Characteristics and Sources of Single Particles in the Urban Liaocheng of North China during the Heating Period

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ABSTRACT

Liaocheng represents one of the most serious polluted cities in Northern China. To investigate the impact of residential heating activities on atmospheric particles, the chemical composition, size distribution, and evolution process of single particles collected during the wintertime of 2019 were investigated using a single-particle aerosol mass spectrometer (SPAMS). The results showed that the concentrations of four air pollutants including PM_{2.5}, SO₂, NO₂, and CO during the heating period were 1.1–1.2 times higher than those before the heating period largely due to the increase of pollutant emissions from coal combustion, while O₃ concentration during the heating period decreased by 40.2%. The mass spectra and unscaled size distributions of single particles suggested that the particles had undergone a significant aging process during the whole observation period. The acidity of single particles was calculated by the relative acidity ratio (R_{ra}), which increased from 36.1 ± 13.9 before the heating period to 64.8 ± 43.9 during the heating period, implying that the single particles were more acidic and less aged during the heating period, mainly due to the enhanced formation of sulfate and nitrate and the decreased O₃ concentration during the heating period. Moreover, R_{ra} decreased from clean days to polluted days before and during the heating period, suggesting that the atmospheric particles in polluted days were less acidic and more aged. The percentage of elemental carbon (EC) particles increased by 13.6% and 11.5% from clean days to polluted days before and during the heating period, respectively, suggesting the significant contribution of EC particles to the polluted days. Source identification results showed that single particles before the heating period were mostly derived from secondary inorganic source (26.5%) and vehicle exhaust (21.4%), whereas those during the heating period were largely from coal combustion (24.0%) and secondary inorganic source (21.4%).

Keywords: Size distribution, Online source analysis, Aerosol acidity (R_{ra}), The heating period, Single particle aerosol mass spectrometer (SPAMS)

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1 INTRODUCTION

In recent years, severe pollution incidents occurred frequently in northern China during the winter, mainly due to residential heating activities by coal combustion during the heating season, which has raised great public concerns (Liu *et al.*, 2016; Chen *et al.*, 2017; Hong *et al.*, 2018; Hu *et al.*, 2018b; Xu *et al.*, 2018; Luo *et al.*, 2019). It has been reported by the National Bureau of Statistics of China (NBSC, 2016) that China contributed to approximately half of the global annual coal consumption, which emitted a large quantity of air pollutants (e.g., PM_{2.5}, SO₂, NO_x, and CO), resulting in severe atmospheric pollution (Zhang *et al.*, 2017a; Zhang *et al.*, 2017d). At the same time, the enhancement of air pollutants has a significant impact on air quality, human health, visibility, and global climate change, which are closely related to the chemical composition and

size distributions of the single particles (Zhang *et al.*, 2017b; Hu *et al.*, 2018a; An *et al.*, 2019; Meng *et al.*, 2020).

The mass concentration, chemical composition, and size distribution of single particles have been studied extensively using the traditional filter sampling method, which usually requires a long sampling time to enable the thorough reaction of single particles with each other (Cheng *et al.*, 2020). In recent years, single particle aerosol mass spectrometer (SPAMS) has been used to monitor the single-particle aerosol online at a high time resolution (Li *et al.*, 2020; Meng *et al.*, 2021). It not only avoids the disadvantages of the traditional offline analysis method, but also excludes the tedious sample pretreatment processes. In addition, the information of particle size, chemical composition and source resolution of single particles can be obtained quickly by SPAMS (Bi *et al.*, 2015; Ma *et al.*, 2016; Zhang *et al.*, 2018; Peng *et al.*, 2019; Shen *et al.*, 2020).

Many studies have been carried out to investigate the sources and the formation mechanism of PM_{2.5} during the heating period. For example, Beijing suffered from severe PM_{2.5} pollution due to the stagnant weather in the heating season of 2016 (Li *et al.*, 2018). Lin *et al.* (2015) reported that the main sources of PAHs were coal combustion and biomass burning during the heating period. In 2017, the air quality of Beijing had improved significantly through the regional joint prevention and control (Pang *et al.*, 2021). However, air quality was still bad during the heating period in most parts of northern China (e.g., the Harbin-Changchun megalopolis) (Zhao *et al.*, 2020). Both the local pollutant emissions and convective motion of aerosol were considered as key contributors to air pollution in the Harbin-Changchun megalopolis during the heating season (Zhao *et al.*, 2020). Liu *et al.* (2020) found that secondary inorganic aerosol and coal combustion were the spatial sources of PM₁₀ and PM_{2.5} during the heating season in Tianjin, China. Although residential coal combustion emissions have been proposed as an especially vital contributor to the haze formation in winter, there still has been little information about the size distribution, mixing state, and aging process of single particles in northern China, especially during the heating season (Li *et al.*, 2020).

