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Insights into chemical composition, abatement mechanisms and regional transport of atmospheric pollutants in the Yangtze River Delta region, China during the COVID-19 outbreak control period

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\textbf{A B S T R A C T}

To investigate chemical characteristics, abatement mechanisms and regional transport of atmospheric pollutants during the COVID-19 outbreak control period in the Yangtze River Delta (YRD) region, China, the measurements of air pollutants including fine particulate matter (PM\textsubscript{2.5}) and volatile organic compounds (VOCs) on non-control period (NCP, 24 December 2019–23 January 2020) and control period (CP, 24 January–23 February 2020) were analyzed at the urban Pudong Supersite (PD) and the regional Dianshan Lake Supersite (DSL). Due to the stricter outbreak control, the levels of PM\textsubscript{2.5} and VOCs, and the occurrence frequencies of haze-fog episodes decreased substantially from NCP to CP, with average reduction rates of 31.6%, 38.9% and 35.1% at PD, and 34.5%, 50.7% and 37.9% at DSL, respectively. The major source for PM\textsubscript{2.5} was secondary sulfate & nitrate in both periods, and the emission control of primary sources such as coal burning and vehicle exhaust decreased the levels of precursors gas sulfur dioxide and nitrogen oxide, which highly contributed to the abatement of PM\textsubscript{2.5} from NCP to CP. The higher levels of ozone at both PD and DSL on CP might be due to the weak nitrogen monoxide titration, low relative humidity and high visibility compared with NCP. Vehicle exhaust and fugitive emission from petrochemical industry were the major contributors of ambient VOCs and their decreasing activities mainly accounted for VOCs abatement. Moreover, the high frequency of haze-fog events was closely impacted by medium-scale regional transport within Anhui and Jiangsu provinces. Therefore, the decreasing regional transported air pollutants coincided with the emission control of local sources to cause the abatement of haze-fog events in YRD region on CP. This study could improve the understanding of the change of atmospheric pollutants during the outbreak control period, and provide scientific base for haze-fog pollution control in YRD region, China.

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1. Introduction

Atmospheric pollution has aroused global concern due to the presence of harmful particles and gases that can present health threat to human, living organisms and ecosystems (IARC, 2016; WHO, 2016). Air pollutants like particulate matter (PM), toxic metals, volatile organic compounds (VOCs) are the result of natural processes and human activities such as burning of fuels by power plants and motor vehicles, and industrial production (WHO, 2016). Outdoor air pollution and PM are carcinogenic to humans (group 1) (IARC, 2013), and have been proved to pose an increasing risk for respiratory and cardiovascular diseases (IARC, 2013; Thurston, 2017). On account of the adverse effect, outdoor air pollution carries the responsibility for the premature death of about 3 million people annually (WHO, 2016) and also causes economic loss (OECD, 2016). In China, assessments for the diseases burden and premature deaths from exposure to air pollution have been critically over-viewed, highlighting the ability of air pollution to cause hazards for Chinese population (GBD, 2015 Risk Factors Collaborators, 2016; Hu et al., 2015; Liu et al., 2016; Yang et al., 2013; Zhao et al., 2019).

With the rapid development of industries, urbanization and

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economics, the Yangtze River Delta (YRD) region is emerging as a world-class urban agglomeration and one of the major economic contributors in China. YRD covers an area of 217,700 square kilometers, which had a regional gross domestic product of 12.67 trillion CNY and a population of 150 million, accounting for 18.5 percent and 11.0 percent of China’s total in 2014, respectively (NDRC and MHURD, 2016). Megacity Shanghai is an important international gateway and industrial production center in YRD, with the permanent population of 24.18 million and vehicle ownership nearly 3.92 million in 2017 (SMB and SONBS, 2018). Meanwhile, there are also a number of coal-fired power plants and industrial boilers to meet the development demands of industries and urban in this region (Jiangsu Provincial People’s Government, 2014; Shanghai Municipal People’s Government, 2018; Zhejiang Provincial Development and Reform Commission, 2018). However, intensive industrial and traffic activities caused the serious regional air pollution problems such as haze-fog events, resulting in a deterioration of air quality and public health in YRD (Haque et al., 2020; Li et al., 2016a; Liu et al., 2018; Ouyang et al., 2019; Zhang et al., 2020; Li et al., 2016b). Since December 2019, a novel coronavirus pneumonia (COVID-19) had caused the outbreak in Wuhan, China. The effective control measures were made rapidly by the Chinese government to contain the epidemic (The State Council Information Office of the People’s Republic of China, 2020). Shanghai Municipal People’s Government has initiated the top-level response mechanism for major public health emergencies in 24 January 2020. The resumption of production work by enterprises and the opening of schools have been deferred in Shanghai (Shanghai Municipal People’s Government, 2020). However, the understanding of chemical composition, abatement mechanisms, and source variation of atmospheric pollutants remains unknown during the special control period in YRD region, China. Therefore, the aims of this study were to comprehensively investigate the variations on levels and chemical compositions of PM$_{2.5}$ and VOCs on two Supersites during the non-control period and control period, to identify their potential sources and study the abatement mechanisms, and to assess the impact of regional transport on haze-fog pollution in YRD region, China.

2. Methodology

2.1. Sampling sites

The sampling sites are the urban Pudong (PD) and the regional Dianshan Lake (DSL) Supersites, situated geographically at the center of YRD region, China (Fig. 1). The PD Supersite (31.23°N, 121.52°E), near the Lujiazui Financial District, is located in downtown area of Shanghai, which is surrounded by the prosperous commerce, dense population and high traffic volume. DSL Supersite (31.09°N, 120.98°E) is situated in the southwest suburban of Shanghai and is adjacent to Jiangsu and Zhejiang Provinces. Siting on the edge of Shanghai, DSL Supersite is considered as the suitable site to investigate the regional air quality and transport of air pollutants in YRD region.

