PM$_{2.5}$ Chemical Composition Analysis in Different Functional Subdivisions in Tangshan, China

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ABSTRACT

In this study, the 24-h PM$_{2.5}$ (i.e., the fine particles with aerodynamic diameter of $\leq$ 2.5 $\mu$m) samples were collected at two different functional subdivisions in the city of Tangshan during the period of July 2012 to April 2013. The months of July, October, January, and April were chosen to represent four different typical seasons. The total PM$_{2.5}$ mass was measured. PM$_{2.5}$ samples were used for the analysis of inorganic elements, ions, Organic Carbon (OC) and Elemental Carbon (EC). PM$_{2.5}$ concentration in the industrial subdivision were generally higher than those in the residential subdivision. The annual mean PM$_{2.5}$ concentrations were 196 $\mu$g m$^{-3}$ for the industrial subdivision and 116 $\mu$g m$^{-3}$ for the residential subdivision. The coefficients of divergence (CD) calculated for spring, summer, autumn and winter were 0.67, 0.35, 0.65, and 0.33, respectively. The Enrichment Factor Method (EFM) was used to help determine the original sources of these inorganic elements. Secondary water-soluble ions ($\text{SO}_4^{2-}$, $\text{NO}_3^-$, and $\text{NH}_4^+$) were the major water soluble ions in the PM$_{2.5}$ of Tangshan, and they are present in the atmosphere as $(\text{NH}_4)\text{SO}_4$ and $\text{NH}_4\text{NO}_3$. The Sulfur Oxidation Ratio (SOR) and Nitrogen Oxidation Ratio (NOR) show that the precursor conversion ratio was highest in summer. At both subdivisions, winter had the highest monthly average OM concentration while summer had the lowest.

Keywords: PM$_{2.5}$ pollution; Chemical composition; Residential subdivision; Industrial subdivision.

INTRODUCTION

PM$_{2.5}$ pollution has become a severe environmental challenge facing China in the past decades. For example, in January 11$^{th}$–13$^{th}$ 2013, the region of BTH (Beijing-Tianjing-Hebei) experienced over 50 hours in which its hourly average PM$_{2.5}$ concentrations were over 300 $\mu$g m$^{-3}$, which was 4 times of PM$_{2.5}$ Level II value (75 $\mu$g m$^{-3}$) of National Air Quality Standard of China. The mass of PM$_{2.5}$ is comprised of various cations, anions, metallic elements, and organic materials, some of which are toxic. PM$_{2.5}$ can not only make the sky ‘grey’ or ‘brown’, and bring unpleased feelings, but also poses a great threat to human health due to its chemical composition (Cao et al., 2012). It is found that extreme PM$_{2.5}$ episodes have become the 4$^{th}$ leading factors endangering the public health in eastern China, particularly for the at-risk population with respiratory and cardiovascular system problems (Yang et al., 2013). In 2010, almost 3 million people in China lost their lives due to air pollution problems (GBD, 2013). PM$_{2.5}$ pollution is getting more and more attention from the Chinese government and the public. A series of air pollution control plans have been issued by both central and local Chinese governments in order to effectively control regional PM$_{2.5}$ pollution and to improve the overall regional air quality. For example, on September 12, 2013, a plan titled “National Action Plan for Air Pollution Prevention and Control” was released by the Central Government of China. According to this plan, the Key Regions need to reduce the annual average concentration of PM$_{2.5}$ by 25% in 2017 (compared to their 2012 PM$_{2.5}$ concentration levels) (China State Council 2013). Local province also released its own Provincial Air Pollution Prevention and Control Action Plan, which is even more stringent than the national control target. As one of the most PM-polluted cities in
Hebei Province, the Plan requires the city of Tangshan to reduce its annual average PM$_{2.5}$ concentrations in 2017 by 33% instead of 25% in 2017 (Provincial Government, 2013). These actions mark crucial steps taken by the Chinese government in response to a more and more severe PM$_{2.5}$ pollution issue.