Shandong Province, situated in the mid-eastern part of northern China, has become one of the areas suffering from regional haze pollution in China (Meng *et al.*, 2020). Liaocheng City, located in the southwest of Shandong Province, was ranked as the top 32th most polluted city among 365 Chinese cities with the average PM_{2.5} concentration of 103 $\mu\text{g m}^{-3}$ from October to December in 2019 (<https://www.aqistudy.cn/>). The regional transport of air pollutants from Liaocheng has a significant effect on the regional atmospheric pollution of Beijing-Tianjin-Hebei region in China (Zhang *et al.*, 2017c). The winter in Liaocheng is harsher and colder than other cities of China, the heating period in Liaocheng lasts from November to March of the next year. In this study, SPAMS was used to conduct the real-time observation of single aerosol particles in Liaocheng during the wintertime, focusing on the chemical composition, size distribution, relative aerosol acidity, and source analysis of single aerosol particles before and during the heating period. In addition, the characteristics and evolution processes of single particles on clean and polluted days were analyzed. The results will provide an important theoretical base for energy control and emission reduction in northern China, especially for the improvement of air quality during the heating period.

2 METHODS

2.1 Field Measurement

Liaocheng, located in the western part of Shandong province, is regarded as one of the “2 + 26” air pollution transmission channel cities in Beijing-Tianjin-Hebei, China. Field observations were conducted at a national air quality monitoring station on the rooftop of a six-story building (36.43°N, 116.01°E) in Liaocheng University, which is situated in the southeast of Liaocheng City. The sampling site is surrounded by residential areas, main roads and schools without obvious pollution sources and tall buildings. The single particles were analyzed per hour using a single-particle aerosol mass spectrometer (SPAMS, 0515R Model, Hexin Analytical Instrument Co., Ltd., China). The heating period of Liaocheng during the winter of 2019 began on November 15 and lasted for four months. To investigate the effect of heating period on the chemical composition, size distribution and source of individual particles in the urban atmosphere of northern China during the wintertime, the whole sampling period was divided into “before the heating” (0:00 on

24 October to 24:00 on 7 November, 2019) and “during the heating” (from 0:00 on 23 November to 24:00 on 7 December, 2019). In addition, the hourly mass concentration of meteorological parameters, gaseous pollutants, and PM_{2.5} was obtained from Environmental Protection Bureau of Liaocheng (<http://www.lchbj.gov.cn>).

2.2 Descriptions of Observational Instruments

The principle and structure of SPAMS have been described in detail (Li *et al.*, 2011). In short, the aerosol particles will first enter the instrument aerodynamics lens through a metal orifice with a diameter of 0.1 mm at a flow rate of 75 mL min⁻¹. The accelerated particles are firstly measured and counted by a dual beam 532 nm laser, and the aerodynamic diameter of each particle is determined via its time of flight. Then, particles are ionized by a 266 nm ultraviolet pulse laser to produce positive and negative ions. Meanwhile, the ionized ion fragments are detected by bipolar time-of-flight mass spectrometry, which captures the chemical composition and particle diameter of single aerosol synchronously. To ensure the effectiveness and accuracy of the instrument measurement results, polystyrene beads with particle sizes of 0.23, 0.51, 0.96 and 1.96 μm are used to calibrate the instrument before sampling, and a fitting curve is drawn to ensure the calibration coefficient $R^2 > 0.99$. At the same time, in order to ensure the accuracy of particle size measurement results, the particles will pass through a drying pipe before being detected to reduce the influence of humidity.

2.3 Data Analysis

Data analysis was conducted using Matlab 2014b (Math Work Inc., Natick, MA, USA). When the single-particle mass spectra data were imported into Matlab 2014b, the data were first classified through an adaptive resonance theory neural network algorithm (ART-2a). This algorithm can group similar particles into the same class according to the particle mass spectrometry information. Then the CoCo V1.4 package was used to process the size and mass spectra information. In this study, we set up a learning rate of 0.05, a vigilance factor of 0.7, and a maximum of 20 iterations. Meanwhile, data from online sources were obtained using the tracer ions method.

3 RESULTS AND DISCUSSION

3.1 Overview of the Observations

3.1.1 Variations in air quality and meteorological conditions

The temporal variations of meteorological parameters, gaseous pollutants (e.g., SO₂, NO₂, O₃ and CO), PM_{2.5}, and the number counts of total single particles during the whole observation period are shown in Fig. 1. Temperature decreased drastically from $12.6 \pm 4.7^\circ\text{C}$ before the heating to $2.7 \pm 4.2^\circ\text{C}$ during the heating period, and relative humidity (RH, $67.1 \pm 22.4\%$) was higher before the heating than that ($58.7 \pm 20.8\%$) during the heating period (Table 1). Similarly, solar radiation presented a decreasing trend, with an average of $118.2 \pm 176.8 \text{ W m}^{-2}$ before the heating and $78.9 \pm 130.5 \text{ W m}^{-2}$ during the heating period, respectively (Table 1). The average wind speed ($1.0 \pm 0.6 \text{ m s}^{-1}$) before the heating period was almost equivalent to that ($1.2 \pm 0.6 \text{ m s}^{-1}$) during the heating period. Wind speed lower than 1.5 m s^{-1} is considered as stagnant air condition (Chen *et al.*, 2018), indicating that the effect of long-distance transport on the atmospheric particles was minor. Therefore, local emissions and subsequent heterogeneous oxidation might play a leading role in the air quality in this area.

