Chemical Characteristics and Potential Sources of PM_{2.5} in Shahe City during Severe Haze Pollution Episodes in the Winter

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ABSTRACT

In recent years, North China has suffered from severe air pollution. Hence, this study performed a comprehensive field experiment during Dec. 2017 in Shahe (114.5°N, 36.85°E), a typical industrial city in this region that is characterized by intensive NO_x emission from the local glassmaking industry. During the study period, the mass concentration of the PM_{2.5} (fine particulate matter) averaged $121.6 \pm 91.8 \mu\text{g m}^{-3}$, whereas the mass concentrations of the nitrate and sulfate in the PM_{2.5} averaged 21.4 ± 16.3 and $15.9 \pm 20.9 \mu\text{g m}^{-3}$, respectively. The high sulfate mass concentration primarily resulted from the oxidation of SO₂, which was mainly due to gas-phase and heterogeneous reactions during low relative humidity (RH; < 40%) and enhanced aqueous reactions during high RH (> 40%). In addition, because the nitrogen oxidation ratio (NOR) increased as the RH decreased during the day, the nitrate was largely generated through photochemical reactions. The mass concentrations of the optical organic carbon (OC), elemental carbon (EC), and water-soluble organic compounds (WSOCs) equaled 50.4 ± 31.1 , 5.8 ± 4.4 , and $12.8 \pm 10.1 \mu\text{gC m}^{-3}$, respectively, and applying the EC tracer method revealed that primary emissions contributed approximately 72% of the total OC. Furthermore, intense industrial activities were detected in a nearby area to the northeast, which potential source contribution function (PSCF) analysis identified as the main potential source area for PM_{2.5} during haze.

Keywords: Air pollution; Chemical composition; North China Plain; Potential source analysis.

INTRODUCTION

In recent decades, China has experienced rapid economic development. However, its success involves vast fossil fuel consumption, which resulted in degraded air quality, including air pollution and water contamination. Regional haze pollution occurs frequently in China and has attracted enormous attention from the public, government, and scientists (Zhang *et al.*, 2015). Long-lasting and large-scale regional haze events imposed a great threat to public health and sustainable economic development. According to recent research, the origin of air pollution in China has gradually shifted from typical coal combustion to a combination of pollution from

fossil fuel combustion, vehicle emission, and industrial discharge. Among the different pollutants of PM_{2.5}, PM₁₀, SO₂, NO₂, O₃, and CO, PM_{2.5} is of particular interest because PM_{2.5} could cause the serious respiratory problem of humans (Lu *et al.*, 2016; Kelley *et al.*, 2020). Airborne particles could also suppress the development of the planetary boundary layer, worsening the regional pollution. The formation of haze is unclear due to the complicated chemistry and feedback mechanisms.

Due to the coupling effects of strong pollutant emissions, unfavorable meteorological conditions and unique topography, the Beijing-Tianjin-Hebei (BTH) region became one of the most seriously polluted regions in China (Cai *et al.*, 2017; Huang *et al.*, 2017; Deng *et al.*, 2018; Huang *et al.*, 2018). Recently, many studies about mass concentration, chemical components, sources of PM_{2.5} in BTH have been reported (Wang *et al.*, 2014; Sun *et al.*, 2019; Xie *et al.*, 2019; Liu *et al.*, 2020a). However, those studies were mainly performed

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in megacities and large cities of BTH, such as Beijing, Tianjin, Shijiazhuang. There are not enough studies related to haze pollution in industrial cities, especially areas characterized as distinct industry in the Hebei Province, limiting our knowledge about haze formation in BTH. The Ministry of Environmental Protection of the People's Republic of China has formulated the scheme of air pollution prevention and control in the BTH region and surrounding areas in 2017 (Feng *et al.*, 2018). Thus, it is urgently necessary to conduct studies on typical industrial cities in Hebei Province, which is an important part of this scheme.

Shahe is a typical industrial city located in the southern Hebei Province, facing serious haze pollution. Shahe is famous for glassmaking and accounts for ~20% of total national glass production. The mean mass concentration of PM_{2.5} in Shahe was 91 $\mu\text{g m}^{-3}$ in 2017 (<http://hbmis.atcloud.cn>), which is approximately 1.57 times that of Beijing. However, very few studies have been pursued to understand the characteristics and formation mechanisms of pollution episodes in Shahe. In this work, a comprehensive field campaign was performed in Shahe. Hourly continuous concentrations of pollutants, including PM_{2.5}, the chemical components, as well as the gaseous pollutants were measured. Based on the observed data, we investigated the characteristics and formation of the haze and studied the impact of pollutant transport in Shahe. Our findings will help to expand the knowledge of haze formation in BTH.