2.2. Measurements and data analysis

2.2.1. Measurements of meteorological parameters and atmospheric pollutants

The meteorological parameters, including temperature (T), wind direction (WD), wind speed (WS), atmospheric pressure (P), relative humidity (RH), and visibility were monitored at PD and DSL Supersites, respectively. Gaseous pollutants, i.e., sulfur dioxide (SO$_2$), nitrogen monoxide (NO), nitrogen dioxide (NO$_2$), ozone (O$_3$), and fine particles (PM$_{2.5}$) were measured by Thermo Scientific gas analyzers. The concentrations of 8 water-soluble inorganic ions (WSIs) (SO$_{4}^{2-}$, CI$^-$, NO$_3^-$, Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$) in PM$_{2.5}$ were measured by an online Monitor for AeRosols and Gases (MARGA, Model ADI2080, Metrohm Applikon B.V., The Netherlands). Organic carbon (OC) and elemental carbon (EC) were observed with a thermo-optical OC/EC analyzer (Model RT-4, Sunset Lab, USA). The concentrations of 17 elements (Si, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Ag, Cd, Ba, Pb, and Hg) in PM$_{2.5}$ were determined by an ambient continuous multi-metals monitor (Model Xact 625, Cooper Environmental Services, Beaverton, OR, USA). Continuous measurements of 56 VOC species, including 29 alkanes, 10 alkenes, 16 aromatics, and 1 kind of alkylene (acetylene) (Table S1) were conducted by gas chromatograph with flame ionization detector systems. The calibration of VOC species was performed with the photochemical assessment monitoring station and TO-15 standard mixtures, and the correlation coefficient of calibration curves of target compounds was >0.99. The detailed information on VOCs measurement and quality assurance was described elsewhere (Zheng et al., 2019). The measurement data was presented at 1-h time resolution for statistics. To distinctly investigate the variation of atmospheric pollutants, the observation campaign was divided into the non-control period (NCP, 24 December 2019–23 January 2020), control period (CP, 24 January–23 February 2020). Based on the meteorological industry standard of China, haze is defined as an atmospheric turbid phenomenon, which is characterized by the low visibility less than 10 km and the RH below 80% (CMA, 2010). When the visibility is below 1 km and RH more than 90%, the fog weather occurs, and when RH is between 80% and 90%, the visibility is reduced by haze and fog (CMA, 2003; Liu et al., 2018). To conveniently study the characteristics of atmospheric composition during the fog-haze events, the visibility was applied to characterize the pollution levels, which was generally classified into five categories: ≥10 km, clear; ≥5.0 km, and <10 km, slight fog-haze (SFH); >3.0 km, and <5.0 km, low fog-haze (LHF); ≥2.0 km, and <3.0 km, medium fog-haze (MHF); <2.0 km, heavy fog-haze (HFH).

2.2.2. Calculation of sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR)

To assess the degrees of secondary formation of SO$_4^{2-}$ and NO$_3^-$, sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) were calculated by the following equation (Xu et al., 2017):

$$\text{SOR} = \frac{n - \text{SO}_4^{2-}}{n - \text{SO}_4^{2-} + n - \text{SO}_2}$$

$$\text{NOR} = \frac{n - \text{NO}_3^-}{n - \text{NO}_3^- + n - \text{NO}_2}$$

where n- SO$_4^{2-}$ and n-NO$_3^-$ are the molar concentrations of SO$_4^{2-}$ and NO$_3^-$, n-SO$_2$ and n-NO$_2$ are the molar concentrations of SO$_2$ and NO$_2$, respectively.

2.2.3. Calculation of enrichment factor (EF)

To evaluate the relative contributions of crustal and anthropogenic origins of the elements, the enrichment factor (EF) of each element was estimated by the following formula (Gao et al., 1992; Ramirez et al., 2020):

$$\text{EF} = \frac{C_{\text{sample}}}{\text{EPA Background}} = \frac{C_{\text{mean}}}{C_{\text{geo}} + C_{\text{B}}},$$

where $C_{\text{sample}}$ is the measured concentration of element in the sample, $C_{\text{mean}}$ is the mean concentration of the element in the background, and $C_{\text{geo}}$ and $C_{\text{B}}$ are the concentrations of the element in the crust and background, respectively.
where \((X/Ref)_{\text{sample}}\) represents the mass ratio of element X to the reference element in PM2.5 sample, and \((X/Ref)_{\text{crust}}\) represents the mass ratio of element X to the reference element in the crust. Here, Fe is used as the reference element (Gao et al., 1992; Ramirez et al., 2020). The crustal element data in the continental of eastern China was given by Gao et al. (1999). Generally, EF value of above 10 is considered indicative of the significant anthropogenic origin, and EF value lower than 10 implies the dominant crustal source (Ramirez et al., 2020; Wang et al., 2018).

2.2.4. Calculation of secondary OC and secondary organic aerosol (SOA)

Primary OC (POC) and secondary OC (SOC) were estimated using EC as a tracer by the following relation (Turpin and Huntzicker, 1995):

\[
POC = EC \times (OC/EC)_{\text{pri}} \\
SOC = OC - EC \times (OC/EC)_{\text{pri}}
\]

where \((OC/EC)_{\text{pri}}\) is the OC/EC ratio from primary sources. The mean of the lowest 1% value of OC/EC ratio was chosen as the representative of \((OC/EC)_{\text{pri}}\) in this study. Further, organic matter (OM) and secondary organic aerosol (SOA) were calculated respectively through multiplying the OC and SOC by a conversion factor between organic carbon to organics, and the mean value of conversion factor for atmospheric aerosols is 1.6 suggested by Turpin and Lim (2001).

