Comparison of PM_{2.5} Chemical Compositions during Haze and Non-haze Days in a Heavy Industrial City in North China

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ABSTRACT

This study aimed to determine the chemical composition, sources and contributing factors of airborne PM_{2.5} (particulate matter with an aerodynamic diameter $\leq 2.5 \mu\text{m}$) during a haze episode in Zibo, a heavy industrial city in China. Samples of PM_{2.5} were collected 8–27 January 2018 and analyzed for water-soluble inorganic ions (WSIs), trace elements (TEs), organic carbon (OC) and elemental carbon (EC). The PM_{2.5} concentration was 76.78% higher during the haze (mean $\pm$ standard deviation [SD] = $211 \pm 39 \mu\text{g m}^{-3}$) than before it ($49 \pm 38 \mu\text{g m}^{-3}$), and the dominant ions were NO_3^- , SO_4^{2-} and NH_4^+ . Additionally, an elevated TE concentration was observed during the episode (exceeding the pre- and post-haze values by 54.70% and 31.98%, respectively), with crustal elements (K, Al, Ca, Si, Na, Fe and Mg), the most abundant elemental components, accounting for 88.64%. Carbonaceous species (OC and EC) contributed 15.45% of the PM_{2.5} on haze days and slightly more on non-haze days. The $\text{NO}_3^-/\text{SO}_4^{2-}$ and OC/EC ratios indicated that coal combustion and motor vehicle emission were the primary sources of pollution, and back-trajectory analysis revealed that the air masses over Zibo on haze days mainly originated in adjacent areas in Shandong Province and the Beijing-Tianjin-Hebei region (BTH). The haze episode was caused by a combination of unfavorable meteorological conditions, secondary formation, the accumulation of local pollutants, and peripheral transmission.

Keywords: Chemical composition; PM_{2.5}; Haze episode; Heavy industrial city.

INTRODUCTION

With the development of large-scale industrialization and accelerated urbanization, China has experienced rapid economic growth (Ji *et al.*, 2014). Meanwhile, China is facing serious air pollution issues. Particulate matter pollution is one of the most urgent problems to be solved, especially in developed megalopolises, which are severely affected by emissions from industry, motor vehicle exhaust and other urban air pollution sources. Suspended particulate matter with an aerodynamic diameter $\leq 2.5 \mu\text{m}$ (PM_{2.5}) is of great significance because of its unique physical and chemical

characteristics (Taghvaei *et al.*, 2019). Previous studies have shown that PM_{2.5} is a major cause of haze and can scatter and absorb sunlight, reduce atmospheric visibility and increase radiation forcing, leading to global climate change and harm to ecosystems and human health (Menon *et al.*, 2002; Chan and Yao, 2008; Yang *et al.*, 2011; Gens *et al.*, 2014; Lin *et al.*, 2014; Tan *et al.*, 2016; Zou *et al.*, 2017; Joharestani *et al.*, 2019).

Many studies have been done on the chemical characteristics and source apportionment of PM_{2.5} worldwide (Tan *et al.*, 2016, 2017; Turap *et al.*, 2019). The chemical composition of PM_{2.5} is very complicated, and mainly includes organic substances, water-soluble inorganic salts, carbonaceous substances, trace elements, water, mineral dust, acidic substances, heavy metals and polycyclic aromatic hydrocarbons (PAHs) (Turpin and Lim, 2001; Tao *et al.*, 2017b; Zou *et al.*, 2017). As the chemical composition of PM_{2.5} is complex and diverse, it has become increasingly important to conduct an in-depth study on it and determine the key information necessary for effective emission reduction (Taghvaei *et al.*, 2019).

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Though the overall air quality has improved significantly in China, serious air pollution issues still occur frequently in heavy industrial cities in China. However, few studies have focused on the chemical composition of PM_{2.5} before, during and after haze episodes in such cities. With the development of industry, air pollution in this region has become quite serious (Zhang *et al.*, 2018). However, few studies have focused on the chemical composition of PM_{2.5} in this area, especially during haze episodes.

Zibo is a heavy industrial city upwind of the Beijing-Tianjin-Hebei region (BTH). Serious pollution occurs in winter (Li *et al.*, 2017), so there is an urgent need to learn more about the characteristics of PM_{2.5} pollution. Monitoring data show that the annual average PM_{2.5} concentrations in Zibo in 2015, 2016, 2017 and 2018 were 88 $\mu\text{g m}^{-3}$, 74 $\mu\text{g m}^{-3}$, 63 $\mu\text{g m}^{-3}$ and 55 $\mu\text{g m}^{-3}$, respectively, which all exceed the national annual secondary standard (35 $\mu\text{g m}^{-3}$). Zibo is often listed as one of the top ten most polluted cities in China, especially in winter (Li *et al.*, 2017; Luo *et al.*, 2018). Zibo is a typical heavy industrial city with petrochemical, ceramics, pharmaceutical, and building material industries (Li *et al.*, 2017; Luo *et al.*, 2018). It is undeniable that these industries produce a great deal of pollution.

