, S., Yang, Y., Wang, H., Smith, S.J., Qian, Y., Rasch, P.J., 2019. Black carbon amplifies haze over the North China Plain by weakening the East Asian winter monsoon. Geophys. Res. Lett. 46 (1), 452–460.

Luo, J., Zhang, J., Huang, X., Liu, Q., Luo, B., Zhang, W., et al., 2020. Characteristics, evolution, and regional differences of biomass burning particles in the Sichuan Basin, China. J. Environ. Sci. 89, 35–46.

Nakada, L.Y.K., Urban, R.C., 2020. COVID-19 pandemic: Impacts on the air quality during the partial lockdown in São Paulo state. Brazil. Sci. Total Environ., 139087.

Qu, W., Wang, J., Zhang, X., Sheng, L., Wang, W., 2016. Opposite seasonality of the aerosol optical depth and the surface particulate matter concentration over the north China Plain. Atmos. Environ. 127, 90–99.

Quinn, P.K., Bates, T.S., 2003. North American, Asian, and Indian haze: Similar regional impacts on climate? Geophys. Res. Lett. 30 (11), doi:10.1029/2003GL016934.

Shen, L., Wang, H., Lü, S., Zhang, X., Yuan, J., Tao, S., et al., 2017. Influence of pollution control on air pollutants and the mixing state of aerosol particles during the 2nd World Internet Conference in Jiating, China. J. Clean. Prod. 149, 436–447.

Shen, L.J., Wang, H.L., Zhao, T., Liu, J., Bai, Y., Kong, S.F., et al., 2020. Characterizing regional aerosol pollution in central China based on 19 years of MODIS data: Spatiotemporal variation and aerosol type discrimination. Environ. Pollut., 114556.

Sicard, P., De Marco, A., Agathokleous, E., Feng, Z., Xu, X., Paolletti, E., et al., 2020. Amplified ozone pollution in cities during the COVID-19 lockdown. Sci. Total Environ., 139542.

Song, C., Wu, L., Xie, Y., He, J., Chen, X., Wang, T., et al., 2017. Air pollution in China: status and spatiotemporal variations. Environ. Pollut. 227, 334–347.

Sun, Y., Lei, L., Zhou, W., Chen, C., He, Y., Sun, J., et al., 2020. 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. Sci. Total Environ., 140739.

Tang, M., Liu, Y., He, J., Wang, Z., Wu, Z., Ji, D., 2020. In situ continuous hourly observations of wintertime nitrate, sulfate and ammonium in a megacity in the North China Plain from 2014 to 2019: temporal variation, chemical formation and regional transport. Chemosphere, 127745.

Tian, H., Liu, Y., Li, Y., Wu, C.H., Chen, B., Kraemer, M.U., et al., 2020a. An investigation of transmission control measures during the first 50 days of the COVID-19 epidemic in China. Science 368 (6491), 638–642.

Wang, C., Horby, P.W., Hayden, F.G., Gao, G.F., 2020b. A novel coronavirus outbreak of global health concern. Lancet 395 (10223), 470–473.

Wang, H., Zhu, B., Shen, L., Zhang, Z., Liu, X., 2014a. The mass concentration and chemical compositions of the atmospheric aerosol during the Spring Festival in Nanjing. China Environ. Sci. 34 (1), 30–39.

Wang, N., Zhu, H., Guo, Y., Peng, C., 2018. The heterogeneous effect of democracy, political globalization, and urbanization on PM$_{2.5}$ concentrations in G20 countries: Evidence from panel quantile regression. J. Clean Prod. 194, 54–68.

Wang, P., Chen, K., Zhu, S., Wang, P., Zhang, H., 2020c. Severe air pollution events not avoided by reduced anthropogenic activities during COVID-19 outbreak. Resour. Conserv. Recy. 158, 104814.

Wang, T., Nie, W., Gao, J., Xue, L., Gao, X., Wang, X., et al., 2010. Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact. Atmos. Chem. Phys. 10 (16), 7603–7615.

Wang, Y., Gao, W., Wang, S., Song, T., Gong, Z., Ji, D., et al., 2020d. Contrasting trends of PM$_{2.5}$ and surface ozone concentrations in China from 2013 to 2017. Natl. Sci. Rev. doi:10.1093/nsr/nwaa032.

Wang, Y., Yao, L., Wang, L., Liu, Z., Ji, D., Tang, G., et al., 2014b. Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China. Sci. China Earth Sci 57 (1), 14–25.

Wang, Y., Zhang, Y., Schauer, J.J., de Foy, B., Gao, B., Zhang, Y., 2016. Relative impact of emissions controls and meteorology on air pollution mitigation associated with the Asia-Pacific Economic Cooperation (APEC) conference in Beijing, China. Sci. Total Environ. 571, 1467–1476.

Wen, L., Yue, L., Wang, X., Xu, C., Chen, T., Yang, L., et al., 2018. Summertime fine particulate nitrate pollution in the North China Plain: increasing trends, formation mechanisms and implications for control policy. Atmos. Chem. Phys. 18 (15), 11261–11275.

Xu, P., Chen, Y., Ye, X., 2013. Haze, air pollution, and health in China. Lancet 382 (9910), 2067.

Xu, R., Tang, G., Wang, Y., Tie, X., 2016. Analysis of a long-term measurement of air pollutants (2007–2011) in North China Plain (NCP): Impact of emission reduction during the Beijing Olympic Games. Chemosphere 159, 647–658.

Yang, Q., Yuan, Q., Yue, L., Li, T., Shen, H., Zhang, L., 2019. The relationships between PM$_{2.5}$ and aerosol optical depth (AOD) in mainland China: About and behind the spatio-temporal variations. Environ. Pollut. 248, 526–535.

Zhang, F., Wang, Y., Feng, J., Chen, L., Sun, Y., Duan, L., et al., 2020. An unexpected catalyst dominates formation and radiative forcing of regional haze. Proc. Natl. Acad. Sci. U.S.A. 117 (8), 3960–3966.

Zhang, J., Sun, Y., Liu, Z., Ji, D., Hu, B., Liu, Q., et al., 2014. Characterization of submicron aerosols during a month of serious pollution in Beijing, 2013. Atmos. Chem. Phys 14 (6), 2887–2903.

Zhang, J., Wang, L., Wang, Y., Wang, Y., 2016. Submicron aerosols during the beijing asia–pacific economic cooperation conference in 2014. Atmos. Environ. 124, 224–231.

Zheng, H., Kong, S., Chen, N., Yan, Y., Liu, D., Zhu, B., et al., 2020. Significant changes in the chemical compositions and sources of PM$_{2.5}$ in Wuhan since the city lockdown as COVID-19. Sci. Total Environ., 146000.
Zhu, T., Shang, J., Zhao, D., 2011. The roles of heterogeneous chemical processes in the formation of an air pollution complex and gray haze. Sci. China Chem. 54 (1), 145–153.

Zeng, Y., Cao, Y., Qiao, X., Seyler, B.C., Tang, Y., 2019. Air pollution reduction in China: Recent success but great challenge for the future. Sci. Total Environ. 663, 329–337.