2.2.5. Estimation of ozone formation potential (OFP) and secondary organic aerosol potential (SOAP) for VOCs

Ozone formation potential (OFP) is a key indicator to evaluate the reactivities of photochemical ozone formation of VOCs. The OFP of individual VOC species was estimated using the maximum incremental reactivity (MIR) value, which is the amount of \(O_3\) formation by adding a weight of VOC species under the representative atmosphere with the relative high \(NO_x\) condition (Carter, 1994, 2010, 2013):

\[
OFP_i = VOC_i \times MIR_i
\]

where \(OFP_i\) is the OFP of VOC species i, \(VOC_i\) is the concentration of individual VOC i, MIR is the MIR value of the corresponding VOC i, as described in Carter (2013).

To better reflect the propensities of VOCs to SOA formation, Derwent et al. (2010) developed the secondary organic aerosol potential (SOAP), which defined the yield capacity of SOA for each VOC species on the mass basis relative to toluene, as described by the following relation (Derwent et al., 2010):

\[
SOAP_i = \frac{\text{Increment in SOA mass concentration with VOC species } i}{\text{Increment in SOA with toluene}} \times 100
\]

where \(SOAP_i\) is the SOAP factor for VOC species i, as showed in elsewhere (Derwent et al., 2010).

The contribution of individual VOC species to SOA formation can be calculated by multiplying the emission of each VOC species with the specific SOAP factor. There are 44 VOC species with the specific SOAP factors in this study. Thus, the total SOAP of 44 VOC species was estimated as follows (Niu et al., 2016):

\[
SOAP = \sum_{i=1}^{k} E_i \times SOAP_i
\]

where \(E_i\) is the concentration of individual VOC i for 44 VOC species.

2.2.6. Statistical analysis

Descriptive statistics, Spearman correlation analysis and Mann-Whitney \(U\) test were conducted by SPSS version 22 (IBM Corp., USA). The positive matrix factorization (PMF) 5.0 model was used to perform the source apportionments of VOCs and PM2.5, respectively (Paatero and Tapper, 1994; U.S. EPA, 2014), and concentration below the method detection limit (MDL) was determined as 1/2 of
3. Results and discussion

3.1. Characteristics of air pollutants and meteorological parameters

Fig. 2 shows the time series of hourly data for meteorological parameters, SO2, NOx, O3, PM2.5 and VOCs during the observation period at PD and DSL Supersites, respectively. On CP, the hourly concentrations of SO2, NOx, PM2.5, O3 and total 56 VOCs (Σ56VOCs) were $4.88 \pm 2.05 \text{ mg m}^{-3}$, $24.5 \pm 12.5 \text{ mg m}^{-3}$, $35.5 \pm 26.2 \text{ mg m}^{-3}$, $67.7 \pm 20.5 \text{ mg m}^{-3}$ and $14.6 \pm 7.05 \text{ ppbv}$ at PD, and $5.68 \pm 3.11 \text{ mg m}^{-3}$, $27.4 \pm 7.76 \text{ mg m}^{-3}$, $39.5 \pm 25.7 \text{ mg m}^{-3}$, $72.0 \pm 23.0 \text{ mg m}^{-3}$ and $10.5 \pm 4.56 \text{ ppbv}$ at DSL, respectively (Fig. S1a). The concentrations of SO2, NOx, PM2.5, Σ56VOCs and O3 generally presented a similar variation tendency at both PD and DSL ($p < 0.01$). Compared with NCP, the levels of NOx, PM2.5 and Σ56VOCs had the significant reduction rates of 56.2%, 31.6% and 38.9% at PD, and 58.2%, 34.5% and 50.7% at DSL on CP, respectively, which were higher than those at the same periods during 2017–2019 (Fig. S2). Moreover, Mann-Whitney U test result showed that the levels of visibility at PD (value: $14,500 \pm 9430 \text{ m}$) and DSL (value: $13,600 \pm 11,100 \text{ m}$) on CP were significantly above those of NCP (values: $9340 \pm 7010 \text{ m}$ and $7310 \pm 7440 \text{ m}$) ($p < 0.01$), and the occurrence frequencies of haze-fog events decreased by 35.1% and 37.9% at PD and DSL in CP, respectively, as compared to NCP (Fig. S1b). In particular, the concentrations of O3 increased by 67.8% and 90.9% at PD and DSL, respectively, which were higher than those at the same periods on 2017–2019 (Fig. S2). Because the time division of NCP and CP was almost coincided with the vacation of Chinese Spring Festival, the declines of NOx, PM2.5 and Σ56VOCs and the increase of O3 were generally observed in the same periods during 2017–2019 (Fig. S2). Meanwhile, due to the impact of COVID-19 outbreak, the vacation of Chinese Spring Festival was highly extended and the resumption of production work by enterprises was deferred in the control period during 2019–2020. Thus, the stricter outbreak control measures contributed significantly to the variations of air pollutants.