PM_{2.5} concentration ($71.9 \pm 42.9 \mu\text{g m}^{-3}$) during the heating period was 1.2 times higher than that ($62.5 \pm 34.3 \mu\text{g m}^{-3}$) before the heating period, reflecting that the air quality became worse due to the enhancement of pollutant emissions from coal combustion during the heating period. PM_{2.5} concentration exhibited a pronounced diurnal profile with two rush-hour peaks in the morning (10:00) and in the nighttime (22:00), respectively (Fig. 2). Similarly, the concentrations of SO₂, NO₂ and CO during the heating period were expected to be 1.1–1.2 times higher than those before the heating period (Table 1, Fig. 1), due largely to the increased coal combustion during the heating period. Interestingly, NO₂ was correlated robustly with CO ($r > 0.5$, $p < 0.01$) before and during the heating period, suggesting that both species shared common sources

Fig. 1. Temporal variations of meteorological parameters, concentrations of gaseous pollutants, and PM_{2.5} during the whole observation period.

(e.g., vehicle exhausts). O₃ is primarily derived from the photochemical oxidation of NO_x and volatile organic compounds (VOCs), thus it can be used to evaluate the atmospheric oxidation capacity (Meng *et al.*, 2021). Being opposite to the variations of the other four air pollutants, the concentration of O₃ ($23.2 \pm 20.0 \mu\text{g m}^{-3}$) during the heating period decreased by 40.2% compared to that ($38.8 \pm 46.7 \mu\text{g m}^{-3}$) before the heating period, suggesting that the oxidation capacity of atmosphere became weaker during the heating period. The relatively low temperature and weak solar radiation conditions during the heating period limited the formation of O₃ (Xu *et al.*, 2020). It has been reported that O₃ was negatively correlated with PM_{2.5} mass concentration because of the impact of aerosol radiative on the photochemistry production of O₃ (Wu *et al.*, 2020), thus the higher PM_{2.5} concentration during the heating period was another significant reason for the reduced O₃.

3.1.2 The characterization of single particles

A total of 1856200 and 2817180 single particles were collected before and during the heating period, respectively. As shown in Fig. 3, the single particles before and during the heating period had obvious signals of ³⁹K⁺, carbon ions, ²³Na⁺, ¹⁸NH₄⁺, and OC fragments (e.g., ²⁷C₂H₃⁺, ³⁹C₃H₃⁺, ⁴¹C₃H₅⁺, ⁵¹C₄H₃⁺, ⁶³C₅H₃⁺, and ⁷⁴C₆H₂⁺) in the positive spectra, and the negative spectra were characterized by strong signals of ²⁶CN⁻, ⁴²CNO⁻, and secondary inorganic ions (e.g., ⁴⁶NO₂⁻, ⁶²NO₃⁻, ⁸⁰SO₃⁻, and ⁹⁷HSO₄⁻). The signal peaks of OC fragments were more obvious during the heating period than those before the heating period, but the signal intensities of carbon ions

Table 1. Concentrations of PM_{2.5} and gaseous pollutants, meteorological parameters, and count of each type of single particles during the whole observation period.

	Before heating	During heating	Whole period
PM _{2.5} (μg m ⁻³)	62.5 ± 34.3	71.9 ± 42.9	67.2 ± 38.8
Count	1856200	2817180	4673380
Sample classification (number of count)			
EC	709770	562870	1272640
OC	301510	853340	1154850
ECOC	88820	387290	476110
Dust	174850	268940	443790
BB	297600	474840	772440
Sec	184510	142490	327000
HM	99140	127410	226550
Meteorological parameters			
Temperature (°C)	12.6 ± 4.7	2.7 ± 4.2	7.5 ± 6.5
Relative humidity (%)	67.1 ± 22.4	58.7 ± 20.8	62.9 ± 22.1
Wind speed (m s ⁻¹)	1.0 ± 0.6	1.2 ± 0.6	1.1 ± 0.6
Solar Radiation (W m ⁻²)	118.2 ± 176.8	78.9 ± 130.5	98.6 ± 156.6
Gaseous pollutants			
O ₃ (μg m ⁻³)	38.8 ± 46.7	23.2 ± 20.0	34.9 ± 33.0
NO ₂ (μg m ⁻³)	49.2 ± 25.3	60.1 ± 19.9	54.6 ± 23.4
SO ₂ (μg m ⁻³)	14.2 ± 8.6	17.6 ± 8.5	15.9 ± 8.7
CO (μg m ⁻³)	0.9 ± 0.4	1.0 ± 0.4	0.9 ± 0.4

Fig. 2. Hourly variations in PM_{2.5} and RH, gaseous pollutants (NO₂, O₃ and CO), EC and BB particles (a) before the heating period, and (b) during the heating period.