The city of Tangshan is located in the northeast part of Hebei Province. The city has experienced rapid industrialization and urbanization processes in the past three decades, which have led to a dramatic increase of local air pollutant emissions and thus deteriorated local ambient air quality. In the 2013 and 2014 annual air quality report released by the Ministry of Environmental Protection of China, the city of Tangshan was one of the top ten poorest air quality cities in China among a total of 74 reported cities (MEP, 2013; MEP, 2014). In the past two decades, a number of air pollution control studies and projects have been conducted for the city of Tangshan (Li et al., 2013a; Li et al., 2013b; Xue et al., 2013). However, most of them have focused on the pollution control of SO$_2$, O$_3$, and NO$_x$. The chemical composition can also be detected directly by on-line measurement instruments such as rapid collection of matter samples collected by membranes (Duan et al., 2007; Pathak et al., 2011; Song et al., 2012). The membrane sampling method used instruments such as X-ray fluorescence, chromatography, spectrometry to detect the particulate matter samples collected by membranes (Duan et al., 2006; Gilardoni et al., 2007; Pathak et al., 2011; Song et al., 2012). The chemical composition can also be detected directly by on-line measurement instruments such as rapid collection of fine particles and ion chromatography (RCFP-IC), HR-TOF-AMS and single particle mass spectrometry (Wen et al., 2006). Cheng et al. (2012) investigated the concentrations of water soluble cations/anions and inorganic elements in PM$_{2.5}$ samples collected from 14 major cities in China. Zhao et al. (2009) conducted a continuous 3-year measurement of PM$_{2.5}$ mass concentration in Beijing to evaluate its seasonal and diurnal variations during 2005–2007. Zhao et al. (2013) used over 400 PM$_{2.5}$ samples collected from the BTH region to analyze the spatial variations of organic carbon and black carbon in this region. The compensative chemical composition was presented by many recently studies, especially when the source apportionments were applied in China. For example Zhang et al. (2013) conducted delicate investigation PM$_{2.5}$ chemical measurements in Beijing, which included a suite of crustal and anthropogenic elements, major water-soluble ions, and OC/EC. Tao et al. (2014) characterized seasonal PM$_{2.5}$ chemical compositions in southwest China.

However, there is a lack of PM$_{2.5}$ studies in the most polluted city of Tangshan China, especially incorporated a complete chemical composition spectrum into one chemical speciation study framework. Moreover, it’s needed an insight into the overall chemical composition and its variations in the different functional subdivisions of the city. Since PM$_{2.5}$ levels and emission sources in a city could be dramatically different in a variety of functional subdivisions, it becomes important that the characteristics of PM$_{2.5}$ composition and the spatial variations of PM$_{2.5}$ concentration are well understood on the functional- subdivision basis, in order for the city to better control PM$_{2.5}$ pollution and achieve their goal. In addition, as one of the effective tools for supporting PM$_{2.5}$ emission control strategy decision making, the source apportionment can only be performed relying on the results from comprehensive chemical composition and speciation studies. This fact makes a comprehensive chemical composition/speciation study even more essential. This paper aims to characterize the overall chemical composition of the PM$_{2.5}$ from two subdivisions as well as the seasonal variations of each component in PM$_{2.5}$. The composition and speciation analysis will provide the knowledge and database for the study of PM$_{2.5}$ pollution control and further such as PM$_{2.5}$ source apportionment. It is expected that the results obtained from this study will be useful for the government of Tangshan by providing them with scientific bases for improving their performance in their regional air quality management practices.

THE STUDY AREA - THE CITY OF TANGSHAN

The city of Tangshan is located in the northeast part of Hebei Province of China (38°55′N–40°28′N, 117°31′E–119°19′E), with a population of approximately 7.6 million (Fig. 1). The city covers a total area of 13,472 km$^2$, with 11 districts. It is one of the major industrial bases for manufacturing steel products in northern China. In 2012, the steel production of Tangshan was 170 million tons, accounting for 10.8% of total steel production in China (NBS, 2012). The city is facing serious environmental pollution challenges due to its rapid industrialization and urbanization. The total coal consumption in Tangshan was 9.552 million tons in 2011 (TBS 2012), and the total vehicles has increased to 1.86 million by March 2013. Both are the major emission sources of different air pollutants. With a distance of 154 km to Beijing, Tangshan’s pollution emission could transport a significant amount of its air pollutants to Beijing through regional atmospheric circulations (Su et al., 2004).

SAMPLING AND CHEMICAL ANALYSIS

Sampling Program

Over the calendar year of 2012–2013, a PM$_{2.5}$ Observation Program was initiated and carried out for collecting the PM$_{2.5}$ samples from different functional subdivisions in the city of Tangshan. The PM$_{2.5}$ samples were collected in July and October of 2012 and January and April of 2013, representing
all four seasons of a year, and more than 480 samples were obtained, with almost 17,000 data points being measured. At least 25 samples were obtained from each month. In this study, the data collected were used for the comprehensive composition and speciation analysis of PM$_{2.5}$, as well as the source identification and apportionment. The Observation Program included two ground stations: one was located in a steel factory, representing the industrial subdivision and the other one was located in the municipal environmental monitoring station of Tangshan, representing the residential subdivision. The 24-h (09:00 to 09:00 local time) PM$_{2.5}$ samples were collected at both functional subdivisions in the city of Tangshan (as shown in Fig. 1). The industrial subdivision is located in the northeast suburb of Tangshan, with many steel and iron manufacturing plants in it. The industrial subdivision is surrounded by farmlands in all directions. The observation station installed at the industrial subdivision was located on the roof of a building which is 30 m above ground. The residential subdivision is located in the center of Downtown Tangshan. The observation station was installed on the roof of a building (15 m above ground) inside the municipal environmental monitoring station. Nearby this observation station are many residential apartment buildings and shopping malls; the traffic on the roads nearby is very busy. The distance between two observation stations is approximately 10.5 km.