MATERIALS AND METHODS

Description of the Field Campaign

The measurements were conducted from Dec. 14 to Dec. 30, 2017, on the eighth floor of a building (114.52°N, 36.88°E), approximately 28 m above the ground. This site is located north of downtown Shahe city. As shown in Fig. S1(a), NO_x emissions from industrial areas in Shahe and its surrounding cities were intensive. Cities around Shahe, e.g., Xingtai (Xu *et al.*, 2019) and Handan (Meng *et al.*, 2016), are severely polluted as well. A large number of glass factories are located in the northeast of the monitoring site, approximately 5 km away (Fig. S1(c)).

Instruments

Mass concentrations of PM_{2.5} and water-soluble components (e.g., sulfate, nitrate, and water-soluble organic compounds [WSOCs]) were measured using a continuous dichotomous aerosol chemical speciation analyzer (ACSA-12; Kimoto Electric Co., Ltd.) at a time resolution of 1 h and flow rate of 16.7 L min⁻¹ (Pan *et al.*, 2018). The mass concentrations of PM_{2.5}, SO₄²⁻ and NO₃⁻ were detected using the β -ray absorption method, BaSO₄-based method and ultraviolet absorption photometric method, respectively. The mass concentrations of WSOCs were detected using the ultraviolet absorption photometric method as well. The mass concentrations of organic carbon (OC) and elemental carbon (EC) were measured by a particulate carbon analyzer (APC-710; Kimoto Electric Co., Ltd.) at a time resolution of 1 h and a flow rate of 16.7 L min⁻¹. The OC and EC samples were collected on the banded Teflon filter membrane by the

APC-710. Then, the samples were analyzed by near-infrared and ultraviolet light. The mass concentrations of OC and EC were calculated based on the attenuation of transmitted light and reflected light. Mass concentrations of CO, CO₂, and volatile organic compounds (VOCs) were measured by using CA-752 and VOC-770 systems (Kimoto Electric Co., Ltd.) respectively based on non-dispersive infrared methods. CH₄ was measured by a flame ionization detector (FID) using HA-771 (Kimoto Electric Co., Ltd.). All instruments were calibrated for flow before measurement. ACSA-12 was calibrated by a standard solution. ASCA-12 and APC-710 passed blank membrane experiments at a flow rate of 16.7 L min⁻¹. CA-752, VOC-770, and HA-771 were calibrated by corresponding standard reference gas. Routine maintenance and regular calibration on the instruments were performed in the field campaign. More information about data quality assurance/quality control measures of the above instrument has been illustrated in previous studies (Yang *et al.*, 2018, 2019; Ye *et al.*, 2019).

PM₁₀ mass concentration and mixing ratios of SO₂ and NO₂ were collected from a national air monitoring station which was in the same building that the sampling site located (on the sixth floor and approximately 21 m above the ground). Meteorological parameters, including wind direction (WD), wind speed (WS), temperature (T), atmospheric pressure (P), and relative humidity (RH), were measured by the automatic meteorological station. A micro-pulse LIDAR (AGHJ-I; Wuxi CAS Photonics Co., Ltd.) was installed at the monitoring site. The LIDAR had two receiving channels, with a laser wavelength of 532 nm. After range and overlap correction, the LIDAR signals were processed automatically. The LIDAR had a 20 MHz analog-to-digital conversion rate and a 7.5 m vertical resolution. The extinction coefficient of aerosols was retrieved based on the Fernald method (Fernald, 1984).

Backward Trajectory and PSCF Analysis

Backward Trajectory

The HYSPLIT model developed by the U.S. National Oceanic and Atmospheric Administration Air Resources Laboratory (NOAA ARL) was usually employed to identify the potential source regions and transport pathways of air masses (Yang *et al.*, 2017b). 24-h back trajectories, starting at the arrival level of 100 m from the monitoring site (114.52°N, 36.88°E) in Shahe were calculated during the study period. The Final (FNL) Operational Global Analysis data were obtained from the National Centers for Environmental Prediction's Global Data Assimilation System (GDAS) wind field reanalysis (<http://www.arl.noaa.gov/>). The backward trajectory model was run every hour of the day.