Overall, the values of WS and RH were $1.20 \pm 0.877 \text{ m s}^{-1}$ and $80.7\% \pm 16.2\%$ on NCP, and $1.34 \pm 0.937 \text{ m s}^{-1}$ and $74.6\% \pm 23.8\%$ on CP at PD, and $1.80 \pm 1.17 \text{ m s}^{-1}$ and $76.4\% \pm 21.4\%$ on CP at DSL, respectively. Generally, WS decreased and RH increased from the clear weather to haze-fog events, which had the highest change rates of 69.5% and 25.7% on NCP, and 39.3% and 51.1% on CP at PD, and 54.6% and 33.0% on NCP, and 53.3% and 51.2% on CP at DSL, respectively (Fig. S3), indicating that the haze-fog episodes were heavily characterized by the stagnant meteorological conditions, such as the low WS and high RH. As showed in Fig. S3, the concentrations of SO2, NOx, PM2.5 and Σ56VOCs at PD and DSL mostly presented the higher levels at NCP than those of CP on each fog-haze level. On average, the concentrations of NOx and PM2.5 had the remarkable increases from the clear weather level to haze-fog events, especially for NCP with the highest increments of $34.5 \text{ mg m}^{-3}$ and $77.4 \text{ mg m}^{-3}$ at PD, and $41.2 \text{ mg m}^{-3}$ and $67.3 \text{ mg m}^{-3}$ at DSL, respectively, which were higher than those of PD ($5.10 \text{ mg m}^{-3}$ and $30.1 \text{ mg m}^{-3}$) and DSL ($3.40 \text{ mg m}^{-3}$ and $43.9 \text{ mg m}^{-3}$) on CP. The decline in the levels of these air pollutants from NCP to CP indicated the decreasing...
contribution of primary emission sources to the high concentrations of air pollutants and the formation of haze-fog events. Therefore, these results highlighted that the stringent control measures played an important role on reducing air pollutants and improving air quality due to the COVID-19 lockdown.

3.2. Variation characteristics of PM$_{2.5}$

3.2.1. Chemical composition

The hourly data for EC, OC, and 8 WSIIs in PM$_{2.5}$ during the two periods at PD and DSL are given in Figs. S4 and S5. The concentrations of OC and EC were 5.17 ± 1.75 µg m$^{-3}$ and 1.02 ± 0.555 µg m$^{-3}$ at PD, and 4.14 ± 2.23 µg m$^{-3}$ and 1.44 ± 0.769 µg m$^{-3}$ at DSL on CP, respectively. Compared with NCP, it was highly characterized by the obvious increase of mean values of OC/EC by 39.1% and 42.5% at PD and DSL on CP, highlighting the decline of the relative contribution of primary emission to carbonaceous pollutants (Turpin and Huntzicker, 1995). The concentrations of total 8 WSIIs (Σ$_8$WSIIs) were $22.9 ± 16.4$ µg m$^{-3}$ and $21.7 ± 14.6$ µg m$^{-3}$ at PD and DSL on CP, respectively, which were averagely decreased by 29.8% and 48.6% at PD and DSL respectively as compared with NCP. The PM$_{2.5}$ and Σ$_8$WSIIs masses were heavily featured by the high fractions of sulfate-nitrato-ammonium (SNA: the sum of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ ) at both PD and DSL for each period. The SNA proportions averaged 60.0% and 52.2% of PM$_{2.5}$ mass on CP, and 58.9% and 56.6% on NCP at PD and DSL respectively. Additionally, the concentrations of NH$_4^+$ showed a significant correlation with those of SO$_4^{2-}$ and NO$_3^-$ at both PD and DSL for each period ($R = 0.860 − 0.985$, $p < 0.01$), depicting the consistency of NH$_4^+$ variation with SO$_4^{2-}$ and NO$_3^-$, which was also similar to previous studies in Shanghai (Wang et al., 2006) and Hangzhou (Cao et al., 2009). NH$_4^+$ was combined with SO$_4^{2-}$ and NO$_3^-$ to form (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$, respectively. The NCP and CP were highly characterized by the low temperature and high RH, which might favor the formation of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ (Shao et al., 2019; Squizzato et al., 2013; Toro et al., 2014). The visibility was significantly negatively correlated with the concentrations of SNA species at both PD and DSL on each period ($p < 0.01$), which showed the contributions of SNA to the decline of visibility (Pitchford et al., 2007). As showed in Fig. S5, during the morning rush hours (around 6:00−8:00), the high levels of SNA species caused the low visibility (less solar radiation), and then made a low height of planetary boundary layer and resulted in the increase of SNA species concentrations (Pan et al., 2019). Then as the temperature, solar radiation and planetary boundary layer height increased, the concentrations of SNA species decreased and visibility increased to the peak level at afternoon (around 13:00−17:00). Meanwhile, the concentrations of PM$_{2.5}$ and SNA species showed the significant correlations at both PD (NCP: $R = 0.975$, $p < 0.01$; CP: $R = 0.934$, $p < 0.01$) and DSL (NCP: $R = 0.839$, $p < 0.01$; CP: $R = 0.932$, $p < 0.01$), highlighting that SNA species dominated the variation of PM$_{2.5}$.

The average data for 17 elements during the two periods at PD and DSL are depicted in Fig. S6. The concentrations of total 17 elements were $1320 ± 989$ ng m$^{-3}$ and $1290 ± 1070$ ng m$^{-3}$ at PD and DSL on CP, which were significantly decreased by 12.9% and 16.6% respectively at PD and DSL as compared to NCP ($p < 0.01$). K, Si, Fe and Ca were major species, totally accounting for 84.8% and 84.3% of all 17 elements mass on NCP, and 90.5% and 89.9% on CP for PD and DSL respectively. Moreover, the concentrations of most elements such as Cr, Mn, Fe, Ni, Cu, Zn, As, Ag, Cd, Pb, Hg and Ca had the obvious reduction rates with 73.2%, 80.6%, 52.8%, 31.8%, 21.1%, 66.2%, 47.0%, 38.2%, 16.2%, 40.2%, 10.0% and 30.5% at PD, and 77.9%, 73.1%, 60.8%, 50.1%, 17.5%, 71.5%, 46.3%, 37.9%, 7.50%, 49.8%, 23.5% and 46.5% at DSL from NCP to CP, which might be associated with the declining activities of the related sources. As showed in Fig. S7, Ni, Cu, Zn, As, Ag, Cd, Pb and Hg generally had the high EFs with the mean values of above 10, thus indicating the significant impact from anthropogenic origin. Meanwhile, compared with NCP, the EFs of elements including Hg, Pb, Ni, Cu, Ag, Cd, Ba, Se, V, K and Si all increased averagely more than 20% on CP, which implied that the relative contribution of crustal source decreased more than that of anthropogenic origin.