Fig. 3. Mass spectra of detected particles (a) before the heating period, and (b) during the heating period. Color bars represent each peak area corresponding to a specific fraction in individual particles.

were relatively weak. Meanwhile, the proportion of $^{80}\text{SO}_3^-$ and $^{97}\text{HSO}_4^-$ increased during the heating period, indicating that the heterogeneous reaction with SO_2 increased to form sulfate (Wang *et al.*, 2019a). Nevertheless, the signals of both $^{46}\text{NO}_2^-$ and $^{62}\text{NO}_3^-$ were stronger than that of $^{97}\text{HSO}_4^-$ both before and during the heating period, which illustrated that the single particles were subject to the formation of nitrate in the aging process. The single particles have been regarded to be aged when the negative mass spectra were dominated by the high abundances of secondary species including $^{46}\text{NO}_2^-$, $^{62}\text{NO}_3^-$, and $^{97}\text{HSO}_4^-$, or more abundant signals of nitrate than sulfate as observed in the same mass spectrum (Meng *et al.*, 2021). As shown in Fig. 3, both the secondary species and the stronger signals of nitrate than sulfate were observed before and during the heating period, indicating that single particles have been suspended in the atmosphere for a long time and undergone a significant aging process during the whole observation period. The single particles before and during the heating period presented unimodal distributions with a peak at a smaller size ($\sim 0.46\ \mu\text{m}$) during the heating period than that ($\sim 0.48\ \mu\text{m}$) before the heating period, which was attributed to different sources and formation mechanisms (Fig. 4(b)).

3.2 Characteristics of Major Particles Types

The single particles were manually classified into seven types by ART-2a according to the characteristics of the respective ion peak, including elemental carbon (EC), organic carbon (OC), EC and OC combined particles (ECOC), dust particles (Dust), biomass burning (BB), secondary (Sec), and heavy metals (HM). The mass spectra of the particle types throughout the entire sampling period are shown in Fig. 5. In the positive spectrum, the signal peak of $^{39}\text{K}^+$ was commonly found in all particle types because of the extreme sensitivity of the SPAMS instrument to K^+ (Wang *et al.*, 2019b). And the signal peaks of nitrate (m/z –46 and –62) and sulfate (m/z –97) were obvious in the negative spectrum, suggesting that all types of particles experienced different degree of aging. As presented in Table 1 and Fig. 6, the dominant particle type was EC (38.3%), followed by OC (16.2%) and BB (16.0%) before the heating period. However, the contribution of OC (30.3%) became the most important during the heating period, while EC (20.0%) and biomass burning (16.9%) were still at high levels.

Fig. 4. Unscaled size distributions of single particles before and during the heating period.

3.2.1 Carbonaceous particles

Carbonaceous species mainly include three types, including EC, OC, and ECOC particles, whose peaks in the positive spectra did not change significantly before and during the heating period. Three kinds of carbonaceous species in the negative spectra before the heating period were dominated by $^{62}\text{NO}_3^-$, but these particles during the heating period were pronounced in $^{97}\text{HSO}_4^-$ except for EC particles (Fig. 5), indicating that carbonaceous particles favored the sulfate formation during the heating period (Shen *et al.*, 2020). EC particles, which are mainly derived directly from the incomplete combustion of fossil and biomass fuels (Lin *et al.*, 2017; Huang *et al.*, 2018), had obvious signals of $\text{C}_n^{+/-}$ ($n = 1, 2, \dots, 6$) in the positive and negative mass spectra. They showed the similar variations with CO and peaked at 9:00 during the heating period (Fig. 2), suggesting that they had the common prevalence. The count of EC decreased from 709770 before the heating period to 562870 during the heating period, accounting for 36.3% and 20.0% of the total detected particles, respectively. Thus, both the count of EC particles and its percentage contribution to the total particles were higher before the heating period than those during the heating period, mainly owing to the reduction in the direct emissions of primary single particles during the heating period. As listed in Fig. 7, EC particles had a strong correlation ($r = 0.77$, $p < 0.01$) with HM particle before the heating period, implying that they had similar sources before the heating period. However, such a robust correlation was not obtained during the heating period ($r = 0.47$, $p < 0.01$).

Fig. 5. Average mass spectra of seven types of single particles (a) before the heating period, and (b) during the heating period.

Fig. 6. (a) Temporal variations in the fractions of each type of single particles; (b) average percentages of single particle types during the four stages: clean days before the heating period, polluted days before the heating period, clean days during the heating period and polluted days during the heating period.

Fig. 7. Correlation coefficients (r) of single particle types (a) before the heating period, and (b) during the heating period.

The positive mass spectra of OC particles presented strong signals of $^{27}\text{C}_2\text{H}_3^+$, $^{37}\text{C}_3\text{H}^+$, $^{39}\text{C}_3\text{H}_3^+$, $^{50}\text{C}_4\text{H}_2^+$, $^{63}\text{C}_5\text{H}_3^+$, and $^{74}\text{C}_6\text{H}_2^+$. This particle type is typically attributed to the primary combustion such as biomass burning, vehicular emissions, and coal combustion as well as the secondary formation via the atmospheric photochemical reaction of anthropogenic and biogenic volatile organic precursors (Chang *et al.*, 2017; Mao *et al.*, 2018). Being opposite to the variations of EC particles, the number counts of OC particles during the heating (853340) increased by 14.1% compared to that before the heating (301510) (Table 1). As an indicator for secondary organic species (Meng *et al.*, 2021), oxalic acid (m/z –89) showed the stronger signal before the heating period than that during the heating period, largely due to the stronger atmospheric oxidizing capacity (O_3 concentration), the higher temperature, and the stronger solar radiation conditions before the heating period. In addition, OC particles were correlated strongly with BB particles and dust particles before ($r > 0.60$, $p < 0.01$) and during the heating period ($r > 0.86$, $p < 0.01$), respectively (Fig. 7). And the correlations during the heating period were significantly higher than that before the heating period, suggesting that OC particles were strongly associated with BB particles during the heating period. In addition, traffic dust around the sampling site is an important contributor to the OC particles (Wang *et al.*, 2019b).