Two simultaneous filters were collected for each daily sample with one of the Whatmans 41 filter and the other of the quartz filter. The Whatmans 41 membrane was not tolerant to high temperature, while it’s blank value was low and the adsorption efficiency of acid gas was very high. It was suitable for elements and ions analysis. The quartz filters were high temperature tolerance and high efficiency of complement, but containing elements Si and Al. The samples collected on the quartz filters were used for the detection of Organic Carbon (OC) and Element Carbon (EC). The comparing these two filters for PM$_{2.5}$ collecting efficiency and their effects on chemical analysis was studied by He et al. (2011). All the samplers (Wuhan Instrument Cooperation Ltd.) were operated at a flow rate of 100 L min$^{-1}$. All the filters were weighed before and after sample collections in the lab using a one over ten-thousand Analytical Balance. The filters were equilibrated in a constant temperature (20 ± 5°C) and humidity (40 ± 2%) chamber for 48-h. Before placing the filters back into the samplers, all flow meters were calibrated and the sampler passed the tightness test. The sample measurements were conducted in a certified lab (Key Laboratory of Beijing on Regional Air Pollution Control, Beijing). The laboratory had carried out lots of research on PM$_{2.5}$ in recent years (Cheng et al., 2013; Lang et al., 2013; Wang et al., 2015). The data of SO$_2$ and NO$_x$ concentration were provided by the Tangshan Environmental Monitoring station. The meteorological data (temperature, humidity and rain condition) were recorded for each sampling day.

Chemical Analysis and Methods

Each Whatmans 41 filter (with PM$_{2.5}$ samples on it) was cut into four identical pieces, PM$_{2.5}$ samples on one piece were extracted for the analysis of inorganic elements (i.e., Na, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, S, Fe, Ni, Cu, Zn, As, Se, Sr, Cd, Sb, and Pb). PM$_{2.5}$ samples on the second piece were used to analyze the ions (SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$). The inorganic elements were measured by inductively coupled plasma-mass spectrometry (ICP-MS, 7500a, Agilent). The ions were analyzed by ion chromatograph (Metrohm 861 Advanced Compact IC). The high concentration samples were diluted 10 times for measurement. Quartz-fiber filter samples were extracted for the analysis of the Organic Carbon (OC) and Elemental Carbon (EC). The OC and EC were measured using a Thermal/Optical Carbon Analyzer (DRI, Model 2001). SOC was calculated by EC tracer method (Castro et al., 1999).

Quality assurance and quality control tests (e.g., analysis of blanks, method detection limit, recovery efficiency) were conducted. During the laboratory analysis, a blank filter fiber and the standard chemical samples were tested by ICP-MS, ion chromatograph and Thermal/Optical Carbon
Analyzer to ensure data quality. For inorganic elements test, the RSD value of internal standard elements (72Ge 89Y 103Rh 115In 159Tb) was kept less than 5%, otherwise the sample needed to be redetected. Standard Reference Materials (SRMs) obtained from the National Research Center for Certified Reference Materials, China, were analyzed for quality assurance purposes. For ion chromatograph test, the relative standard deviation of each ion was less than 5% for reproducibility test. The limits of detection (S/N = 3) were less than 0.04 mg L⁻¹ for anions and 0.006 mg L⁻¹ for cations. The detailed methods for analysis can be found in Han et al. (2007), Wang et al. (2007) and Chow et al. (2007).

In this study, the coefficient of divergence (CD) was calculated to illustrate the distance between two sets of inorganic element data collected at the industrial and residential subdivisions (Zhang et al., 2000).

\[
CD_{jk} = \sqrt{\frac{1}{p} \sum_{i} \left( \frac{X_{ij} - X_{ik}}{X_{ij} + X_{ik}} \right)^2}
\]

where j and k stand for industrial and residential subdivisions, p is the number of investigated components, and X_{ij} and X_{ik} represent the average mass concentrations of a chemical component I at sites j and k. If the CD approaches zero, the two sampling sites are similar. If the CD approaches one, the two sampling sites are very different.

The Enrichment Factor Method (EFM) was used in this study, to help determine the original sources of these inorganic elements (Gao et al., 1992). The EFM uses the element Al as the reference element for calculating the enrichment factor value, and the equations is given as follows:

\[
EF = \frac{\left( \frac{E}{Al} \right)_{samples}}{\left( \frac{E}{Al} \right)_{crust}}
\]

where E represents the annual average concentration of a specific inorganic element; EF is the enrichment factor; Samples represents PM_{2.5} samples collected in this study; Crust represents standard crust in earth; \((E/Al)_{crust}\) is the standard ratio of a specific element E to Al in the crust of Hebei Province (MEP, 1990). If the EF is higher than 10, the element is believed to be from anthropogenic sources; If the EF is in between 1 to 10, the element is from the natural sources such as soil dust (He et al., 2002).