In this study, the chemical composition of PM_{2.5} was studied before, during and after a haze episode, and the causes of the haze episode are discussed. PM_{2.5} samples and meteorological data were collected and systematically analyzed. This study increases our understanding of the chemical composition of PM_{2.5} during haze episodes and provides a scientific basis for the prevention and control of atmospheric pollution in such heavy industrial cities.

METHODS

Sample Collection

Zibo is located in the central part of Shandong Province,

China. It covers an area of 5965 km² and has a population of about 4.32 million. Zibo has a warm temperate continental monsoon climate with northwesterly, westerly and southwesterly winds dominating in winter (Luo *et al.*, 2018). There were more than 1.237 million vehicles in Zibo in 2018 (*Statistical Communiqué of Zibo on the 2018 National Economic and Social Development*). There is diverse terrain with mountains in the southern, eastern and western regions and low land to the north. A central depression in the north is not conducive to the spread of air pollutants.

Air quality will be recorded as *polluted* when it exceeds the Grade II limit (75 $\mu\text{g m}^{-3}$) for daily average PM_{2.5} concentration stipulated by the Chinese National Ambient Air Quality Standard (GB 3095-2012). A *haze episode* is defined here as a weather phenomenon with horizontal visibility of ≤ 10 km, relative humidity (RH) of $\leq 90\%$ (Wu *et al.*, 2007), and a daily PM_{2.5} concentration of $> 75 \mu\text{g m}^{-3}$ for ≥ 5 days. There was a haze episode from 15–21 January 2018 in Zibo. Atmospheric PM_{2.5} samples were collected on 8–27 January 2018. The sampling site was approximately 6 m above the ground on the second rooftop of the Nanding Ambient Air Quality Monitoring Station, Zhangdian District, Zibo (36°48'10.67"N, 118°01'28.19"E) (Fig. 1). The sampling site was surrounded by residential and administrative agencies and located about 50 m from Xincun Road, with no other obvious sources of pollution. The sampling time was from 10:00 a.m. on the first day to 9:00 a.m. on the second day. Daily PM_{2.5} samples were collected with a Teflon filter (diameter = 47 mm; Whatman, USA) and a quartz filter (diameter = 47 mm; Pall, USA) at a flow rate of 16.7 L min⁻¹ by a particulate sampler with two parallel channels (ZR-3930; Zhongrui Inc., China).

Before sampling, the quartz filters were baked in a muffle furnace at 550°C for 4 hours to remove carbonaceous pollutants. Before and after sampling, the filters were balanced under constant temperature ($20 \pm 1^\circ\text{C}$) and humidity ($50 \pm$

Fig. 1. Location of the sampling site in Zibo.

5%) for over 24 hours and weighed using an automatic filter weighing system (AWS-1; Comde-Derenda GmbH, Germany). The difference between two consecutive measurements was not more than 5 µg. After sampling, the filters were stored at −20°C until analysis to prevent volatilization of volatile components (Xiao *et al.*, 2014).

Chemical Analysis

One quarter of each quartz filter was extracted via ultrasonication to analyze the concentration of water-soluble inorganic ions (WSIs). The sample was added to 10 mL of deionized water and sonicated for 20 minutes, centrifuged for 5 minutes, and then filtered through a microporous membrane (pore size = 0.45 µm; diameter = 25 mm). The concentrations of six anions (F^- , Cl^- , NO_2^- , NO_3^- , $C_2O_4^{2-}$ and SO_4^{2-}) and five cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) were analyzed by ion chromatography (Dionex ICS-1100; Thermo Fisher Scientific, USA) (Wang *et al.*, 2005; Yang *et al.*, 2017).

In order to analyze the concentration of elements, each Teflon filter was divided into two parts, which were separately dissolved in acid and alkali solution (Kong *et al.*, 2010). The elements Li, Be, Na, P, K, Sc, As, Rb, Y, Mo, Cd, Sn, Sb, Cs, La, V, Cr, Mn, Co, Ni, Cu, Zn, Ce, Sm, W, Tl, Pb, Bi, Th and U were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; 7500a; Agilent, USA), while the elements Zr, Al, Sr, Mg, Ti, Ca, Fe, Ba and Si were analyzed by an inductively coupled plasma optical spectrometer (ICP-OES; Agilent, USA).