ECOC particles, mainly derived from the vehicle emission in urban areas (Liu *et al.*, 2016; Yang *et al.*, 2017), were characterized by C_n^+ and C_nH_m^+ in both the positive and negative mass spectra. The signal of sulfate signals was more obvious in the negative spectra during the heating period than that before the heating period, which may be associated with the enhancement of coal combustion (Wang *et al.*, 2019b). Moreover, a total of 387290 ECOC particles were determined during the heating, which was 4.4 times higher than that before the heating (Table 1). And this particle type accounted for 13.7% of the total particles during the heating period, which increased by 8.9% compared with that (4.8%) before the heating period.

3.2.2 Dust particles

Dust particles, mainly derived from construction, re-suspended road dust and natural soil (Luo *et al.*, 2019), were characterized by strong peak of $^{40}\text{Ca}^+$ and weak peaks of $^{60}\text{SiO}_2^-$ and $^{76}\text{SiO}_3^-$. Moreover, the stronger peak of nitrate ($^{46}\text{NO}_2^-$ and $^{62}\text{NO}_3^-$) than that of sulfate ($^{97}\text{HSO}_4^-$) was observed both before and during the heating period, suggesting that the more dust particles had heterogeneous reactions with NO_x rather than SO_2 (Sullivan *et al.*, 2007; Mao *et al.*, 2018). The relative abundance of dust particles in the total detected particles (9.4%) before the heating period was equivalent to that (9.5%) during the heating period. Given that the wind speed in the observation period was less than 2 m s^{-1} , dust particles were mainly emitted from road dust (Wang *et al.*, 2019b). In addition, dust particles were correlated well with BB particles before ($r = 0.74$, $p < 0.01$) and during ($r = 0.90$, $p < 0.01$) the heating period (Fig. 7), respectively, suggesting the significant impact of biomass burning on the dust particles.

3.2.3 Biomass burning particles

BB particles showed a representative peak of levoglucosan ion fragments (e.g., $^{45}\text{CHO}_2^-$, $^{59}\text{C}_2\text{H}_3\text{O}_2^-$, $^{71}\text{C}_3\text{H}_3\text{O}_2^-$, and $^{73}\text{C}_3\text{H}_5\text{O}_2^-$), which are important tracers of biomass burning (Chen *et al.*, 2017; Wu *et al.*, 2018) in the mass spectrum (Fig. 5). In addition, BB particles contained abundant signals of K^+ and secondary inorganic ions. The signal peak of nitrate was stronger than that of sulfate before and during the heating period, indicating the existence of aged biomass particles. BB particles started to increase at 5:00 and 7:00 before and during the heating period, respectively, and reached the first peak at 10:00 (Fig. 2). The other peak rose greatly at 18:00 before the heating period and at 17:00 during the heating period, which was attributed to the cooking and heating by biomass burning. Similar to the percentage of dust particles, the proportion of BB before the heating period (16.0%) was approximately equal to that (16.9%) during the heating period.

3.2.4 Secondary particles

As shown in Fig. 5, secondary particles were characterized by the strong intensities of $^{23}\text{Na}^+$, $^{39}\text{K}^+$, $^{46}\text{NO}_2^-$, $^{62}\text{NO}_3^-$ and $^{97}\text{HSO}_4^-$. The count of secondary particles decreased from 184510 before the heating period to 142490 during the heating period, largely due to the unfavorable meteorological conditions, such as the lower temperature, weaker solar radiation, and weaker atmospheric

oxidation capacity (Table 1) during the heating period. Secondary particles were strongly correlated with dust particles, ECOC particles, OC particles and BB particles before the heating period ($r_{\text{Sec-Dust}} = 0.67$, $r_{\text{Sec-ECOC}} = 0.53$, $r_{\text{Sec-OC}} = 0.49$, $r_{\text{Sec-BB}} = 0.81$, $p < 0.01$) and during the heating period ($r_{\text{Sec-Dust}} = 0.69$, $r_{\text{Sec-ECOC}} = 0.66$, $r_{\text{Sec-OC}} = 0.67$, $r_{\text{Sec-BB}} = 0.65$, $p < 0.01$), respectively (Fig. 7), suggesting that these types of particles were mixed with secondary particles as discussed above.

3.2.5 Heavy metal particles

HM particles are mainly derived from industrial emissions, coal and oil-fired power plant emissions, fossil fuel combustion, and steel plant processes (Liu *et al.*, 2016). HM particles accounted for only 5.0% of the total detected particles, indicating the minor contribution of industrial and combustion sources to the atmospheric particles. As shown in Fig. 5, HM particles were characterized by the strong intensity of $^{56}\text{Fe}^+$, $^{55}\text{Mn}^+$, and $^{206,207,208}\text{Pb}^+$ in the positive mass spectrum. The negative mass spectrum was dominated by $^{46}\text{NO}_2^-$, $^{62}\text{NO}_3^-$, and $^{97}\text{HSO}_4^-$. The more abundant signals of nitrate than sulfate was observed during the whole observation period, suggesting that HM particles experienced a significant aging process.