RESULTS AND DISCUSSION

Spatial and Temporal Variations of PM_{2.5}

The sampling program generated 119 samples at the residential subdivision and 106 samples at the industrial subdivision. In some days, the samples were not available due to mechanical failure of the samplers. If we met with mechanical failure, we will extend the sampling time to ensure the 25 samples collected in each season.

The annual mean concentrations of PM_{2.5} for both subdivisions were calculated. The industrial subdivision had a value of 196 µg m⁻³, which was 5.6 times of PM_{2.5} Level II National Air Quality Standard (35 µg m⁻³) (MEP, 2012). The residential subdivision was 116 µg m⁻³, which was 3.2 times of the same standard. As a comparison, the average PM_{2.5} concentration at the industrial base in middle west US was 17 µg m⁻³ (Lazaridis et al., 2001).

Fig. 2 presents the temporal variations of PM_{2.5} mass concentration in each monitoring month, which can represent to some extent the changes of PM_{2.5} in different seasons.

According to the data measured, the monthly average concentrations of PM_{2.5} at the industrial subdivision were 130 µg m⁻³ for summer, 155 µg m⁻³ for autumn, 304 µg m⁻³ for winter, and 195 µg m⁻³ for spring. On the other hand the monthly average concentrations of PM_{2.5} at the residential subdivision were 81 µg m⁻³ for summer, 98 µg m⁻³ for autumn, 145 µg m⁻³ for winter, and 101 µg m⁻³ for spring. It is found that the monthly PM_{2.5} concentration change has the same trend at both subdivisions, i.e., winter > spring > autumn > summer. Winter seasons have the highest PM_{2.5} concentrations mainly due to increased coal consumptions in winter for heating purpose as well as the superior atmospheric stability which impedes the diffusion and dispersion for PM_{2.5}. Spring seasons were ranked the second in term of PM_{2.5} pollution due mainly to the fugitive dust emissions from the bare land and construction sites caused by the frequent spring winds. Summer seasons have the best PM_{2.5} quality during the year mainly because more precipitations occur in summer and wash the PM_{2.5} out of the air, and also the increased BLH (Boundary Layer Height) helps the air disperse (Guinot et al., 2007). In autumn as the BLH and precipitation gradually decrease, PM_{2.5} concentration becomes a little higher than summer. Also, since autumn seasons have less windy days, the PM_{2.5} contribution from fugitive dust in autumn is less than spring.

The correlation analysis for PM_{2.5} concentrations between two subdivisions were conducted in this study. The correlation coefficient obtained is 0.68, indicating that both sites experienced similar PM_{2.5} pollution processes for the sampling period. Also, this observation was confirmed by the similar trends of PM_{2.5} changes with time (as shown in Fig. 2). This observation demonstrated that the PM_{2.5} pollution could possibly be characterized as a regional issue.

Fig. 2 also shows that the PM_{2.5} concentrations in the industrial subdivision were generally higher than that in the residential subdivision, and the elevated emissions from the intensive industrial activities could be the obvious reason. However, there were a total of 19 days during which the residential subdivision had higher PM_{2.5} concentrations than the industrial subdivision. The study showed that the heavy local traffic at the residential subdivision located at the downtown core as well as the favorable local weather conditions at the industrial subdivision could be the two possible causes. For example, on the 10th of January, the residential subdivision had a higher PM_{2.5} concentration than the industrial subdivision, with a difference of 83 µg m⁻³. On July 15th, the PM_{2.5} concentration at the industrial subdivision began to decrease, but the concentration at the residential subdivision increased. According to the meteorological data recorded, the pollutant dispersion condition of industrial...
subdivision was better than that of residential subdivision. The industrial subdivision was with showers on July 15th. And PM$_{2.5}$ in the air was washed by the rainfall. Besides the wind speed is 4 m s$^{-1}$ in industrial subdivision, 0 m s$^{-1}$ for residential subdivision.

**Characterization of Inorganic Elements in PM$_{2.5}$**

Fig. 3 presents the scatter plots to compare the monthly average concentrations of inorganic elements identified in the PM$_{2.5}$ samples collected at the industrial and residential subdivisions for summer, autumn, winter and spring, respectively. It shows a total of 18 inorganic elements were identified from the PM$_{2.5}$ sample, including Na, Mg, Al, S, Ca, Fe, Zn, Pb, Mn, Ti, Cu, Cr, Ni, Sr, V, As, Sb, and Cd. Fig. 3 shows that the concentrations of all inorganic elements at the industrial site were higher than that of the residential site in the months of spring, summer and autumn. In winter some of the inorganic elements had higher concentrations at the residential site while the others had higher concentrations at the industrial site. It is understood that the industrial emissions (e.g., the steel manufacturing processes) played a major role in contributing to the elevated concentrations of these elements in all months. According to the meteorological data record (Micaps, China Meteorological Administration), the west-northwest and northeast wind direction of Tangshan is frequently in the month of January 2013 (as Fig. 4 shown). There were a number of construction projects undertaken in the west-northwest direction of sampling station, which is upwind direction of the residential subdivision. It brought more elements from the construction sites (such as Ca, Al, Mg, Ti) and the diesel fueled vehicles (such as V) in the residential subdivision. This resulted in higher concentrations of those elements at the residential site than the industrial site.