The thermal/optical reflectance (TOR) carbon analysis method was used based on the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol (Chow *et al.*, 2004; Yang *et al.*, 2017). The Desert Research Institute (DRI) Model 2001A was used for analysis. An area of 0.5 cm² was punched from each filter sample and analyzed for organic carbon (OC) in a helium (He) atmosphere and elemental carbon (EC) in a 2% O₂/98% He atmosphere. In this process, the pyrolytic carbon was identified by reflected laser (Tao *et al.*, 2017b; Turap *et al.*, 2019). The method detection limits (MDLs) of OC and EC were 0.81 µgC cm⁻² and 0.12 µgC cm⁻², respectively.

Quality Assurance and Quality Control

All analytical processes were conducted under strict quality assurance (QA) and quality control (QC) to avoid any possible pollution. Before and after sampling, as well as during compositional analysis, the quartz filters were confirmed to be intact, and broken filters were excluded. The background was regularly monitored by blank testing, which was used to verify and correct the corresponding data (Turap *et al.*, 2019).

RESULTS AND DISCUSSION

Mass Closure and Concentration of PM_{2.5}

Six conventional pollutants (O₃, CO, SO₂, NO₂, PM₁₀ and PM_{2.5}) and meteorological parameters (wind direction [WD], wind speed [WS], visibility, relative humidity [RH] and temperature [T]) were recorded simultaneously at Nanding Ambient Air Quality Monitoring Station near the sampling site. Table 1 shows a summary of the mass concentrations of PM_{2.5} and average meteorological parameters in sampling periods. Fig. 2 shows the time series of WS, WD, visibility, T and RH, and six conventional pollutants over the sampling period. The daily concentrations of PM_{2.5} were 20–129 µg m⁻³, 147–256 µg m⁻³, and 39–124 µg m⁻³ before, during, and after the haze episode, respectively, with means ± standard deviations (SDs) of 49 ± 38 µg m⁻³, 211 ± 39 µg m⁻³ and 58 ± 33 µg m⁻³. The concentration of PM_{2.5} was 76.78% higher during the haze episode than before it. The highest PM_{2.5} value was 256 µg m⁻³ on 19 January, which may be related to low WS (1.57 m s⁻¹), high RH (62.21%) and T (2.83°C). In contrast, the minimum value of PM_{2.5} was 20 µg m⁻³ on 10 January, which may be related to high WS (1.98 m s⁻¹), low (RH 27.33%) and T (−4.4°C).

PM_{2.5} concentrations were strongly affected by meteorological parameters such as wind direction, wind speed, temperature and RH. At low wind speeds, the atmosphere tends to stabilize and spread slowly and discharged contaminants easily accumulate, resulting in a higher concentration of particulate matter (Zhang *et al.*, 2007). Lower wind speeds might inhibit the dispersion of pollutants in vertical and horizontal directions, while higher temperatures and RH promote gas-to-particle conversion and generate secondary aerosols (Wang *et al.*, 2018). Using SPSS Statistics 22.0 software, the correlations between PM_{2.5} concentration and meteorological parameters were analyzed (Table 2). PM_{2.5} was significantly negatively correlated with wind speed and visibility, and positively correlated with RH and temperature. Similar results have been found by previous investigations (Li *et al.*, 2017).

In order to ensure data quality, the method proposed by Wang *et al.* (2016) was used to reconstruct the PM_{2.5} mass from measurements of mineral dust, organic matter (OM), EC, trace elements, water-soluble inorganic ions and other chemical substances. The OM mass was calculated by multiplying the OC mass by a factor of 1.6 (Wang *et al.*, 2016). The mass closure is shown in Fig. 3. There was a significant correlation between the measured and reconstructed PM_{2.5} masses ($R^2 = 0.96$) with a slope of 0.82. This result indicates that the chemical analysis was reliable.

Table 1. PM_{2.5} mass concentrations and mean meteorological parameters before, during and after a haze episode.

Parameter	Before	During	After
PM _{2.5} (µg m ⁻³)	49	211	58
Wind speed (m s ⁻¹)	2.7	1.3	1.7
T (°C)	−1.8	1.5	−6.2
RH (%)	33.9	61.8	63.0
Visibility (km)	28.9	5.1	22.7

Fig. 2. Time series of (a) wind speed (WS), (b) temperature (T) and relative humidity (RH), and (c) visibility; online monitoring of (d) CO and SO₂, (e) O₃ and NO₂, and (f) PM_{2.5} and PM₁₀ concentration.

Table 2. Correlations between PM_{2.5} and meteorological parameters.