3.3 Size Distribution

The size distribution was determined by SPAMS with the size range of 0.2–2.0 μm . Note that larger particles were seldom detected due to the low detection efficiency of the instrument. The unscaled size distributions of different types of particles are shown in Fig. 4. The number fraction of EC particles peaked at $\sim 0.5 \mu\text{m}$ before and during the heating period. The number fraction of EC particles decreased significantly over the entire size range during the heating period compared to that before the heating period. It has been reported that the EC particles transferred into the larger size during the aging processing, mainly because the oxidized organic species, nitrate, and sulfate were mixed with EC particles (Chen *et al.*, 2018). It is worth noting that the size distribution of EC particles before the heating period became broader than that during the heating period, suggesting that the EC particles underwent more aging process before the heating period. Meanwhile, the number fraction of EC particles ranging from 0.2 to 0.4 μm was low, which was detected to be less than 13.3% of all detected particles throughout the observation period, suggesting the negligible contribution of fresh vehicle exhaust to the EC particles (Li *et al.*, 2020). Simultaneously, OC particles contributed nearly one half of the total particles with the size smaller than 0.5 μm , and decreased to $\sim 20\%$ with a larger size ($> 0.5 \mu\text{m}$) (Fig. 4(a)), suggesting that the contribution of the primary emission was more significant than that of the secondary sources. As shown in Fig. 4, OC particles peaked at 0.46 μm in the whole observation period, and their number fraction decreased with the larger particle size before and during the heating period, indicating that the formation mechanism of OC particles in these two periods was similar. The size distribution of ECOC particles peaked at 0.46 μm and 0.44 μm before and during the heating period, respectively. The number fraction was higher during the heating period compared to that before the heating period when the size was smaller than 1.0 μm . In addition, dust particles had a peak at 0.48 μm both before and after the heating period, and their size distribution shifted towards the larger size rapidly due to the heterogeneous photochemical reactions during the long-distance transport (Nie *et al.*, 2014). BB particles displayed the same size distribution before and during the heating period, which was mainly attributed to the same forming process or the same sources during these two observation periods. The highest number fraction of HM particles before and during the heating period peaked at 0.52 and 0.50 μm , respectively.

3.4 Evolution of Single Particles on Clean and Polluted Days

To better understand the effect of residential heating supply on the chemical compositions and sources of atmospheric particles, we divided the observation period into four stages: clean days before the heating period (C1, $\text{PM}_{2.5} < 75.0 \mu\text{g m}^{-3}$), polluted days before the heating period (P1, $\text{PM}_{2.5} \geq 75.0 \mu\text{g m}^{-3}$), clean days during the heating period (C2, $\text{PM}_{2.5} < 75.0 \mu\text{g m}^{-3}$) and polluted days during the heating period (P2, $\text{PM}_{2.5} \geq 75.0 \mu\text{g m}^{-3}$) according to daily $\text{PM}_{2.5}$ concentration. C1, P1, C2, and P2 experienced 9.8, 5.3, 9.4, and 5.7 d, with average $\text{PM}_{2.5}$ concentrations of 41.7, 100.7, 42.1, and 109.5 $\mu\text{g m}^{-3}$, respectively.

3.4.1 Chemical compositions

The fractions of particle type during the different kinds of observation period are shown in Fig. 6. EC particles (38.3%) were the dominant species, followed by OC (16.2%) and BB (16.0%) particles before the heating period, while OC particles (30.3%) were the most abundant species, followed by EC (20.0%) and BB (16.9%) particles during the heating period. The contribution of EC particles in polluted days increased by 1.4 and 1.8 times than that in clean days before and during the heating period, respectively, suggesting that primary sources played an important role in the forming of polluted events. In contrast to the variations of EC particles, the percentage of OC particles in polluted days decreased by 41.8% and 21.6% than that in clean days before and during the heating period, respectively. Meanwhile, the relative abundance of OC particles in the detected total particles (26.5%) in P2 was 2.3 times higher than that (11.7%) in P1. The reduction of EC particles and the increase of OC particles in P2 was mainly attributed to the accumulation of primary contaminants caused by adverse meteorological conditions, as well as the stronger secondary reactions. Similar to OC particles, the contribution of BB particles also showed a decreasing trend from the clean days to the polluted days, but they were still the second or third dominant species in the polluted days, largely because biomass burning is now still widely used for cooking and heating in the rural areas of northern China. ECOC particles accounted for 13.4% and 14.0% in C2 and P2, which were 2.7 and 3.0 times higher than that in C1 and P1, respectively. The proportions of secondary particles slightly decreased from C1 to P1, but they showed an increasing trend from C2 to P2, suggesting that the C1 was enhanced by the adverse meteorological conditions and C2 was driven by the enhanced secondary oxidation.