3.2.2. Formation and abatement of haze-fog events

Fig. 3 presents the average concentrations and fractions of PM$_{2.5}$ chemical components under the different levels of fog-haze episodes at PD and DSL on each period. Overall, the SNA concentrations increased with the meteorology from clear level to haze-fog, especially for NCP with the higher increments of 50.5 µg m$^{-3}$ and 51.0 µg m$^{-3}$ at PD and DSL respectively. The mass ratios of NO$_3^-$/SO$_4^{2-}$ were 1.74 ± 0.895 and 1.56 ± 1.07 at PD, and 2.13 ± 0.922 and 1.77 ± 1.26 at DSL on NCP and CP, indicating the declining predominance of mobile source for these pollutants on CP (Animoto et al., 1996; Wang et al., 2006, 2015). The average values of SOR and NOR were greater than 0.10 at both PD and DSL on each period, which showed the occurrence of atmospheric photooxidation of SO$_2$ or NO$_2$ (Uli et al., 2016b; Ohta and Oikita, 1990). The values of SOR at PD were $0.470 ± 0.136$ and $0.436 ± 0.167$ at PD, and $0.442 ± 0.124$ and $0.394 ± 0.138$ at DSL on NCP and CP, respectively and the values of NOR on CP were significantly lower than those of NCP at both PD and DSL ($p < 0.01$), depicting the decrease of secondary formation of SO$_2$ to SO$_4^{2-}$ on CP, which might be related to the reduction of SO$_2$ emission due to the serious control measures for pollution sources. As showed in Fig. S8, during the NCP, SOR significantly increased by 67.6% and 50.6% with the levels of haze-fog events and RH at PD and DSL, respectively ($p < 0.01$), indicating the more active secondary conversion during haze-fog episodes with the higher levels of RH, which was conducive to the occurrence of aqueous-phase oxidation of SO$_2$ (Xu et al., 2017; Zhang et al., 2018a). By contrast, SOR all significantly increased first ($p < 0.01$) and then decreased with the levels of haze-fog at PD and DSL on CP, which showed the lacking capacity for secondary formation of SO$_2$ to SO$_4^{2-}$, especially on MHN and HFN. The values of NOR averaged $0.171 ± 0.118$ and $0.215 ± 0.128$ at PD, and $0.216 ± 0.122$ and $0.209 ± 0.105$ at DSL on NCP and CP, respectively, which showed the increasing secondary formation of NO$_2$ to NO$_3^-$ at PD, and the slightly decreasing secondary nitrate formation at DSL on CP. NOR can show a strong O$_3$ concentration dependency (Chiwa, 2010; Xu et al., 2017; Zhang et al., 2018a). Compared with SOR, the values of NOR were significantly correlated with the O$_3$ concentrations at PD and DSL on both periods ($p < 0.01$) in this study. Therefore, the increase of NOR at PD and slight decrease of NOR at DSL on CP might be contributed to the increased gas-phase oxidation of NO$_2$ at the high O$_3$ concentration (Chiwa, 2010; Creasey et al., 2001). Under the different levels of fog-haze episodes, NOR showed the similar variations with SOR on PD and DSL on each period (Fig. S9).

The relative contributions of six sources for PM$_{2.5}$ at PD and DSL on two periods are showed in Fig. 4a, and the source identification of PM$_{2.5}$ is provided in Supplemental materials. Overall, secondary sulfate & nitrate was the dominant contributor of ambient PM$_{2.5}$, accounting for 58.0% and 51.9% at PD, and 55.8% and 36.8% at DSL on NCP and CP, respectively. The obvious decrease of the contribution of secondary sulfate & nitrate at DSL reflected the more efficiency of regional joint control on PM$_{2.5}$ abatement as compared to PD, which was relatively impacted by local sources. Meanwhile, it should also be noticed that primary sources such as heavily oil combustion and coal & biomass burning also contributed highly to PM$_{2.5}$ mass. The average concentrations of six sources to PM$_{2.5}$ were estimated according to the source profiles from PMF output. As
showed in Fig. 4b, PM$_{2.5}$ masses from secondary sulfate & nitrate, coal & biomass burning and crustal sources had the obvious reduction rates of 38.8%, 31.6% and 19.7% at PD, and 56.8%, 77.1% and 81.2% at DSL, respectively. Moreover, the decrease of secondary formation of sulfate & nitrate highly accounted for PM$_{2.5}$ abatement, with the average masses of 11.7 $\mu$g m$^{-3}$ and 19.1 $\mu$g m$^{-3}$ from NCP to CP at PD and DSL, respectively. The precursors of secondary sulfate and nitrate were SO$_2$ and NO$_x$, which mainly emitted from coal combustion and vehicle exhaust (Li et al., 2016b; Tao et al., 2014). Therefore, these results indicated the decreasing activities of primary sources emission and secondary formation of sulfate and nitrate.