Parameter	PM _{2.5}	T	RH	WS	Visibility
PM _{2.5}	1				
T	0.661**	1			
RH	0.554**	-0.016	1		
WS	-0.542*	0.106	-0.638**	1	
Visibility	-0.907**	-0.635**	-0.691**	0.509*	1

** $P < 0.01$, * $P < 0.05$.

Fig. 3. Correlation between reconstructed and measured PM_{2.5} masses.

Water-soluble Inorganic Ions

As shown in Table 3, the total concentrations (mean $\pm$ SD)

of water-soluble inorganic ions (TWSIs) were $24.70 \pm 19.07 \mu\text{g m}^{-3}$, $131.97 \pm 54.29 \mu\text{g m}^{-3}$ and $30.08 \pm 17.56 \mu\text{g m}^{-3}$, accounting for 50.74%, 61.47% and 51.61% of the PM_{2.5} before, during and after the haze episode, respectively. The concentrations of water-soluble inorganic ions followed the order $\text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{Cl}^- > \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{F}^- > \text{C}_2\text{O}_4^{2-} > \text{Mg}^{2+} > \text{NO}_2^-$. The highest concentration during the haze episode was of NO_3^- ($60.45 \pm 27.67 \mu\text{g m}^{-3}$). A favorable distribution of NO_3^- from the gas phase to the particle phase may lead to high NO_3^- concentration in PM_{2.5} at relatively low temperatures in winter (Luo *et al.*, 2018). The SO_4^{2-} was mainly produced by the chemical reaction of gaseous precursors (such as SO_2 gas, dimethyl sulfide in the ocean), which occur in the gas phase with OH radicals or in cloud drops with H_2O_2 or ozone (Pandis *et al.*, 1990). The NH_4^+ was mainly caused by the reaction between NH_3 and the acidic components of NO_3^- and SO_4^{2-} (He *et al.*, 2012). NH_3 emissions mainly derive from human activities and natural sources (Yang *et al.*, 2017). The NO_3^- , SO_4^{2-} and NH_4^+ (SNA) were the dominant ions in PM_{2.5}. The SNA concentrations were $19.55 \pm 17.59 \mu\text{g m}^{-3}$, $120.58 \pm 52.57 \mu\text{g m}^{-3}$ and $26.71 \pm 16.31 \mu\text{g m}^{-3}$, accounting for 79.5%, 91.5% and 89.0% of TWSIs before, during and after the haze

Table 3. Mass concentration of major chemical components in PM_{2.5} (μg m⁻³).

Species	Before	During	After
	Mean ± SD	Mean ± SD	Mean ± SD
<i>Water-soluble inorganic ions</i>			
F ⁻	0.15 ± 0.11	0.20 ± 0.14	0.09 ± 0.11
Cl ⁻	2.49 ± 1.71	7.15 ± 1.57	1.81 ± 0.59
NO ₂ ⁻	0.05 ± 0.06	0.03 ± 0.01	0.02 ± 0.01
NO ₃ ⁻	8.82 ± 9.94	60.45 ± 27.67	9.90 ± 7.78
SO ₄ ²⁻	5.06 ± 3.04	31.83 ± 14.55	9.41 ± 5.34
NH ₄ ⁺	5.67 ± 4.61	28.30 ± 10.35	7.40 ± 3.19
C ₂ O ₄ ²⁻	0.05 ± 0.05	0.12 ± 0.08	0.02 ± 0.00
Na ⁺	0.37 ± 0.16	0.87 ± 0.18	0.36 ± 0.17
K ⁺	0.57 ± 0.43	2.16 ± 0.74	0.55 ± 0.49
Mg ²⁺	0.08 ± 0.09	0.09 ± 0.01	0.07 ± 0.07
Ca ²⁺	1.40 ± 2.13	0.78 ± 0.19	0.46 ± 0.25
<i>Elements</i>			
Na	0.20 ± 0.17	0.77 ± 0.20	0.39 ± 0.20
P	0.01 ± 0.01	0.05 ± 0.02	0.02 ± 0.01
K	0.40 ± 0.42	1.61 ± 0.47	0.64 ± 0.56
Cr	0.01 ± 0.00	0.02 ± 0.01	0.02 ± 0.01
Mn	0.02 ± 0.01	0.06 ± 0.02	0.03 ± 0.02
Cu	0.01 ± 0.01	0.03 ± 0.01	0.01 ± 0.01
Zn	0.11 ± 0.10	0.37 ± 0.15	0.64 ± 1.25
Pb	0.03 ± 0.04	0.10 ± 0.05	0.06 ± 0.05
Al	0.75 ± 0.11	1.44 ± 0.44	1.07 ± 0.26
Mg	0.44 ± 0.13	0.39 ± 0.06	0.18 ± 0.06
Ti	0.10 ± 0.07	0.24 ± 0.34	0.03 ± 0.01
Ca	0.57 ± 0.08	1.11 ± 0.43	0.81 ± 0.23
Fe	0.27 ± 0.08	0.50 ± 0.22	0.20 ± 0.05
Si	0.55 ± 0.27	0.97 ± 1.24	1.11 ± 0.35
Ni	0.02 ± 0.01	0.06 ± 0.02	0.03 ± 0.01
Other elements	0.0011 ± 0.0020	0.0034 ± 0.0053	0.0016 ± 0.0024
<i>OC and EC</i>			
OC	7.54 ± 5.09	21.46 ± 4.94	6.57 ± 1.72
EC	4.09 ± 2.46	11.14 ± 1.74	3.79 ± 0.75
TC	11.63 ± 6.95	32.59 ± 5.48	10.36 ± 2.24
SOC	2.22 ± 1.97	7.11 ± 4.09	0.71 ± 0.62