Potential Pollution Source Model

The potential source contribution function (PSCF) is widely used to identify the probable locations of emission sources (Ashbaugh *et al.*, 1985; Wang *et al.*, 2009; Peng *et al.*, 2019). The domain being researched is divided into small equal grid cells (*ij*). The PSCF value for each cell can be defined as:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (1)$$

where n_{ij} represents the total number of trajectory endpoints fall in the grid cell (i, j) , and m_{ij} represents the number of trajectory endpoints at the grid cell (i, j) with pollutant concentrations higher than the threshold criterion. In this study, the pollutant is $PM_{2.5}$ and its mass concentration is the threshold criterion. The study domain is in the range of 103° – 120° E, 31° – 51° N, with a spatial resolution of $0.2^{\circ} \times 0.2^{\circ}$. When n_{ij} is 3 times smaller than each grid average number of trajectory endpoints (n_{ave}), an arbitrary weight function $W(n_{ij})$ is multiplied into the PSCF value to reduce the uncertainty in cells (Dimitriou et al., 2015; Liu et al., 2016). The weighted potential source contribution function (WPSCF) is defined below.

$$WPSCF_{ij} = \frac{m_{ij}}{n_{ij}} W(n_{ij}) \quad (2)$$

$$W(n_{ij}) = \begin{cases} 1.00, & 3n_{ave} < n_{ij} \\ 0.70, & 1.5n_{ave} < n_{ij} \leq 3n_{ave} \\ 0.4, & n_{ave} < n_{ij} \leq 1.5n_{ave} \\ 0.17, & n_{ij} \leq n_{ave} \end{cases} \quad (3)$$

Data Analysis

Sulfur and Nitrogen Oxidation Ratio

To evaluate the sulfur and nitrogen oxidation, sulfur oxidation ratio (SOR) and the nitrogen oxidation ratio (NOR) are employed (Yang et al., 2015; Liu et al., 2016), which are defined as:

$$SOR = n\text{-SO}_4^{2-} / (n\text{-SO}_4^{2-} + n\text{-SO}_2) \quad (4)$$

$$NOR = n\text{-NO}_3^- / (n\text{-NO}_3^- + n\text{-NO}_2) \quad (5)$$

where n refers to the molar concentration.

Estimated Mass Concentration of Secondary Organic Carbon

An EC tracer method was employed to estimate the mass concentration of secondary organic carbon (SOC) and primary organic carbon (POC) from the following equation (Cao et al., 2007; Zhao et al., 2013; Zheng et al., 2019):

$$POC = (OC/EC)_{pri} \times EC + b \quad (6)$$

$$SOC = OC - POC \quad (7)$$

where $(OC/EC)_{pri}$ is the OC/EC ratio in primarily emitted combustion aerosols and b represents non-combustion POC. The $(OC/EC)_{pri}$ and b are often determined by regressing the OC and EC concentrations on a fixed percentile of the lowest OC/EC ratio (usually 5–20%; Yao et al., 2016, 2020).

F-factor

F-factor was established to understand the roles

carbonaceous gases and particles had played in haze formation (Yang et al., 2019). F-factor is defined as:

$$F = \frac{S}{G} = \frac{\sum \lg(S_i)}{\sum \lg(G_j)} \quad (8)$$

where S and G refer to the sum of calculated results for solid phase and gaseous phase respectively. S_i includes OC and EC. G_i includes CO_2 , CO, CH_4 , and VOCs. As in the previous study (Yang et al., 2019), the concentrations of each carbonaceous species were converted to the same unit ($\mu\text{gC m}^{-3}$). Wu et al. (2016) reported that all the VOC species could be represented by an equalized molecular formula of $C_{3.51}H_{6.78}O_{0.24}N_{0.02}Cl_{0.31}$ (molecular weight of 62.38). We adopted 62.38 (Yang et al., 2019, also adopted this value) as the molecular weight of VOCs.