The scatter plots in Fig. 3 also show that the 18 inorganic elements could be divided into two groups. The group of Na, Mg, Al, S, Ca, Fe, Zn, Pb, Mn, Ti had relatively higher concentrations, and the group of Cu, Cr, Ni, Sr, V, As, Sb, and Cd had relatively lower concentrations. In this study, the coefficient of divergence (CD) was calculated for each month to illustrate the distance between two sets of inorganic element data collected at the industrial and residential subdivisions. The CD takes the values of (0, 1), and the smaller the CD values are, the more similarity exists between two sets of data (Zhang et al., 2000). It was found that the CD values for spring, summer, autumn and winter were 0.67, 0.35, 0.65, and 0.33, respectively. It indicates that spring and autumn had more difference in the pattern of inorganic element pollution, while summer and winter had less difference in this regard. As Fig. 4 shown, in summer and winter, the northeast, south and southwest wind directions in the city of Tangshan were frequently. The two sampling sites relative position were located in the upwind and downwind direction of dominant wind at two seasons. The completely wind directions in these two seasons could help exchange the air pollutants between two subdivisions. Thus, it is more advantageous to the uniform distribution of pollution elements.

These inorganic elements were either from the natural sources or anthropogenic sources. In this study, the Enrichment Factor Method (EFM) was used to help determine the original sources of these inorganic elements Fig. 5 presents the calculated enrichment factors for each inorganic element in the PM$_{2.5}$ samples collected from two subdivisions. The elements of Fe, Ca, Na, Al, Mg, and Ti at both subdivisions were all less than 10, and this is in line with the fact that these elements are the major elements in the crust. All other elements came from various anthropogenic emission.
sources in the city of Tangshan, particularly from major industries such as steel manufacturing, ceramic production, and copper and zinc metallurgy. For example, elements of V, Cr, and Sr originated from the metal smelting process (Gu et al., 2011); elements of Mn, Cu, Zn, and Pb came from the ceramic production, road traffic, and copper and zinc metallurgy (Querol et al., 2007). Among all the elements emitted from the anthropogenic sources, S had the highest monthly average concentrations at both sites throughout the entire year. In winter, the monthly average S concentration reached as high as 16.62 µg m⁻³ at the industrial site while that at the residential site was 11.00 µg m⁻³. This observation demonstrated that the city of Tangshan relies heavily on coal combustion for its winter heating and industrial processes.

**Secondary Water Soluble Ions (SWSI)**

Secondary water-soluble ions include \( \text{SO}_4^{2-}, \text{NO}_3^- \), and \( \text{NH}_4^+ \). They were the major water soluble ions in the PM\(_{2.5}\) samples collected from both subdivisions, accounting for 20.56%–45.68% in mass ratio.

Fig. 6 presents the monthly average concentrations of each SWSI in different months at both subdivisions. The SWSI concentrations at the residential site were generally less than that at the industrial site in each respective month. The month of winter had the highest SWSI concentrations, and summer had the second highest SWSI concentrations. The higher SWSI concentrations in winter were associated mainly with the emissions from the coal combustion for winter heating as well as the worse atmospheric conditions for air pollutant dispersion (Li et al., 2013c). In summer, the humid and warm weather could dramatically facilitate the formation of the SWSI through photochemical processes (Gao et al., 2011).

In terms of seasonal variation patterns, different SWSI show commonalities and differences. For example, both \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) had the highest concentrations in winter and the lowest in spring; \( \text{SO}_4^{2-} \) concentration in summer was higher than autumn while \( \text{NO}_3^- \) concentration showed the opposite trend. The highest \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) concentrations occurred in winter due to the increasing emissions of \( \text{SO}_2 \) and \( \text{NO}_x \) from coal combustion. More intensive photochemical reaction under the higher \( \text{O}_3 \) level and temperature in summer would facilitate the secondary formation of \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) (Huang et al., 2015). However in fine particles \( \text{NO}_3^- \) exists mainly in the form of \( \text{NH}_4\text{NO}_3 \), which is thermodynamically unstable. The partitioning of \( \text{NO}_3^- \) between the gas and
particulate phases is affected by temperature. At high temperature, particle-to-gas conversion of NH$_4$NO$_3$ is favored. The particulate NO$_3^-$ could be easily dissociated into gaseous NOx at summer temperatures (Guo et al., 2010).