episode, respectively. These three ions made high contributions to PM_{2.5}, which is consistent with previous studies (Zhang *et al.*, 2013; Luo *et al.*, 2018). Moreover, a good correlation between SO₄²⁻ and NO₃⁻ was found (Pearson's correlation coefficient = 0.979, $P > 0.01$), consistent with an earlier study (Luo *et al.*, 2018). Compared with the other periods, the SNA concentrations were very high during the haze episode (Fig. 4), especially on 20 January with a total concentration of 224.99 μg m⁻³.

The NO₃⁻/SO₄²⁻ ratio in atmospheric particles can be used as a comparative indicator of the contributions of stationary sources (such as coal combustion) and mobile sources (such as automobile exhaust) to sulfur and nitrogen concentrations in the atmosphere (Arimoto *et al.*, 1996; Yao *et al.*, 2002). The ratios of NO_x/SO_x produced by gasoline and diesel combustion were 13:1 and 8:1, respectively (Yao *et al.*, 2002). The ratio of NO_x/SO_x from burning coal was 1:2 when the coal sulfur content was 1% (Yao *et al.*, 2002). Hence, the higher the NO₃⁻/SO₄²⁻, the greater the contribution of mobile sources to PM_{2.5} (Yang *et al.*, 2017). In China, reported

NO₃⁻/SO₄²⁻ ratios in PM_{2.5} include 0.77–0.87 in Zhengzhou (Jiang *et al.*, 2018), 0.14–1.12 in Xinjiang's Dushanzi District (Turap *et al.*, 2019) and 1.2–1.7 in Beijing (Yang *et al.*, 2017). The ratio of NO₃⁻/SO₄²⁻ in some Chinese cities is lower than that in downtown Los Angeles and in Rubidoux in southern California (2–5) (Kim *et al.*, 2000). During the haze episode, the NO₃⁻/SO₄²⁻ ratio was 1.90, which is higher than before (1.73) and after (1.05) the haze episode. As shown in Fig. 4, the concentration of NO₃⁻ was much higher than that of SO₄²⁻ during the haze episode. Due to poor visibility on heavily polluted days, vehicles travel at low speeds and might emit large amounts of NO_x, resulting in high NO₃⁻ concentrations (Jiang *et al.*, 2018).

Other characteristic ions and ion ratios can also reflect the source contribution to PM_{2.5}. The molar ratios of Cl⁻/Na⁺ in PM_{2.5} were 6.70, 8.20 and 4.98 before, during and after the haze episode, respectively. These values are much higher than the ratio in sea-water (1.17), indicating that coal combustion in winter is an important source of Cl⁻ (Yao *et al.*, 2002; Zhang *et al.*, 2013; Tan *et al.*, 2017). K⁺ is used as

Fig. 4. Time series of PM_{2.5} and dominant chemical components.

an indicator of biomass combustion (Yamasoe *et al.*, 2000). During the haze episode, the concentration of K⁺ was 2.16 µg m⁻³, which is 3.79 times higher than before and 3.93 times higher than after the haze episode, suggesting that biomass combustion contributed to PM_{2.5}. The concentration of Mg²⁺ did not change significantly and Ca²⁺ decreased by 44.29% during the haze episode. The major sources of Ca²⁺ are usually soil, road dust and construction. The decrease in Ca²⁺ during the haze episode was probably due to control measures, including cessation of construction and frequent road sweeping (Yang *et al.*, 2017). The concentration of NO₂⁻ did not change much and C₂O₄²⁻ increased by 58.33% in the haze days. The increase of C₂O₄²⁻ may be due to various organic acids generated by the oxidation process of VOCs emitted by combustion, which become organic particulates through homogeneous and heterogeneous nucleation. Luo *et al.* (2018) showed that biomass burning and fossil fuel combustion were important sources of PM_{2.5} in Zibo.