### 3.3. Variation characteristics of VOCs

#### 3.3.1. VOCs and OFP

The statistics of 56 VOC species measured at PD and DSL during the NCP and CP are depicted in Fig. S10. The hourly concentrations of $\Sigma_{56}$VOCs were 23.9 ± 12.6 ppbv and 14.6 ± 7.05 ppbv at PD, and 21.4 ± 13.0 ppbv and 10.5 ± 4.56 ppbv at DSL during the NCP and CP, respectively. Generally, the concentration of $\Sigma_{56}$VOCs at PD was significantly higher than that of DSL ($p < 0.01$). Alkanes were the major components of VOCs at both PD and DSL for two periods, with the mean contribution rates of 70.2% and 60.6% on NCP, and 76.7% and 64.9% on CP, respectively. As showed in Fig. S11, the top ten abundant components of VOCs at PD were consistent with those of DSL for NCP and CP, respectively, which 9 of 10 species were also the same on two periods. Among these VOC species, ethane, propane, ethylene, acetylene, n-butane exhibited the high abundances in VOCs total, which averagely accounted for 26.8%, 24.3%, 8.12%, 7.92% and 5.46% of the volumetric mixture ratio on NCP and 37.7%, 23.8%, 7.36%, 7.58% and 5.34% on CP at PD, and 12.5%, 20.4%, 7.81%, 8.82% and 7.04% on NCP and 19.4%, 23.8%, 11.8%, 9.93% and 6.77% on CP at DSL, respectively. Thus, the composite patterns of VOCs at PD and DSL shared the similarities on both NCP and CP.

The concentrations of OFP for $\Sigma_{56}$VOCs were 48.9 ± 32.3 mg m$^{-3}$ and 53.0 ± 34.4 mg m$^{-3}$ at PD and DSL on CP, respectively, which were significantly lower than those (123 ± 82.4 mg m$^{-3}$ and 159 ± 126 mg m$^{-3}$) on NCP ($p < 0.01$). Inversely, compared with the concentrations of $\Sigma_{56}$VOCs, the OFP of $\Sigma_{56}$VOCs at DSL were higher than those of PD ($p < 0.01$), which suggested the high tendencies of VOCs to O$_3$ formation at DSL. In generally, aromatic hydrocarbons...
and alkenes were both the major contributors to OFP of $\Sigma_{56}$ VOCs, with the mean contribution rates of 42.4% and 34.3% at PD, and 52.7% and 27.4% at DSL on NCP, and 23.1% and 46.0% at PD, and 27.0% and 48.3% at DSL on CP, respectively, which were similar to the results obtained in Shanghai during the 2016 G20 summit (Zheng et al., 2019). It was clear that the relative abundances of OFP by aromatic hydrocarbons decreased, while OFP of alkenes increased on CP as compared with NCP. For the top 10 components to OFP of $\Sigma_{56}$ VOCs at PD and DSL, they shared the nine same species on NCP with the average contributions of 72.2% and 68.4% to the total OFP, and eight same species on CP with the average contributions of 75.2% and 70.6%, respectively (Fig. S12). Moreover, ethylene, $m/p$-xylene, toluene, and propylene were the abundant species for OFP of VOCs, which accounted averagely 17.7%, 16.2%, 10.9% and 8.89% at PD and 11.8%, 18.5%, 15.0% and 5.84% at DSL on NCP, and 24.7%, 8.43%, 8.09% and 16.0% at PD, and 26.5%, 7.38%, 8.60% and 13.0% at DSL on CP, respectively. Compared with NCP, the relative abundances of OFP by ethylene and propylene increased, while OFP by $m/p$-xylene and toluene decreased slightly on CP. These results indicated the variation of composition patterns of VOCs for OFP from NCP to CP.

Fig. 5 shows the concentrations of VOC species, OFP and $O_3$ on the different levels of fog-haze episodes at PD and DSL on each period. Generally, the concentrations of $\Sigma_{56}$ VOCs, OFP and their four subgroups at PD and DSL on fog-haze pollution presented the higher levels than those on clear weather. However, in contrast to OFP, the concentrations of $O_3$ at both PD and DSL on CP were significantly higher than those of NCP ($p < 0.01$). Moreover, the concentrations of $O_3$ at PD and DSL were all significantly negatively correlated with those of NO$_x$, OFP and RH ($p < 0.01$), while the concentrations of $O_3$ were all significantly positively correlated with the availability of $\text{PD}$ and DSL on each period ($p < 0.01$) (Table S2), indicating that the high RH and low visibility weaken the photophysical generation of $O_3$ and reduced the level of $O_3$ (Wang et al., 2020; Wu et al., 2016; Zhang et al., 2015b). It should also be noticed that the concentrations of NO were $8.01 \pm 1.00$ $\mu g \text{m}^{-3}$ and $14.4 \pm 28.6$ $\mu g \text{m}^{-3}$ on NCP at PD and DSL, respectively, which were decreased by 78.0% and 69.7% on CP, indicating the increase of $O_3$ levels due to the weak NO titration on CP (Seinfeld, 1989). Therefore, NO levels and RH decreased and the visibility increased highly on CP, which offered favorable atmosphere to form $O_3$. The ratio values of VOC/NO$_x$ (ppbC/ppbv) were $3.02 \pm 1.24$ and $3.70 \pm 1.62$ at PD, and $2.69 \pm 0.961$ and $2.43 \pm 0.957$ at DSL on NCP and CP, respectively, demonstrating that $O_3$ formation was more inclined to be VOC-sensitive (Seinfeld, 1989; Sillman, 1999), which was also in accordance with the results reported in Shanghai (Gao et al., 2017; Geng et al., 2008) and the Pearl River Delta (Li et al., 2020a). Therefore, $O_3$ formation should be paid more attention in the control of VOCs.

