Online monitoring concentrations of PM at five sites were obtained from 01/01/2016 to 31/12/2016 in Laiwu, China, and PM$_{2.5}$ filters were manually sampled for total 34 days at the same sites in four seasons in 2016. PM pollution sources, including soil dust, urban dust, construction dust, coal-fired power plants dust, steel plant dust and motor vehicle exhaust dust were sampled, respectively. The overall mean PM$_{2.5}$/PM$_{10}$ ratio (0.57) in Laiwu was at a relatively lower level compared with that in other Chinese cities, which was higher in winter, indicating fine particulate was the main contributor of atmospheric pollution in this period. NH$_4^+$ mainly existed in the form of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ during the sampling periods. Higher sulfate and NH$_4^+$ concentrations were in summer while higher nitrate concentrations prevailed in winter. The annual value of OC/EC was (5.38 ± 1.70), higher in summer and lower in winter, and the calculated SOC/OC value (%) was (43.68 ± 12.98)%. The characteristic components were Si, Fe and Ca in urban dust and soil dust; Ca, Mg, and NH$_4^+$ in construction dust; Fe, Ca and SO$_4^{2-}$ in steel dust; OC, EC and Si in motor vehicle exhaust dust; SO$_4^{2-}$, Al and NH$_4^+$ in power plant dust. Compared with other cities at home and abroad, it was found that the concentrations of metal elements in Laiwu were significantly higher than those in foreign cities, and at a medium level in China. With the improved CRAESCMB model, the urban dust was regarded as the receptor and the source of PM$_{2.5}$ and apportioned its secondary sources contributions to PM$_{2.5}$. The CMB results showed the contributions of secondary sources including sulfate (17%), nitrate (17%) and SOC (13%) to PM$_{2.5}$ accounted for nearly half of all sources. Therefore, more attentions should be paid on secondary sources from the primary emission sources of the motor vehicle exhaust, coal combustion sources especially.

In recent decades, the rapid development of China’s economy, which has involved extensive industrialization and urbanization, has triggered many pollution problems. In particular, there has been an increase in the number of haze or smog episodes driven by elevations in atmospheric particulate matter (PM), especially particles with aerodynamic diameters <2.5μm (PM$_{2.5}$) and 10μm (PM$_{10}$). It is commonly known that PM pollution is associated with poor atmospheric visibility, high health risks, and global climate change, light extinction, and traffic accidents at the regional as well as local scale. To improve air quality, the Atmospheric Pollution Prevention and Control Action Plan was enacted by the Chinese government (Chinese Ministry of Environmental Protection) in 2014. Since then, air quality across the country has improved greatly. However, air pollution in many cities containing industrial locations remains severe. To assist with such efforts, many scholars have carried out studies of the characteristics of atmospheric pollution, which have provided a basis for air pollution control and have facilitated sources analyses. Researchers also found that PM$_{2.5}$ concentrations exhibited seasonal variations, wherein the levels were the highest in winter and lowest in summer. Chemical compounds of PM are known to contain ionic species, carbonaceous species, and metals and metalloids. Secondary inorganic species, such as NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$, which are water-soluble ions, are also known to be present in PM$_{2.5}$ and can comprise a large fraction of PM in the atmosphere. Organic carbon (OC), composed of thousands of organic compounds, originates from both natural and artificial sources. Element carbon (EC), with relatively stable chemical properties, is directly emitted from primary combustion and influences the global climate system through its impact.

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on radiative forcing. High correlations between OC and EC have been found in PM$_{10}$ and PM$_{2.5}$\textsuperscript{13}. It is generally acknowledged that local emissions remain an important factor affecting environmental quality. EPA CMB (Chemical Mass Balance) receptor model is a sources resolution technique to indicate the contribution of various pollution sources to receptors\textsuperscript{14,15}, and has been extensively used for the apportionment of PM in the United States, Europe and Asia\textsuperscript{16–20}. Although many researchers have conducted pollution characterization and sources assessment studies of PM$_{10}$ and PM$_{2.5}$ in ambient air, overall, these works were mainly conducted in developed cities and fast-developing areas\textsuperscript{21–23}. Presently, there have been few detailed studies on atmospheric PM pollution in less urbanized and slow-developing cities\textsuperscript{6}. Such studies are necessary because regional atmospheric environments are interconnected, and the ambient air in one city can affect the air quality in other cities via meteorological transport processes. In order to better evaluate the present situation of ambient air in a less developed city, a comprehensive study of the air pollution characteristics and sources of Laiwu must also be conducted.