3.4.2 Online source analysis

Based on the method of tracer ions, the sources of single particles were divided into eight categories: dust, biomass burning, motor vehicle exhaust, coal combustion, industrial processes, secondary inorganic source, cooking, and others (Fig. 8). It is worth noting that coal combustion was the dominant source of the single particles and made up as high as 24.0% of the total sources during the heating period, which was 2.8 times higher than that (8.6%) before the heating period, suggesting that the enhancement of coal combustion for heating was the most important contributor to atmospheric particles during the heating period. However, the most significant source before the heating period was the secondary inorganic source, which accounted for 26.5% of the total sources, primarily because the more favorable meteorological conditions (e.g., including the higher temperature, stronger solar radiation, and atmospheric oxidation capacity) could promote the formation of secondary inorganic species as discussed above. The second highest source of single particles before the heating period was motor vehicle exhaust, accounting for 21.4% of the total sources, followed by industrial processes (13.8%) and dust (11.9%). However, the second dominant source of single particles during the heating period was the secondary inorganic source, contributing to 21.4% of the total sources, followed by industrial processes (14.4%) and motor vehicle exhaust (14.0%). It is interesting to note that the percentage of motor vehicle exhaust during the heating period decreased by 34.6% compared to that before the heating period, which was attributed to the restrictions on vehicle driving by the Liaocheng government during the heating period. The relative abundance (20.0%) of EC particles in detected total particles during the heating period was 1.9 times lower than that (38.3%) before the heating period. Moreover, the diurnal variation of motor vehicle exhaust source was similar to the EC particles (Fig. 6(a) and Fig. 8(a)), indicating that the EC particles were originated from the emissions of motor vehicle exhaust. Similarly, the proportions of coal combustion and OC particles presented the similar diurnal variations during the whole observation period, indicating that coal combustion was an important contributor to the OC particles. The secondary inorganic source during the heating period made less contribution (26.5%) than that (21.4%) before the heating period, again indicating a decreased contribution of secondary inorganic source during the heating period resulting from the weaker atmospheric oxidation capacity and unfavorable meteorological conditions.

As shown in Fig. 8(b), the secondary inorganic source was observed to be the most abundant source in C1, P1, and P2. Moreover, its contribution increased from clean days to polluted days, reflecting that secondary inorganic source contributed significantly to the formation of polluted days. Meanwhile, the contribution of motor vehicle exhaust source also increased by 5.6 and

Fig. 8. (a) Temporal variations in the fractions of online sources; (b) average percentages of online sources during the four stages: clean days before the heating period, polluted days before the heating period, clean days during the heating period and polluted days during the heating period.

9.1% from C1 to P1 and from C2 to P2, respectively, suggesting that the motor vehicle exhaust source is worthy of attention. In contrast, the fraction of industrial processes, dust, and biomass burning showed a descending trend from clean days to polluted days, again suggesting the minor effect of these polluted sources on the formation of polluted days.

3.5 Relative Aerosol Acidity

Aerosol acidity plays an important role in the physical and chemical properties of aerosols (He *et al.*, 2012; Huang *et al.*, 2013). The acidity of the particles cannot be calculated because of the absence of the real-time concentration of inorganic ions in this study. Instead, the relative aerosol acidity (R_{ra}), defined as the ratio of total peak areas of sulfate and nitrate to that of ammonium, can be used to estimate the acidity of aerosols (Hu *et al.*, 2018a; Meng *et al.*, 2021). Our previous study has obtained a robust correlation ($r = 0.85$, $p < 0.01$) between R_{ra} and in situ particle pH (pH_{is}) calculated from inorganic ions using the ISORROPIA-II model, confirming the validity of using R_{ra} for evaluating particle acidity (Meng *et al.*, 2021). R_{ra} increased from 36.1 ± 13.9 before the heating period to 64.8 ± 43.9 during the heating period, implying that the aerosol particles were more acidic during the heating period. Chen *et al.* (2018) has demonstrated that R_{ra} can be used to evaluate aerosol aging. The newly emitted particles are more easily neutralized by the alkalic species as they become aging, thereby resulting in a lower R_{ra} value. As shown in Fig. 9(b),

Fig. 9. (a) Hourly variations in relative acidity before and during the heating period; (b) box plot of relative aerosol acidity on different types of day; box plot of relative aerosol acidity as a function of RH (c) before the heating period, and (d) during the heating period. (^a before the heating; ^b during the heating)

R_{ra} decreased from clean days to polluted days before and during the heating period, which implied that the atmospheric particles in polluted days were less acidic and more aged. It can be concluded that the fresh particles were more acidic in Liaocheng, which was consistent with field measurements in the urban atmosphere of Xi'an, China (Chen *et al.*, 2018). The diurnal variations of R_{ra} before and during the heating period were illustrated in Fig. 9(a). The smallest R_{ra} was observed at 15:00 during the whole observation period. The acidic gases can react with NH_4NO_3 to form HNO_3 in the gaseous phase and then uptake ammonium, leading to the decreased R_{ra} (Chen *et al.*, 2018). The highest R_{ra} appeared around 23:00 both before and during the heating period, which was associated with the increased production of HNO_3 and H_2SO_4 in the aerosol

Table 2. Peak areas of SO_4^{2-} , NO_3^- , and NH_4^+ in different range of RH before and during the heating period.