### 3.3.2. SOA and SOAP

The concentrations of SOA were $2.83 \pm 1.51$ $\mu g \text{m}^{-3}$ and $4.47 \pm 1.00$ $\mu g \text{m}^{-3}$ at PD, and $3.13 \pm 1.76$ $\mu g \text{m}^{-3}$ and $3.41 \pm 2.08$ $\mu g \text{m}^{-3}$ at DSL during the NCP and CP, respectively. On the whole, the SOA concentrations significantly increased by 57.6% and 8.88% at PD and DSL respectively from NCP to CP ($p < 0.05$). The visibility was generally negatively correlated with the concentrations of SOA on the two periods, especially at DSL ($p < 0.01$), indicating the influences of SOA on the deterioration of visibility. Fig. S13 shows the variation of average data for OC, EC and the relative proportions of SOA to OM under the different levels of fog-haze episodes. On the whole, the concentrations of EC and OC generally increased with the meteorology from clear level to haze-fog events on NCP, which had the maximal growth rates of 249% and 124% at PD, and 215% and 152% at DSL, respectively, highlighting the contribution of primary sources on the formation of haze-fog events (Turpin and Huntzicker, 1995; Xie et al., 2019). By contrast, with the increase of haze-fog pollution level, the EC and OC increased first and then decreased, which has the highest growth rates of 77.8% and 41.0% at PD, and 102% and 103% at DSL, respectively, indicating the decreasing activities of primary sources during the haze-fog events on CP as compared with NCP. Overall, the proportions of SOA to OM averaged 38.3% ± 17.0% and 56.6% ± 10.7% at PD, and 36.1% ± 10.9%, 51.4% ± 11.2% at DSL on NCP and CP, which showed the increasing formation of secondary organic aerosols at both PD at DSL on CP. Moreover, the relative

![Fig. 5. The variation of mean concentrations of VOC species, OFP and $O_3$ on the different levels of fog-haze episodes at PD and DSL on NCP and CP.](image-url)
percentages of SOA to OM displayed the different tendencies along with the levels of fog-haze episodes on the two periods. On NCP, the relative proportions of SOA to OM usually decreased with the fog-haze pollution levels, which showed the declining formation of secondary organic aerosols as the haze-fog pollution level increased. However, the proportions of SOA to OM exhibited a fluctuation trend at PD and a low reduction rate on DSL on CP, indicating the relative strong formation of secondary organic aerosols on the haze-fog events.

The concentrations of SOAP for total 44 VOCs ($\Sigma_{44}$ VOCs) were $996 \pm 813$ µg m$^{-3}$ and $297 \pm 197$ µg m$^{-3}$ at PD, and $1650 \pm 1580$ µg m$^{-3}$ and $356 \pm 237$ µg m$^{-3}$ at DSL on NCP and CP, respectively. Aromatic hydrocarbons contributed over 95 percent to the SOAP of $\Sigma_{44}$ VOCs at both PD and DSL on each period, which indicated that aromatics were the key contributors to the SOAP of VOCs. The similar results were also observed in UK (Derwent et al., 2010), Beijing (Sun et al., 2016), and Wuhan (Hui et al., 2019). For the top ten abundant components to SOAP of $\Sigma_{44}$ VOCs at PD and DSL, they also had the considerable similarities between PD and DSL although the lower level of SOAP was presented in CP. Among these VOC species, toluene, benzene, ethylbenzene, o-xylene averagely accounted for 33.8%, 19.5%, 17.6%, 11.2%, 8.78% and 33.2%, 13.5%, 38.1%, 5.90%, 5.10% of the ambient VOCs at PD, and 36.4%, 17.4%, 12.9%, 11.0%, 7.59% and 31.9%, 10.7%, 36.8%, 7.05%, 3.94% at DSL for NCP and CP, respectively (Table S3), highlighting the relative strong formation of secondary organic aerosols as the haze-fog pollution levels, which showed the declining formation of secondary organic aerosols as the haze-fog pollution level increased.

3.3.3. Sources and abatement of VOCs

The details of source identification of VOCs is described in Supplemental information. Fig. 6a illustrates the relative contributions of five sources to VOCs at PD and DSL on each period. Obviously, vehicle exhaust and fugitive emission from petrochemical industry made the major contributions, accounting for 28.7% and 35.1%, 34.0% and 33.2% of the ambient VOCs at PD, and 45.7% and 22.2%, 36.7% and 30.2% at DSL on NCP and CP, respectively, followed by industrial process, solvent usage, and fuel evaporation. The average concentrations of five sources to VOCs were estimated according to the source profiles from PMF output. As showed in Fig. 6b, the amounts of VOCs from vehicle exhaust, fugitive emission from petrochemical industry and industrial process showed the significant reduction rates of 27.6%, 42.1% and 31.0% at PD, and 60.4%, 32.8% and 69.1% at DSL, respectively. Moreover, the decreases of vehicle exhaust, fugitive emission from petrochemical industry mainly accounted for VOCs abatement from NCP to CP, with the average VOCs amounts of 1.89 ppbv and 3.53 ppbv at PD, and 5.90 ppbv and 1.56 ppbv at DSL, respectively, highlighting the decreasing activities of these emission sources due to the strict regulations on the outbreak control period.