RESULTS AND DISCUSSION

Overview of the Haze Pollution Period

General Description

The temporal variations in the mass concentrations of the $PM_{2.5}$ chemical composition, the meteorological parameters and the aerosol extinction coefficient are displayed in Fig. 1. The mean mass concentrations of $PM_{2.5}$ over the whole study were $121.6 \pm 91.8 \mu\text{g m}^{-3}$, which was almost 1.6 times the second grade of Chinese National Ambient Air Quality Standards ($75 \mu\text{g m}^{-3}$, an average of 24 h). The average mass concentrations of NO_3^- and SO_4^{2-} were $21.4 \pm 16.3 \mu\text{g m}^{-3}$ and $15.9 \pm 20.9 \mu\text{g m}^{-3}$, respectively. The mean mass concentrations of CO_2 were $968.0 \mu\text{g m}^{-3}$. The average concentrations of VOCs observed in this study (195.9 ppbC) were much higher than that of Beijing (151.3 ppbC) (Yang et al., 2019), suggesting that there were stronger VOC emissions in Shahe. Besides, the dominant wind was northern, with a frequency of 74.5%. The mean wind speed was 1.6 m s^{-1} , which was not favorable for the diffusion of pollutants. It has been reported that relative humidity plays an important role in haze formation (Pathak et al., 2009; Liu et al., 2013; Cheng et al., 2016). A positive correlation between RH and $PM_{2.5}$ concentrations ($r = 0.7$, $p < 0.01$) was found in this study. When the mass concentration of $PM_{2.5}$ was above $75 \mu\text{g m}^{-3}$ continuously, the period was considered to be a haze episode. Combining the profiles of the aerosol extinction coefficient (Fig. 1(h)) and the $PM_{2.5}$ variations (Fig. 1(a)), three different pollution episodes (gray shadows in Fig. 1) were selected for the further study: EP-I (11 a.m. on Dec. 14 to 5 a.m. on Dec. 16, 2017), EP-II (3 a.m. on Dec. 21 to 2 a.m. on Dec. 24, 2017) and EP-III (9 a.m. on Dec. 25 to 4 p.m. on Dec. 30, 2017). EP-I was a short-term pollution episode that occurred for approximately two days. In EP-I, RH was continuous at a high level with a mean value of $79.4 \pm 14.8\%$, and the mass concentrations of $PM_{2.5}$ increased from 93 to $382 \mu\text{g m}^{-3}$ in 37 hours. In EP-II, the average RH was $38 \pm 9\%$, and the $PM_{2.5}$ mass concentrations varied less than in EP-I and EP-III (the standard deviation of $PM_{2.5}$ concentration in EP-I, II, III was 72.3 , 44.1 , and $99.5 \mu\text{g m}^{-3}$ respectively). EP-III, a long pollution episode, lasted approximately

Fig. 1. Time series of observed (a) particulate matter; (b) NO_2 , SO_2 , sulfate, and nitrate; (c) CO and CO_2 ; (d) VOCs and CH_4 ; (e) OC, EC, and WSOCs; (f, g) meteorological parameters; and (h) vertical profiles of aerosol extinction coefficient in Shahe from Dec. 14 to Dec. 30, 2017. The red horizontal dashed line in (a) represents the second grade of the Chinese National Ambient Air Quality Standards for $\text{PM}_{2.5}$.

five days. During EP-III, RH and $\text{PM}_{2.5}$ mass concentrations increased slowly but steadily in general. There were clean periods (CPs) with a mean $\text{PM}_{2.5}$ mass concentration of $17.5 \mu\text{g m}^{-3}$ (blue shadows in Fig. 1).

Chemical Composition of $\text{PM}_{2.5}$

As shown in Fig. 2(a), secondary inorganic aerosols (NO_3^- and SO_4^{2-}) accounted for $30.2 \pm 10.1\%$ of the $\text{PM}_{2.5}$ on an average for the whole observation period. During the haze episodes (when $\text{PM}_{2.5}$ mass concentrations were more than $75 \mu\text{g m}^{-3}$), the average mass fractional contribution of NO_3^- and SO_4^{2-} to $\text{PM}_{2.5}$ was $18.1 \pm 4.2\%$ and $11.8 \pm 6.9\%$, respectively. In Beijing due to the vehicles increasing and the coal use controlling, the mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ in winter decreased from 2010 at 1.2 (Zhao et al., 2013) to 2015 at 1.43 (Zhang et al., 2018). In this study, $\text{NO}_3^-/\text{SO}_4^{2-}$ was on an average of 2.0 ± 1.3 (Fig. 2(b)). We inferred that the high value of $\text{NO}_3^-/\text{SO}_4^{2-}$ observed in Shahe was due to intense NO_x emission from industrial sources rather than from vehicles. As depicted in Fig. 2(c), the average values of SOR and NOR during the whole study were 0.19 ± 0.19 and 0.17 ± 0.09 , respectively. Previous studies reported that when SOR and NOR were greater than 0.1, SO_4^{2-} and NO_3^- mainly came from the secondary transformation of SO_2 and NO_2 respectively, rather than primary source emissions