RH	0–40%	40–60%	60–80%	80–100%
Before heating				
SO_4^{2-}	91403	104025	126933	137149
NO_3^-	3815083	5323351	5900973	7589426
NH_4^+	127198	174418	180360	211987
During heating				
SO_4^{2-}	5506309	6790379	6844294	4220429
NO_3^-	5316773	8846695	8994814	6419335
NH_4^+	164159	303234	278178	241925

droplets at night (Luo *et al.*, 2019). In addition, the value of R_{ra} in nighttime was higher than that in daytime during these two periods, because the diurnal variation of relative acidity was less affected by the heating (Luo *et al.*, 2019).

As shown in Fig. 9, R_{ra} showed a similar diurnal variation with RH, indicating that RH had a significant effect on the aerosol relative acidity (Zhou *et al.*, 2012). To understand fully the effect of RH on R_{ra} , we divided RH into four parts: 0–40%, 40–60%, 60–80% and 80–100%. The absorption of acidic species such as HSO_4 , HNO_3 and SO_2 can be promoted with the increase of water content (Chen *et al.*, 2018), which can lead to a stronger aerosol acidity. Therefore, R_{ra} increased from 31.5 to 38.2 with the increase of RH before the heating period (Fig. 9(c)), consistent with the larger peaks of nitrate and sulfate (Table 2). Zhang *et al.* (2021) have reported that the conversion rate of SO_2 to SO_4^{2-} , and NO_2 to NO_3^- become faster with the increase of RH. We found that the absolute-peak-areas of SO_4^{2-} and NO_3^- before the heating increased by 45746 and 3774343 with the increase of RH, respectively (Table 2). However, the relationship between R_{ra} and RH was complicated during the heating period. R_{ra} decreased from 92.9 to 57.5 when $\text{RH} < 60\%$, because the absolute-peak-areas of ammonium (303234) was 1.8 times higher when RH falling in the range of 40–60% than that (164159) when $\text{RH} < 40\%$ (Table 2). Although nitrate and sulfate also increased, the increasing amplitude of these two species was smaller than that of ammonium, largely because the enhancement of sulfur oxidation ratios and nitrogen oxidation ratios contributed the creation of atmospheric particulates, especially the transformation of NH_3 to NH_4^+ (Zhang *et al.*, 2021). When $\text{RH} > 60\%$, the peak area of NH_4^+ began to decrease, which was attributed to the unchanged gas-particle partitioning ratio of ammonium with the increase of water content when water content was higher than $100 \mu\text{g m}^{-3}$ (Zhang *et al.*, 2021). When RH was in a range of 60–80%, R_{ra} kept increasing up to a mean value of 63.7, which is attributed to the increase of SO_4^{2-} (6844294) and NO_3^- (8994814) and the decrease of NH_4^+ (278178) (Table 2). Previous studies found that the relative aerosol acidity can increase due to an increase in sulfate produced by the non-catalytic SO_2 oxidation in the presence of NH_3 when RH is in the 75–80% range (Turšič *et al.*, 2004). This implied that the increase in sulfate production was one of the important reasons for the elevating R_{ra} when RH was in the range of 60–80%. When $\text{RH} > 80\%$, R_{ra} began to decrease due to the significant reduction of nitrate and sulfate (Table 2), which was ascribed to the limit of sulfate production by acidity effect (Wang *et al.*, 2016; Zhang *et al.*, 2021).

4 CONCLUSIONS

To fully understand the impact of residential heating activities on the characteristics of atmospheric single particles in the city of Liaocheng, two typical sampling periods (i.e., before the heating, and during the heating) were compared to investigate the difference in chemical compositions, size distributions, and sources of single particles. A total of 1856200 and 2817180 single particles were collected with both positive and negative mass spectrum before and during the heating period, respectively. These single particles were classified into seven types: EC, OC, ECOC, Dust, BB, Sec, and HM particles. Compared with those before the heating period, the average concentrations of $\text{PM}_{2.5}$, CO, SO_2 , and NO_2 increased during the heating period, while the concentration of O_3 decreased, suggesting the weaker oxidation capacity during the heating period. In addition, the signal peaks of OC fragments were more obvious during the heating

period than those before the heating period, but the signal intensity of carbon ions was weaker. Meanwhile, the proportion of $^{80}\text{SO}_3^-$ and $^{97}\text{HSO}_4^-$ signal peak was higher during the heating period than that before the heating period, indicating an increased heterogeneous reaction with SO_2 to form sulfate. EC particles had greater impact on $\text{PM}_{2.5}$ in polluted days, but the fraction of OC particles decreased from clean days to polluted days. The diurnal variation trends of the motor vehicle exhaust source and EC particles proportions were similar, indicating that motor vehicle exhaust contributed significantly to EC particles. The relatively high R_{ra} during the heating period suggested that particle acidity during the heating period was stronger and the aging degree was lower than that before the heating period. The R_{ra} value was closely related to the counts of H_2SO_4 , HNO_3 , and RH, while the effect of heating activities was minor. Source identification results showed that single particles before the heating period were mostly affected by the secondary inorganic source and vehicle exhaust, whereas those during the heating period were influenced by coal combustion and the secondary inorganic source.

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