3.4. Impact of regional transport

To evaluate the influence of regional transport on air pollutants, 36-h backward trajectories with 1-h time interval were clustered using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model on NCP and CP (Fig. S16). It was observed that back trajectories of air masses were divided into four clusters on CP: 15% and 14% originated from north-northeast (Cluster 1), 18% and 32% originated from north-northwest (Cluster 2), 39% and 36% originated from northwest (Cluster 3), 28% and 19% originated from south (Cluster 4) for PD and DSL, respectively. Compared with NCP, the percentages of long-distance air mass (Cluster 2) increased and medium-distance air mass (Cluster 1) decreased obviously on CP. The air mass was dominated by Cluster 3 on two periods, passing over Anhui and Jiangsu provinces, reflecting the medium-distance transport of air pollutants. The average data of VOCs, PM$_{2.5}$ and

![Fig. 6. The source contributions of VOCs (a), and the average concentrations of sources estimated from PMF output (b) at PD and DSL on NCP and CP.](image-url)
meteological parameters (T, RH, WS and visibility) corresponding to four trajectory clusters at PD and DSL on NCP and CP are showed in Fig. S17. When the air mass of Cluster 3 prevails, the concentrations of VOCs and PM$_{2.5}$ presented the higher levels and the meteorological conditions were heavily characterized by the low T and WS, which might account for the high frequency of haze-fog and the lower visibility on this trajectory cluster during the NCP and CP. However, due to the serious regional joint control on CP, the clear reductions of PM$_{2.5}$ and VOCs levels and the frequencies of haze-fog events were generally showed on air mass clusters, especially for Cluster 3 with the average rates of 39.0%, 43.9% and 57.5% at PD, and 50.3%, 55.1% and 34.0% at DSL. Thus, such variation of the regional transported air pollutants in conjunction with the emission reduction of local sources resulted in the decreasing occurrence of haze-fog events and increasing visibility at PD and DSL from NCP to CP.

4. Conclusions

This study examined the chemical compositions of PM$_{2.5}$ and VOCs at the urban PD and regional DSL Supersites to investigate the sources variations, abatement mechanisms and regional transport of PM$_{2.5}$ and VOCs in YRD region during the outbreak of COVID-19. The concentrations of PM$_{2.5}$ and VOCs, and the occurrence frequencies of haze-fog events showed the average reduction rates of 31.6%, 38.9% and 35.1% at PD, and 34.5%, 50.7% and 37.9% at DSL, respectively, indicating the substantial reduction of these air pollutants and the improvement of air quality due to the special control measures. The PM$_{2.5}$ mass was dominated by sulfate, nitrate and ammonium. The PMF model identified six potential sources and secondary sulfate & nitrate, heavy oil combustion, and coal & biomass burning presented the higher contributions to PM$_{2.5}$ mass on both NCP and CP, in which secondary sulfate & nitrate was the predominant contributor of PM$_{2.5}$, accounting for 58.0% and 51.9% at PD, and 55.8% and 36.8% at DSL on NCP and CP, respectively. The decrease of secondary formation of sulfate & nitrate highly accounted for PM$_{2.5}$ abatement, with the average masses of 11.7 µg m$^{-3}$ and 19.1 µg m$^{-3}$ from NCP to CP at PD and DSL, respectively. Sulfate and nitrate exhibited a decrease, associated with the decrease in their precursor gases SO$_2$ and NO$_x$, which were mainly attributable to the decreasing activities of coal burning and vehicle exhaust from NCP to CP. Meanwhile, PM$_{2.5}$ masses from coal & biomass burning and crustal sources also had the obvious reduction rates of 31.6% and 19.7% at PD, and 77.1% and 81.2% at DSL, respectively.

On average, alkanes showed the higher concentration levels, but aromatic hydrocarbons and alkenes were the major contributors to OAP and SOAP of VOCs at both PD and DSL. The higher level of O$_3$ was presented on both PD and DSL on CP although them also had the lower OAP of VOCs, which might be attributed to the weak NO titration and advantageous meteorological conditions such as low relative humidity and high visibility on CP. Meanwhile, the higher level of O$_3$ might play a role in the increase of SOA at both PD and DSL on CP. Vehicle exhaust and fugitive emission from petrochemical industry made the major contributions for VOCs, accounting for 28.7% and 35.1%, 34.0% and 33.2% at PD, and 45.7% and 22.2%, 36.7% and 30.2% at DSL on NCP and CP, respectively. Moreover, the decreasing activities of vehicle exhaust and fugitive emission from petrochemical industry mainly accounted for VOCs abatement, with the average VOCs amounts of 1.89 ppbv and 3.53 ppbv at PD, and 5.90 ppbv and 1.56 ppbv at DSL, respectively. Back trajectories analysis showed that the haze-fog pollution was highly impacted by medium-distance transported air masses passing over Anhui and Jiangsu provinces. Due to the stringent regional control, the clear reduction of VOCs and PM$_{2.5}$ levels was generally presented on the air masses on CP. Therefore, the regional control on air pollutants in conjunction with the emission reduction of local sources resulted in the decreasing occurrence of haze-fog events and improving air quality in YRD region from NCP to CP. Therefore, the results demonstrated that YRD region has the significant abatement potentials on PM$_{2.5}$ and VOCs through the strict controls on the activities of coal burning, traffic and fugitive emission from petrochemical industry. This work provided the scientific support to improve the control strategies for regional haze-fog pollution in YRD region, China.

Declaration of competing interest

The authors declare no competing interest.

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Appendix A. Supplementary data

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Authorship Contribution Statement

Haohao Jia: Methodology, Formal analysis, Writing - original draft, Writing - review & editing. Juntao Huo: Methodology, Data curation, Formal analysis, Writing - review & editing. Qingyan Fu: Resources, Data curation, Formal analysis, Writing - review & editing. Yufen Duan: Resources, Data curation, Formal analysis, Writing - review & editing. Xiaodan, Jin: Formal analysis. Xue, Hu: Formal analysis, Jinping Cheng: Conceptualization, Funding acquisition, Supervision, Writing - review & editing.

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