In terms of NH$_4^+$ variations at different subdivisions, the residential subdivision had a relatively higher NH$_4^+$ concentration in summer than in autumn, while the industrial subdivision had an opposite trend. The main sources of NH$_3$ in Tangshan are farm-land (fertilizer application), livestock, human excrement, biomass burning. The farmland was the dominant source impacted the monthly variation trend of the NH$_3$ emission (Zhou et al., 2015). As indicated earlier, the industrial subdivision was surrounded by many farmlands, and autumn is the time of fertilizer application.
for crops (wheat) and plants in the city of Tangshan. The high emission rates in this season could be attributed to the basal dressing and top dressing of wheat (Huang et al., 2012). N-fertilizer could be easily dissociated to release NH$_4^+$ to the ambient air, which could cause the elevated concentration of NH$_4^+$ in the industrial subdivision in autumn.

The possible forms of NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ existing in the atmosphere were also examined through the correlation analysis, and the correlations of NH$_4^+$ with NO$_3^-$ and NH$_4^+$ with SO$_4^{2-}$ are provided in Fig. 7. Strong correlations between NH$_4^+$ and NO$_3^-$ and between NH$_4^+$ and SO$_4^{2-}$ have been observed for most of the cases. The high correlation coefficients revealed that (NH$_4$)$_2$SO$_4$ and/or NH$_4$HSO$_4$, and NH$_4$NO$_3$ were major sulfate and nitrate salts (Sun et al., 2006). Ammonia was believed to be neutralized first by sulfuric acid to form ammonium sulfate or ammonium bisulfate, and the excess NH$_3$ could react with nitric acid to form NH$_4$NO$_3$. The strong mean molar ratios of NH$_4^+$ to SO$_4^{2-}$ in two subdivision, indicating that SO$_4^{2-}$ and NO$_3^-$ are sufficiently neutralized by NH$_4^+$ and that particulate sulphate and nitrate could be formed by gas-phase reactions of acid precursors with NH$_3$ and could be enriched in particulate (Li et al., 2013). Some correlation coefficients were less than 0.7, and this could be attributed to certain competing cations (such as K$^+$) emitted into the atmosphere from the biomass burning in July and October (Tao et al., 2013). This could result in less formation of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. Ammonia was believed to be neutralized first by sulfuric acid to form ammonium sulfate or ammonium bisulfate, and the excess NH$_3$ could react with nitric acid to form NH$_4$NO$_3$. The strong mean molar ratios of NH$_4^+$ to SO$_4^{2-}$ in two subdivision, indicating that SO$_4^{2-}$ and NO$_3^-$ are sufficiently neutralized by NH$_4^+$ and that particulate sulphate and nitrate could be formed by gas-phase reactions of acid precursors with NH$_3$ and could be enriched in particulate (Li et al., 2013). Some correlation coefficients were less than 0.7, and this could be attributed to certain competing cations (such as K$^+$) emitted into the atmosphere from the biomass burning in July and October (Tao et al., 2013). This could result in less formation of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. In this study, the equivalent concentration of NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ were also calculated to estimate the neutralization ratio (NR) index. The neutralization ratio was used to estimate the acidity of airborne particulates by calculating the relationship among the NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ present in the particulates (Li et al., 2008). The neutralization ratio equation as follow (Colbeck and Harrison 1984).

$$NR = \frac{NH_4^+ (\text{eq m}^{-3})}{NO_3^- (\text{eq m}^{-3}) + nss.SO_4^{2-} (\text{eq m}^{-3})}$$

where eq m$^{-3}$ denotes equivalent normal concentration. For the case where NR > 1, the excess in NH$_4^+$ and the airborne particulates were considered to be basic. For NR = 1, all three ions and the airborne particulates were considered to be neutral. For NR < 1, the excess in NO$_3^-$ and SO$_4^{2-}$ and the airborne particulates were considered to be acidic. The NR at the residential subdivision were 1.21 for spring, 1.68 for summer, 1.71 for autumn, 1.5 for winter. On the other hand the NR at the industrial subdivision were 1.11 for spring, 1.30 for summer, 1.76 for autumn, 1.51 for winter. The data indicated that NH$_4^+$ was richer compared to SO$_4^{2-}$. This suggested that the dominant compounds of inorganic water-soluble species were (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$.

In PM$_{2.5}$ source apportionment studies, sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) were commonly used to describe the conversion of precursors SO$_2$ and NO$_x$ to SO$_4^{2-}$ and NO$_3^-$, respectively. Higher SOR and NOR indicate the existence of conversion process and more secondary aerosol formation (Wang et al., 2005). Table 1 gives the calculated SOR and NOR in different months for both subdivisions. The table shows that the conversion ratio was highest in summer among the seasons at both subdivisions, due mainly to the conversion-favoring factors in summer such as high temperature and relative humidity. SOR and NOR at the industrial subdivision were generally higher than the residential subdivision. It’s suggested that the secondary formation of secondary water soluble ions from precursor gases were strongly occurred in the industrial subdivision compared to that in residential (except during winter). The precursor gases (i.e., SO$_2$ and NO$_x$), oxidants, cloud, surface area availability, temperature and RH also exerted some influences on these variations of SOR and NOR (Du et al., 2010; Tao et al., 2013).