The ion balance calculation is a good method for studying the acidity of aerosols. It is determined by the anion equivalents (AE) and the cation equivalents (CE) (Xu *et al.*, 2012). If the ratio of CE to AE is ≥ 1 , most of the acids are considered to be neutralized (He *et al.*, 2011). In contrast, a ratio < 1 indicates that the aerosols are acidic. In this study, the slope of the linear regression indicated that the aerosols are acidic, especially during the haze episode (Fig. 5). The slope of the linear regression during haze days was lower than during non-haze days, indicating that the proportion of acidity increased in the atmosphere. Therefore, the emissions of SO₂ and NO_x should be strictly controlled to decrease the formation of SO₄²⁻ and NO₃⁻ (Yang *et al.*, 2017).

Sulfate and nitrate were the major aerosol components in PM_{2.5}. In order to determine the extent of atmospheric conversion of SO₂ to SO₄²⁻ and of NO_x to NO₃⁻, the sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) were used (Fu *et al.*, 2008; Lin, 2002). The higher the SOR and NOR values, the higher the oxidation degree of the gas species (Fu *et al.*, 2008). Earlier studies reported that

Fig. 5. Correlations between cations and anions before, during and after the haze episode.

photochemical oxidation of SO₂ or NO_x in the atmosphere occurs when the SOR or NOR is > 0.10 (Ohta and Okita, 1990). As shown in Table 4, the SOR values were > 0.10 during the haze episode (mean $\pm$ SD = 0.31 ± 0.11) and after it (mean $\pm$ SD = 0.19 ± 0.08). High SOR values demonstrate that secondary formation of SO₄²⁻ from SO₂ occurs in the atmosphere. The values of NOR were ≥ 0.10 before the haze episode (mean $\pm$ SD = 0.13 ± 0.09), during it (mean $\pm$ SD = 0.34 ± 0.09) and afterwards (mean $\pm$ SD = 0.16 ± 0.08). High NOR values suggest that secondary formation of NO₃⁻ from NO₂ occurred in the atmosphere. High NOR and SOR values indicates that there was more active gas-to-particle conversion during the haze episode (Hua *et al.*, 2015). In addition, Sun *et al.* (2013) has shown that RH has a significant effect on SO₄²⁻ and NO₃⁻ because higher RH can promote the formation of secondary inorganic ions in particles. In this study, the average RH during the haze episode was 61.8%,

Table 4. SORs and NORs before, during and after a haze episode in Zibo.

Ratio	Before	During	After
SOR	0.10 ± 0.05	0.31 ± 0.11	0.19 ± 0.08
NOR	0.13 ± 0.09	0.34 ± 0.09	0.16 ± 0.08

which was higher than before (33.9%) and lower than after (63.0%) the haze episode. Although the RH during the haze episode was lower than afterwards, the concentrations of SO_4^{2-} and NO_3^- during the haze episode ($0.30 \mu\text{g m}^{-3}$ and $0.31 \mu\text{g m}^{-3}$, respectively) were higher than after ($0.24 \mu\text{g m}^{-3}$ and $0.14 \mu\text{g m}^{-3}$), while the SOR and NOR were highest during the haze episode.

Trace Elements

Elemental mass accounted for a small percentage (< 20%) of the total $\text{PM}_{2.5}$ mass. However, they are easily absorbed on the surfaces of $\text{PM}_{2.5}$ particulates and are harmful to the human body (Chan and Yao, 2008). Thirty-nine elements in $\text{PM}_{2.5}$ were investigated and the concentrations during the sampling period are given in Table 3. The concentrations of TEs were $3.47 \pm 1.50 \mu\text{g m}^{-3}$, $7.66 \pm 3.67 \mu\text{g m}^{-3}$ and $5.21 \pm 3.07 \mu\text{g m}^{-3}$ before, during and after the haze episode, respectively, making contributions to $\text{PM}_{2.5}$ of 9.55%, 3.74% and 9.24%. During the haze episode, the most abundant elements were crustal elements (e.g., K, Al, Ca, Si, Na, Fe and Mg), which accounted for 88.64% of the TEs. Comparing elemental concentrations before and during the haze episode, the mean concentration of TEs increased by 57.10%, especially for crustal elements such as Na, Al, Ca, Fe and Si, with increases ranging from 43.36% to 74.56%. This increase in elements may be caused by source emissions and low wind velocities, which may cause an accumulation of atmospheric pollutants. While a large amount of particulate matter from the crust may decrease when the wind speed is low enough, crustal elements may still increase due to the build-up of dust re-suspended by road traffic (Gu et al., 2011).