(Yao et al., 2002; Fu et al., 2008; Zhang et al., 2011). This suggested SO_4^{2-} and NO_3^- mainly came from the secondary transformation in Shahe city. As listed in Table 1, SOR value varied greatly in North China in winter. The SOR value in Shahe city (0.19) was lower than observed in Beijing (0.20 in 2014 and 0.27 in 2015) but much higher than that of Handan (approximately 30 km away from Shahe) with 0.10 and Shijiazhuang (the capital city of Hebei Province) with 0.15. This indicated that the secondary formation of sulfate in Shahe was more intensive than its surrounding cities. The NOR value in Shahe (0.17) was similar to that of Handan (0.20) and Beijing (0.20 in 2014 and 0.17 in 2015) and higher than that of Shijiazhuang (0.14). The SOR value varied more than NOR value in North China, which indicated the secondary formation of sulfate was more easily affected by some factors, e.g., weather conditions, anthropogenic emissions. Although the oxidation ratios of sulfur and nitrogen were similar in Shahe, the mass concentration of NO_2 was approximately 1.9 times that of SO_2 , which resulted in a much higher mass concentration of NO_3^- than that of SO_4^{2-} . EC is a primary pollutant that comes from biomass and fossil fuel combustion sources, and OC is a mixture of several particulate organic compounds containing polycyclic aromatic hydrocarbons and other hazardous components (Zhao et al., 2013; Boreddy et al., 2018). The average concentrations of OC, EC and

Fig. 2. Time series of (a) the mass fraction of secondary inorganic aerosols, (b) SO_2/NO_2 and $\text{NO}_3^-/\text{SO}_4^{2-}$, (c) SOR and NOR, and (d) OC/EC and WSOCs/OC from Dec. 14 to Dec. 30, 2017, in Shahe.

Table 1. Comparisons of SOR and NOR in the winter of North China.

Study time	City	Site	SOR	NOR	Reference
Feb. 10–Mar. 19, 2015	Beijing	urban	0.27 ± 0.2	0.17 ± 0.08	Zhang <i>et al.</i> (2018)
Winter 2014 and 2015	Handan	urban	0.10	0.20	Meng <i>et al.</i> (2016)
Winter 2014	Beijing	urban	0.20	0.20	Liu <i>et al.</i> (2016)
Winter 2014–2016	Shijiazhuang	urban	0.15	0.14	Xie <i>et al.</i> (2019)
Dec. 14–30, 2017	Shahe	urban	0.19 ± 0.19	0.17 ± 0.09	This study

WSOCs observed in this study were 50.4 ± 31.1 , 5.8 ± 4.4 and $12.8 \pm 10.1 \mu\text{gC m}^{-3}$ respectively, which were all much higher than that of Beijing in the winter of 2016 (Yang *et al.*, 2019). This suggested more intensive anthropogenic emissions of OC and EC in Shahe than in Beijing.

Investigation of Characteristics and Formation of Haze Oxidation of Sulfur and Nitrogen in Haze Episodes

The mass concentrations of pollutants varied greatly in different episodes. As listed in Table S1, the mass concentration of $\text{PM}_{2.5}$ in the haze episode was approximately 10 times that in the clean period. The NOR and SOR in the haze episode were approximately 4 and 2 times that in the clean period, respectively, which suggested that the secondary transformations of SO_2 and NO_2 were more intense. In EP-II, with the lowest RH among the three haze episodes, the mean mass concentration of NO_3^- was much higher than SO_4^{2-} and the mean NOR was also much higher than SOR. This suggested that the formation of nitrate was

more intensive than sulfate in low RH. The mean RH and wind speed were $19.9 \pm 4.5\%$ and $2.9 \pm 1.4 \text{ m s}^{-1}$ in CPs, respectively, which suggested that lower RH and stronger wind were effective in reducing pollution.

Severe secondary oxidation of SO_2 was found in the haze episodes. When RH was less than 20% (Fig. 3(a)), a high sulfate mass fraction in $\text{PM}_{2.5}$ was found in this study. As shown in Fig. S2, when RH was 0–20%, a high ratio of $\text{SO}_4^{2-}/\text{PM}_{2.5}$ was mainly found under the weak northeastern wind ($< 2 \text{ m s}^{-1}$). This suggested that the local sulfate from the northeastern sampling site caused the high mass fraction of SO_4^{2-} . When RH was under 40%, a negative correlation between SOR and RH was found ($r = -0.15$, $p < 0.01$) in this study. Oxidation pathways of SO_2 include gas-phase reactions with OH radicals or stabilized Criegee intermediates, heterogeneous-phase reactions on the surface of particles, and aqueous-phase reactions with dissolved O_3 , NO_2 , H_2O_2 , and organic peroxides (Liu *et al.*, 2020b). In Shahe, the gas-phase reactions and heterogeneous reactions were probably