The ratio of [NO$_3^-$]/[SO$_4^{2-}$] is commonly used to determine if the dominant pollution sources are mobile or stationary. When the ratios are high (greater than 1), the local dominant sources are mobile; Otherwise the dominant sources are
The correlations of \( \text{NH}_4^+ \) vs \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) vs. \( \text{SO}_4^{2-} \).

**Table 1.** The sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR).

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<tr>
<th></th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re-Sub</td>
<td>0.19</td>
<td>0.06</td>
<td>0.52</td>
<td>0.18</td>
</tr>
<tr>
<td>NOR</td>
<td>0.14</td>
<td>0.12</td>
<td>0.33</td>
<td>0.31</td>
</tr>
<tr>
<td>In-Sub</td>
<td>0.13</td>
<td>0.09</td>
<td>0.66</td>
<td>0.24</td>
</tr>
<tr>
<td>NOR</td>
<td>0.20</td>
<td>0.21</td>
<td>0.36</td>
<td>0.38</td>
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</tbody>
</table>

The ratios of \([\text{NO}_3^-]/[\text{SO}_4^{2-}]\) based on the annual average concentrations at two subdivisions in the city of Tangshan were 0.73 and 0.89, respectively, which indicates that the local dominant pollution sources were stationary. The residential subdivision had a relatively higher \([\text{NO}_3^-]/[\text{SO}_4^{2-}]\) ratio, mainly because the residential site and its surrounding areas had much heavier traffic; thus, more vehicle emissions affect this area.

**Carbon Species in PM2.5 Samples**

The carbon species were important chemical components of PM2.5 in Tangshan. The carbon species are usually classified into organic carbon (OC) and element carbon (EC). The monthly average OC and EC concentrations during the sampling period were between (10.86, 59.43) \(\mu\text{g m}^{-3}\) and (4.65, 11.85) \(\mu\text{g m}^{-3}\), respectively. Organic matter (OM) was converted from OC by multiplying by a coefficient of 1.6. Fig. 8 presents the monthly average OM and EC concentrations from all samples for both subdivisions. At both subdivisions, winter had the highest monthly average OM concentration while summer had the lowest, and their differences were obvious. On the contrary, EC concentration remained constant throughout the year at both subdivisions, which had similar concentration levels. The higher OM concentration in winter was due mainly to more coal combustion (from heating), condensation of volatile organics, atmospheric stability, and more vehicle emissions during auto starting (Chow et al., 1992; He et al., 2006).

The correlation coefficients between OC and EC were calculated for both subdivisions. The residential subdivision had a coefficient sequence of winter (0.97), autumn (0.85), spring (0.83), and summer (0.70). The industrial subdivision had the same order: winter (0.95), autumn (0.79), spring (0.73), and summer (0.69). The levels of correlation coefficients can indicate the source of OC and EC (Turpin et al., 1991). According to the correlation coefficients obtained, the OC and EC might come from the same sources (such as biomass burning and coal combustion) in winter and autumn (Zhang et al., 2009a; Yang et al., 2012).

The ratio of OC/EC was often used to evaluate the formation of secondary organic carbon (SOC). Fig. 8 also presents the ratios of OC/EC in different months at both subdivisions. It shows that the OC/EC ratios in winter,
spring and autumn were greater than 2 at both subdivisions, and summer has the OC/EC ratio slightly lower than 2. Winter had the highest ratio and summer had the lowest ratio, which matches the findings by Zhao et al. (2013). Usually, the SOC can be formed when the ratio of OC/EC is over 2 (Chow et al., 1996). SOC was calculated by EC tracer method, and the formula is given as follows (Castro et al., 1999):

$$SOC = OC - EC \times \left(\frac{OC}{EC}\right)_{\text{min}}$$

(4)

SOA (secondary organic aerosol) can be converted from SOC by multiplying by a coefficient of 1.6. The SOA concentrations in both subdivisions were given in Fig. 8. The annual average SOA concentrations were 24.64 µg m⁻³ and 12.67 µg m⁻³ at the industrial and residential subdivisions, respectively. Photochemical activity was clearly the main factors responsible for SOA formation (Kim et al., 2012). The formation of SOA usually occurs in summer and autumn, which is more intense in the appropriate meteorological conditions (He et al., 2011). However, in this study the highest SOA concentration appeared in winter. Many studies had obtained the same results. It’s mainly due to its low temperature and low mixing layer height in favor of SOC formation (Strader et al., 1999; Huang et al., 2006).

$PM_{2.5}$ Mass Balance

In this study, total $PM_{2.5}$ mass was classified into primary compositions and secondary compositions. Since the inorganic elements/water soluble ions and carbon species were collected by two different filters, the mass balance of total $PM_{2.5}$ was calculated by combining the mass percentage measured from each filter. Primary compositions included soil dust, primary organic matter, elemental carbon, and pollution elements. Pollution elements contain the inorganic elements (e.g., As, V, Mo, Cd, Sr, Ni, Sb, Cr, Cu, Mn, Pb, Zn), which related to anthropogenic activity. The secondary compositions included secondary organic matter, $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ (He et al., 2011). The mass of soil dust was estimated using the oxides of Al, Ca, Ti, Fe, Mg, Na and K, and the equation is given below (Kim et al., 2001):

$$\text{Soil Dust} = 2.20 \times Al + 2.49 \times Si + 1.63 \times Ca + 2.42 \times Fe + 1.94 \times Ti$$

(5)

In this study, Si was not measured due to the lack of a standard solution and method for this element, and its concentration was estimated to be four times that of Al (Yuan et al., 2008).