Element K had the highest concentration ($1.61 \pm 0.47 \mu\text{g m}^{-3}$), which may be related to the biomass combustion. Zn ($0.37 \mu\text{g m}^{-3}$) was the most abundant heavy metal in $\text{PM}_{2.5}$, which may be related to tire wear and automotive lubricant additives (Zhang et al., 2018), followed by Pb, Mn, Cu and Cr. Ni is an indicator of petroleum combustion and is related to oil-fired power and steam boilers, while Fe and Mn are related to the steel industry (Khan et al., 2016; Luo et al., 2018; Zhang et al., 2018). There are petrochemicals, ceramics, pharmaceutical production and building materials in Zibo, so the elements detected in the samples are in line with the characteristics of Zibo's heavy industries.

Carbonaceous Species

The carbonaceous fraction of ambient particulate matter is usually divided into organic carbon and elemental carbon (Park et al., 2001). The OC can be generated by primary emissions and secondary formation, while EC mainly comes from primary emissions (Tao et al., 2017a). The OC in $\text{PM}_{2.5}$ varied from $15.38 \mu\text{g m}^{-3}$ to $30.83 \mu\text{g m}^{-3}$ (mean $\pm$ SD = $21.46 \pm 4.94 \mu\text{g m}^{-3}$), while EC varied from $8.09 \mu\text{g m}^{-3}$ to $13.31 \mu\text{g m}^{-3}$ (mean $\pm$ SD = $11.14 \pm 1.74 \mu\text{g m}^{-3}$) during the

haze episode (Table 3). The OC accounted for 10.18% and the EC accounted for 5.41% of $\text{PM}_{2.5}$ during the haze episode. Compared with before and after the haze episode, the OC concentration was 64.86% and 69.38% higher during it, while the EC concentration was 63.29% and 65.95% higher. OC and EC accounted for 23.73%, 15.45% and 17.86% of the $\text{PM}_{2.5}$ before, during and after the haze episode, respectively.

The relationship between OC and EC was used to determine the source of carbon particles (Ram et al., 2008; Yang et al., 2017). If OC and EC are mainly emitted by primary sources, the correlation between the OC and EC should be high, because the relative emission rates of OC and EC are proportional (Zhang et al., 2007). Fig. 6 shows the correlation between OC and EC concentrations. The correlation between OC and EC was poor during the haze episode ($R^2 = 0.04$), indicating that the sources of OC and EC were different. However, there was a strong correlation between OC and EC both before ($R^2 = 0.93$) and after ($R^2 = 0.91$) the haze episode. This difference may be interpreted as being affected by other sources in addition to local emissions (i.e., secondary OC) (Zhang et al., 2007).

The OC/EC ratio can provide source information. Watson (2002) reported OC/EC ratios of 0.3–7.6 for coal combustion, 0.7–2.4 for motor vehicle emissions and 4.1–14.5 for biomass combustion. In this study, the mean $\pm$ SD OC/EC ratios were 1.81 ± 0.34 , 1.95 ± 0.39 , and 1.72 ± 0.13 before, during and after the haze episode, indicating that coal combustion and vehicle exhaust were the dominant sources of pollution. An OC/EC value ≥ 2 was used to indicate the existence of significant secondary organic carbon (SOC) (Chow et al., 1996). The OC/EC values were about 2.0 during the haze episode, demonstrating that secondary organic carbon might

Fig. 6. Correlations between OC and EC concentrations before, during and after the haze episode.

exist. The SOC calculation method can be found in a previous study (Ram *et al.*, 2008). As shown in Table 3, the mean $\pm$ SD concentrations of SOC were $2.22 \pm 1.97 \mu\text{g m}^{-3}$, $7.11 \pm 4.09 \mu\text{g m}^{-3}$ and $0.71 \pm 0.62 \mu\text{g m}^{-3}$ before, during and after the haze episode, respectively. The ratio of SOC/OC in haze days (0.31 ± 0.15) was slightly higher than before (0.25 ± 0.15) and after (0.10 ± 0.07), which indicates that the photochemical reaction in haze days was more intense than non-haze days (Jiang *et al.*, 2018). There was a significant correlation between SOC and $\text{PM}_{2.5}$ and Pearson's correlation coefficient was 0.815 ($P < 0.01$), indicating SOC is an important component in $\text{PM}_{2.5}$. As a city with heavy industry, there are many petrochemical enterprises and vehicles (1.237 million in 2018), and a great deal of VOCs is released into the atmosphere. Higher concentrations of VOCs produce higher concentrations of secondary organic carbon through photochemical reactions at high temperatures (Wang *et al.*,

2018). The mean temperature was 1.73°C during the haze episode, which is the ideal temperature for SOC formation and accumulation, because evaporation is inhibited at low temperatures (Luo *et al.*, 2018).