the main oxidation pathways of SO_2 in low RH. When RH was above 40% (Fig. 3(a)), SOR increased sharply in this study, which was also found in previous studies (Liu *et al.*, 2019; Liu *et al.*, 2020b). When RH was above 40%, we found the correlation between SOR and RH was strong positive ($r = 0.87$, $p < 0.01$) in this study. This suggested that SO_2 oxidation related to aqueous was enhanced. In high RH, SO_4^{2-} mainly came from the aqueous oxidation of SO_2 due to aerosol water content and surface area increase (Zhang *et al.*, 2015). When RH was 40–60% and above 60% (Fig. 3(a)), the mean SOR value was 0.14 and 0.50, respectively. This indicated that certain potential mechanisms can promote SOR in high RH. When in high RH ($> 60\text{--}70\%$), the trapped SO_2 by aerosols can be oxidized by NO_2 to form sulfate (Cheng *et al.*, 2016; Wang *et al.*, 2016). During 11 a.m. to 8 p.m. LST, RH was under 40% mostly and showed an opposite diurnal trend as SOR (Fig. S3). Thus, we deduced the gas-phase reactions and heterogeneous reactions dominate in this period. During 0 a.m. to 11 a.m. LST (Fig. S2), aqueous oxidation of SO_2 dominated.

As shown in Fig. 3(c), NOR increased with RH ($r = 0.86$, $P < 0.01$). The average NOR was 0.13 at RH of 20–40%, which suggested the secondary transformation of NO_2 in low RH was less important. Generally, the aqueous reactions

will be enhanced with increasing RH. During the daytime in Shahe, RH decreased continuously due to the heating of the sun, but NOR increased (Fig. S3). This suggested that aqueous reaction was not the main mechanism of nitrate formation during the daytime. Instead, nitrate formation is controlled by photochemical production (Ye *et al.*, 2019). At night when photochemical production was poor, nitrate was mainly produced by the hydrolysis of N_2O_5 and gas-particle partitioning (Yang *et al.*, 2017a; Zhang *et al.*, 2018).

Formation and Sources of the Carbonaceous Component

As shown in Fig. 4(a), a strong relationship between OC and EC was found in the four study periods, indicating that OC and EC had similar sources. The lower $\text{PM}_{2.5}$ concentrations were, the stronger the relationship between OC and EC. The ratio of OC to EC is an important indicator that reflects the source type and transformation characteristics (Ji *et al.*, 2019). It has been reported that the OC/EC ratios from vehicle emissions, residential coal combustion, and biomass burning are 1.1–5.0, 8.5–12, and 4.3–80, respectively (Cao *et al.*, 2007; Sandradewi *et al.*, 2008; Ji *et al.*, 2019). In this study, the average OC/EC value was 8.5–9.3 in the four periods, indicating that carbon aerosols mainly came from coal combustion and biomass burning. In this study, to

Fig. 3. (a) SOR and $\text{SO}_4^{2-}/\text{PM}_{2.5}$ under different RH levels. (b) SOR and RH in clean periods and three pollution episodes. (c) NOR and $\text{NO}_3^-/\text{PM}_{2.5}$ under different RH. Median (central horizontal bar within the boxes), 25th and 75th percentiles (lower and upper bars of the boxes), and minimum and maximum (lower and upper whiskers).

estimate the concentration of SOC, 40 samples with the lowest OC/EC ratios were used to calculate $(OC/EC)_{pri}$ and b (Fig. 4(a)). The mean concentration of the estimated SOC was $15.5 \pm 10.7 \mu\text{g C m}^{-3}$. The average SOC/OC value was 27.6% in this study, indicating that OC mainly came from the primary emission in Shahe. The SOC/OC was 10.2% in the clean period and increased to 27% in haze episodes, suggesting enhanced secondary formation processes. Sources of WSOCs are complex, which can be directly from combustion, industrial, and natural sources (primary) and/or formed through secondary processes such as homogeneous gas-phase and/or heterogeneous aerosol-phase oxidation (secondary) (Tang *et al.*, 2016). As listed in Table 2, in this study WSOC/OC value in Shahe was much lower than other cities of North China. We inferred that the intensive emissions from industry caused the low value of WSOCs/OC. Additionally, the correlation between WSOCs and SOC was weak (Fig. S4), which indicated more influences from primary sources. WSOCs correlated better with SOC in the day ($r^2 = 0.16$) than that at night ($r^2 = 0.04$) because reactive photochemical reactions were stronger at day. Low ratios of SOC/OC and WSOCs/OC also suggested that the observation

site was not far from the emission sources.