Table 2 gives the chemical compositions in mass percentage for the $PM_{2.5}$ samples collected at both subdivisions. In spring, the soil dust had the highest mass percentage in the $PM_{2.5}$ total mass, due to high wind speed and dry weather; accordingly, the mass of primary compositions in total $PM_{2.5}$ increased and the mass of secondary compositions in total $PM_{2.5}$ decreased. During the sampling period the mass percentage of secondary compositions out of the total $PM_{2.5}$ ranged from 26.15% to 54.97%, with the highest appearing in summer. The conversion rates of gaseous precursors to secondary particulates were much higher due to the strong radiation, high temperature and humidity in summer.

In this study, the mass percentage of unidentified compositions varied between months, with an estimated range of 12.63% to 25.95%. The levels of unidentified components were affected by a few factors, including the measurement errors, water content in the sample, errors from soil dust and SOC calculations, and more importantly, the actual chemical components which cannot be measured by available laboratory instruments. Previous studies show that unidentified compositions could account for about 20% of total $PM_{2.5}$ mass concentration (He et al., 2001). The detailed distribution of mass percentage for each chemical composition
Table 2. Mass percentage of chemical compositions in PM$_{2.5}$ samples on a monthly basis at both subdivisions (%).

<table>
<thead>
<tr>
<th>Season</th>
<th>Industrial Subdivision</th>
<th>Residential Subdivision</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spring</td>
<td>Summer</td>
</tr>
<tr>
<td>POA</td>
<td>16.25</td>
<td>8.00</td>
</tr>
<tr>
<td>SOA</td>
<td>5.56</td>
<td>9.29</td>
</tr>
<tr>
<td>EC</td>
<td>4.00</td>
<td>5.81</td>
</tr>
<tr>
<td>Soil Dust</td>
<td>22.22</td>
<td>16.61</td>
</tr>
<tr>
<td>Pollution Elements</td>
<td>6.54</td>
<td>2.00</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>8.52</td>
<td>24.01</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>7.00</td>
<td>10.62</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>3.94</td>
<td>11.05</td>
</tr>
</tbody>
</table>

Fig. 9. The mass percentage of chemical compositions in PM$_{2.5}$ on an annual average basis at two subdivisions.

in the PM$_{2.5}$ samples is graphically presented in Fig. 9, and this plot is based on the annual average concentration for each component. Fig. 9 shows that the chemical compositions of PM$_{2.5}$ at two subdivisions had very minor differences during the sampling periods. This indicates that the PM$_{2.5}$ pollution is a regional issue. Among all the compositions, water soluble particles and carbon species were the major component of PM$_{2.5}$, accounting for over 50% of total PM$_{2.5}$ mass concentration.

CONCLUSIONS

During the year of 2012–2013, a PM$_{2.5}$ Monitoring Program was conducted to collect PM$_{2.5}$ samples in four different months at a residential subdivision and an industrial subdivision for the city of Tangshan. The data collected were used for a comprehensive chemical composition analysis of PM$_{2.5}$ as well as its source identification. This paper focuses on the characterization of PM$_{2.5}$ chemical composition and the presentation of the analysis results. The results show that the city of Tangshan is facing serious PM$_{2.5}$ pollution issues, particularly in industrial subdivisions. Winter seasons have the highest PM$_{2.5}$ concentrations, and spring seasons are ranked second, while summer seasons have the best PM$_{2.5}$ quality. Among all the PM$_{2.5}$ components, the inorganic elements of Fe, Ca, Na, Al, Mg, and Ti all originated from crust for both subdivisions, and other inorganic elements were discharged from various anthropogenic emission sources. The SWSI were the major water soluble ions in the PM$_{2.5}$ samples, accounting for 20.56%–45.68% in mass ratio. In addition, NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ were present in the atmosphere in the forms of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ with their conversion ratios being highest in summer. At both subdivisions, winter had the highest monthly average OM concentration while summer had the lowest. EC concentration remained constant throughout the year at both subdivisions,
and their concentration levels were similar. The SOA formed in both subdivisions, with the highest SOA concentration appearing in winter.

ACKNOWLEDGEMENT

This research was supported by the Natural Sciences Foundation of China (No. 41305130&91544232), the Ministry of Environmental Protection Special Funds for Scientific Research on Public Causes (No. 201409006 &201409007), the National Science and Technology Support Project of China (2014BAC23B03). The authors are grateful to the editors and the anonymous reviewers for their insightful comments.

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