Air Mass Backward Trajectory Analysis

To better understand the impact of regional transmission during the haze episode, 24-h air mass back-trajectories were derived for clusters identified from 8–27 January 2018, starting at an altitude of 500 m from the ground (Li *et al.*, 2017). Clusters were computed with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) 4 model developed by the U.S. National Oceanic and Air Administration (NOAA) Air Resources Laboratory (ARL) (Gao *et al.*, 2015). Cluster analysis of 24-h backward trajectories before, during and after the haze episode are shown in Fig. 7. Before the haze episode, 60% (Clusters 1,

Fig. 7. Cluster analysis of 24-h air mass backward trajectories before, during and after the haze episode.

2, 3 and 4) was from the northwest and 39% (Clusters 5 and 6) was from Shandong Province and its adjacent areas. After the haze episode, the air masses were more from the Beijing-Tianjin-Hebei region (46%). During the haze episode, the air mass path was mainly derived from adjacent regions in Shandong Province (57%, Cluster 2), 36% (Cluster 1) was from the Beijing-Tianjin-Hebei region, and 7% (Cluster 3) was from Inner Mongolia and was transmitted to Zibo via Liaoning Province. Air mass backward trajectories for Cluster 2 were short, indicating that air masses moved slowly and pollutants tended to accumulate (Feng *et al.*, 2018). PM_{2.5} concentrations in each air mass during the haze episode showed decreasing trends in the order of Cluster 1 (185.10 $\mu\text{g m}^{-3}$) > Cluster 2 (179.71 $\mu\text{g m}^{-3}$) > Cluster 3 (85.08 $\mu\text{g m}^{-3}$). The above analysis illustrates that large amounts of pollutants from other regions were mixed in the air masses and transported to the research area, thus intensifying its PM_{2.5} pollution level (Jiang *et al.*, 2018). Thus, the regional transport of pollutants has an important impact on PM_{2.5} (Yang *et al.*, 2017).

CONCLUSIONS

The concentration and chemical composition of PM_{2.5} in the heavy industrial city of Zibo were investigated in relation to a haze episode occurring 15–21 January 2018. The concentrations (mean $\pm$ SD) were $49 \pm 38 \mu\text{g m}^{-3}$, $211 \pm 39 \mu\text{g m}^{-3}$ and $58 \pm 33 \mu\text{g m}^{-3}$ before, during and after the episode, respectively, with the TWSIs, TEs and carbonaceous species (OC and EC) accounting for 50.74%, 61.47% and 51.61%; 9.55%, 3.74% and 9.24%; and 23.73%, 15.45% and 17.86%. The TWSIs primarily consisted (79.5–91.5%) of secondary ions (NO_3^- , SO_4^{2-} and NH_4^+), and the TEs displayed an abundance (88.64%) of crustal elements (K, Al, Ca, Si, Na, Fe and Mg) during the episode.

The CE/AE ratio indicated that the acidity increased on haze days, and the $\text{NO}_3^-/\text{SO}_4^{2-}$ and OC/EC ratios suggested that coal combustion and vehicle exhaust emission were the largest sources of pollution. Additionally, the higher SNA and SOC values identified secondary formation as a significant contributor to the elevated PM_{2.5} concentration during the episode, and back-trajectory analysis traced the pollutive aerosols in Zibo on haze days to adjacent areas in Shandong Province (57%) and the Beijing-Tianjin-Hebei region (36%). Finally, unfavorable meteorological conditions were another factor that exacerbated the PM_{2.5} pollution during the haze episode.

ACKNOWLEDGMENTS

This study was supported by the National Research Program for Key Issues in Air Pollution Control (No. DQGG0107-20 and DQGG0107-19), the National Key Research and Development Program of China (2017YFC0212503) and the Special Scientific Research Business of the Central Academy of Public Welfare Research Institute of the Chinese Research Academy of Environmental Sciences (2018-YSKY-041). The authors thank the editor and reviewers for their valuable comments.

DISCLAIMER

The authors declare that they have no conflicts of interest.

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Received for review, December 29, 2019

Revised, April 29, 2020

Accepted, May 26, 2020