Conversion of Carbonaceous Gases to Particles

In this study, the F -factor (mode: 0.3; Fig. S5(a)) was much higher than observed in the winter of Beijing (mode: 0.17) (Yang *et al.*, 2019). This indicated primary emissions of particulate carbon in Shahe was more intensive than in Beijing. In the day, with the temperature raised (Fig. S5(b)), semi-volatile species were more likely to exist as gases, which led to a decrease of F -factor. An obvious positive correlation between $\text{PM}_{2.5}$ concentrations and F -factor was found in this study (Fig. 5(a)). The higher F -factor in more serious haze indicated that (1) more carbonaceous particles were emitted than carbonaceous gases (Yang *et al.*, 2019), and (2) the conversion of carbonaceous gases to particles was more intensive. When RH was 0–60% (Fig. 5(b)), the F -factor increased with the raising of RH and SOC/OC ratio increased, indicating that chemical processes that strengthened the conversion of carbonaceous gases to particles were active. When RH was above 60% (Fig. 5(b)), SOC/OC ratio and F -factor had an opposite variation trend, which suggested that the higher F -factor could be ascribed to greater

Fig. 4. (a) Scatter plot of OC and EC concentrations in the $\text{PM}_{2.5}$ at Shahe. (b) Values of WSOCs/OC, SOC/OC, and OC/EC in clean and haze episodes.

Table 2. Typical values of WSOCs/OC in the winter of North China.

Date	Site	WSOCs/OC (%)	Reference
Winter 2017	Shandong, China	63	Luo <i>et al.</i> (2020)
January–April 2014	Tianjin, China	67	Wen <i>et al.</i> (2018)
2010–2011	Beijing, China	52	Tang <i>et al.</i> (2016)
2015–2016	Qingdao, China	60	Ding <i>et al.</i> (2019)
Winter 2017	Shahe, China	28	This study

Fig. 5. (a) *F*-factor variation with different PM_{2.5} concentrations. (b) Box plots of SOC/OC and *F*-factor under different RH. Median (central horizontal bar within the boxes), 25th and 75th percentiles (lower and upper bars of the boxes), and minimum and maximum (lower and upper whiskers).

emissions of primary aerosols, rather than gas-particle conversion. When RH was 40–80%, the *F*-factor increased slowly, which was not similar to that observed in the winter of Beijing (the *F*-factor increased sharply) (Yang *et al.*, 2019), indicating the different haze formation mechanisms between Beijing and Shahe.

Sources of Air Pollutants

Local Sources

As shown in Figs. 6(a) and 6(c), the mass concentrations of PM_{2.5} and NO₂ were enhanced when the northeasterly wind was experienced at the site, which suggested there were strong sources of pollution in the northeast of the observation site where dozens of glass factories gathered. As for SO₂ (Fig. 6(b)), the high mass concentrations were influenced mainly by the west wind, which might be caused by coal combustion from residential areas. VOCs, NO₃[−] and SO₄^{2−} displayed similar distribution characteristics (Figs. 6(d), 6(e) and 6(f)). The high concentrations mainly appeared under the northeast wind, which indicated the observation site could be influenced by pollutant emissions from industries. The polar plots of OC (Fig. 6(g)) and EC (Fig. 6(h)) showed concentration hotspots under the weak northerly wind, which are different than the polar plot features of NO₃[−] and SO₄^{2−}. This indicated that the sources of OC and EC were different from NO₃[−] and SO₄^{2−}. High mass concentrations of PM_{2.5}, SO₂ and NO₂ appeared at weak winds with speeds of 0–3 m s^{−1}.

Pollution Transmission

As shown in Fig. 7(a), all trajectories in the study period were divided into three groups, C1, C2 and C3, which accounted for 46.1%, 19.9% and 34.1%, respectively. Cluster C1, a short-distance transport, originated in Shijiazhuang and passed through Xingtai city. Cluster C2 started from southern Inner Mongolia and passed through Shanxi Province. When air masses came from directions C1 and C2, the mass concentrations of pollutants were relatively high

(Fig. 7(b)). Cluster C3, which had a long transport across Inner Mongolia and northern Shanxi Province before arriving in Shahe, corresponded to clean air observed in Shahe. There was a negative correlation between the PM_{2.5} concentration and the air mass transport distance (Table 3), with the minimum value in C1 ($r = -0.4$, $p < 0.01$). In C1 and C2, WSOCs/OC was negatively correlated with air mass transport distance. These results suggest that Shahe city may be influenced by pollutant transmission originating in the short distance.

The PSCF model was employed to identify the potential source areas for PM_{2.5} in Shahe. When the PM_{2.5} concentration was greater than 35 μg m^{−3} (Fig. 8(a)), the cells with high WPSCF values were mainly near Shahe and the surrounding area. With the increase in PM_{2.5} concentrations (Fig. 8), the cells with high WPSCF values visibly decreased, indicating the reduction of strong potential source areas. In all cases, Shahe was a strong potential source area for its PM_{2.5}.

CONCLUSIONS

This study investigated the evolution of haze in Shahe from Dec. 14 till Dec. 30, 2017, to identify the pollution characteristics and sources. Comprehensive measurements of the aerosols and the relevant gaseous pollutants, as well as the meteorological conditions, were conducted at the urban atmospheric environment monitoring station in Shahe. The mean mass concentration of the PM_{2.5} was 121.6 ± 91.8 μg m^{−3}, and the maximum concentration was 510.0 μg m^{−3}. The average concentrations of the nitrate and sulfate components were 21.4 ± 16.3 and 15.9 ± 20.9 μg m^{−3}, respectively, accounting for 17.9% and 12.3% of the PM_{2.5}.

NO₂ and SO₂ oxidation, with average oxidation ratios of 0.17 ± 0.09 and 0.19 ± 0.19, respectively, and discovered that the pathway of the latter depended on the RH. When the RH was low (< 40%), SO₂ oxidation was mainly driven by gas-phase and heterogeneous reactions. When the RH was high (> 40%), however, enhanced aqueous reactions became

Fig. 6. Dependence of mass concentrations of (a) $PM_{2.5}$, (b) SO_2 , (c) NO_2 , (d) VOCs, (e) NO_3^- , (f) SO_4^{2-} , (g) OC, and (h) EC on the wind speed and direction from Dec. 14 to Dec. 30, 2017, in Shahe.

Fig. 7. (a) Analytical results of back trajectory clusters and (b) mass concentrations of pollutants under different clusters during observation periods.

Table 3. Spearman correlation coefficients of PM_{2.5}, WSOCs/OC, and NO₃[−]/SO₄^{2−} with transport distance (km), RH, air temperature (°C), wind speed (m s^{−1}), and pressure (Pa) under different back trajectory clusters.

Cluster		D ^a	RH	T ^b	WS ^c	P ^d
C1	PM _{2.5}	−0.40	0.47	−0.12	−0.07	−0.03
	WSOCs/OC	−0.46	0.32	0.30	0.12	−0.32
	NO ₃ [−] /SO ₄ ^{2−}	0.22	−0.49	0.01	−0.03	−0.08
C2	PM _{2.5}	−0.16	0.74	−0.56	−0.21	0.17
	WSOCs/OC	−0.62	0.30	0.24	0.07	−0.06
	NO ₃ [−] /SO ₄ ^{2−}	0.40	−0.56	0.38	0.16	−0.49
C3	PM _{2.5}	−0.31	0.84	−0.24	−0.43	−0.06
	WSOCs/OC	0.06	0.18	0.43	0.15	−0.30
	NO ₃ [−] /SO ₄ ^{2−}	−0.17	0.06	−0.17	−0.35	0.22

^a Transport distance.^b Air temperature.^c Wind speed.^d Pressure. **Fig. 8.** Results of PSCF analysis for PM_{2.5} under different concentration thresholds from Dec. 14 to Dec. 30, 2017, in Shahe: (a) PM_{2.5} concentration $\geq 35 \mu\text{g m}^{-3}$, (b) PM_{2.5} concentration $\geq 75 \mu\text{g m}^{-3}$, (c) PM_{2.5} concentration $\geq 150 \mu\text{g m}^{-3}$, and (d) PM_{2.5} concentration $\geq 250 \mu\text{g m}^{-3}$.

dominant. Additionally, the nitrate largely arose from photochemical reactions during the day but exhibited a different formation mechanism at night.

The OC, EC, and WSOC mass concentrations were 50.4 ± 31.1 , 5.8 ± 4.4 , and $12.8 \pm 10.1 \mu\text{gC m}^{-3}$, respectively, and the SOC mass concentration was estimated using the EC tracer method, which revealed that primary emissions contributed approximately 72% of the total OC. Secondary OC formation potentially increased the gas-to-particle conversion

of carbonaceous species when the RH was 60% or less, but larger primary aerosol emissions played a greater role in determining the *F*-factor when the RH exceeded 60%.

Back trajectories demonstrated the influence of pollutants arriving in Shahe from a nearby area, which potential source contribution function (PSCF) analysis identified as the main potential source area for PM_{2.5} during haze. However, the cities surrounding Shahe also contributed to the high PM_{2.5} concentrations. Thus, measures such as reducing gaseous

precursor emissions, promoting clean energy use, and collaborating on a regional scale are necessary to improve the air quality.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2020.03.0124>

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