Laiwu, an urban residential area of a typical steel industrial city in China, are investigated in this study. To the best of the author’s knowledge, few literatures has reported pollutant results for Laiwu. Laiwu, a medium-sized urban area, is located in the center of Shandong Province at the eastern foot of Mount Tai. This area is an important steel and energy production base in northern China and has experienced rapid development in recent years. Presently, it is one of the most heavily polluted areas in Shandong. Laiwu covers an area of 2,422 km$^2$ and has a population of more than 1.27 million. Coal is the main energy source, and industry consumption accounts for more than 75% of the coal use. Many steel industries, located in the southern, western and northern parts of the city, have different producing processes, such as steel making, iron making, sintering and coking. Two major coal-fired power plants are located in the northeast and central of the city.

In this paper, the characteristics of atmospheric pollution and the chemical compositions of the particles during the monitoring period of one year in Laiwu were analyzed comprehensively. Hourly online monitoring data for PM$_{1.5}$ and PM$_{10}$ at different sites in Laiwu were obtained from the air quality monitoring network for the analysis, and manually sampled monitoring data were also collected. These data enabled us to gain a better understanding of the characteristics and chemical compositions of air pollutants in Laiwu. In addition, the composition spectrum of environmental receptors and seven sources of pollution in Laiwu City were also investigated, including water-soluble ions, inorganic elements and carbon components. The improved Chemical Mass Balance (CMB) model was used to analyze the sources distribution and air pollution levels in Laiwu were compared to those of other major cities. The results were helpful for the government to take effective PM pollution control strategies.

Materials and Methods

Data and samples collection. According to the relevant requirements of the Technical Specifications for Environmental Air Quality Monitoring Points (Trial) (HJ664-2013), fully considering complex factors such as climate, geographical conditions and pollution sources of Laiwu City, five sampling sites (1# Old apartment, 2# New first school, 3# Technical college, 4# Vegetable oil plants, and 5# Steel Environmental Protection Agency) were selected for obtaining online PM$_{1.5}$ and PM$_{10}$ and sampling manually the filters for PM$_{1.5}$ chemical compositions, located in the different direction of the city, affected by the steel industries and power plants. Figure 1 shows the location of Laiwu and the distribution of ambient air sampling sites. Total 170 valid quartz filters (pall 7203, $\varnothing$90mm) and 170 valid organic PTFE filters (Whatman, $\varnothing$90mm) of PM$_{2.5}$ receptor samples were respectively obtained. These PM$_{2.5}$ filter samples were collected for 34 days at every site in 2016 (January 18–24, May 6–17, August 9–15, and October 29–November 5), representing collection in winter, spring, summer, and autumn. Each PM$_{1.5}$ filter sample was collected for 24 hours using a median-flow particle samplers (Tianhong, Wuhan, Co. Ltd) with flow rate of 100 L/min. Model 602 Beta Plus dual-channel particulate matter automatic monitors (API Corporation, USA) were used as the online monitoring instruments for PM$_{10}$ and PM$_{2.5}$. The online hourly monitored concentrations of PM$_{10}$ and PM$_{2.5}$ at the same five sites as manual samples in Laiwu were obtained from 01/01/2016 to 31/12/2016, which indicated the PM pollution temporal characteristics and levels in a typical steel urban site for the whole year.

According to the Technical method guide for analytical monitoring of ambient air particle sources of China\textsuperscript{24}, fully considering local air pollutant emission inventory, the emission pollution sources of PM$_{2.5}$, including soil

![Figure 1. Sketch map of sampling sites chosen in this study (SP and PP stands for steel plant and power plant, respectively).](image-url)
proven to require the ideal results. Sources contribution rate to PM can be calculated as Eq. (1) and Eq. (2). The method is regarded as both a receptor and an emission source by exhaustive fitting calculation method. The method is applied to obtain quartz filters and Telfon filters (ϕ 47 mm) to remove the insoluble materials and then was transferred and fixed to 50 mL in the volumetric flask for the determination of ammonium and anions. An area of 0.526 cm² punched by one quarter of each quartz filter sample was used to analyze carbon composition (OC and EC). The instrument was baked for 30 min to remove residual carbon material before sample analysis. A CH4/CO2 standard gas was used for the calibration of the instrument before and after sample analysis. Organic filters were used for the determination of elements. One half of one filter sample was put into the nickel crucible and ashed at 550 °C for 2 h in the muffle furnace and then melted at 500 °C in alkali fusion process (sodium hydroxide) for 10 minutes in the muffle furnace, finally, the volume was fixed with a certain proportion hydrochloric acid solution to analyze Si and the other part of one organic filter was placed into PTFE digestion vessel for acid treatment (2 mL hydrofluoric acid and 6 mL hydrogen nitrate), then treated by microwave digestion apparatus (CEM Mars 6, USA) for 2 h following the setup routine to analyze metal elements (HJ777-2015). Nineteen elements were determined, including metal elements (Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, Pb) and Si. Table 1 shows the analysis methods and details of equipment used in this study.

**CMB Model.** Based on the theoretical basis of the standard EPACMB 8.0 model, Chinese Academy of Environmental Sciences proposed an improved CRAESCMCMB model (25), which assumes that urban dust source is regarded as both a receptor and an emission source by exhaustive fitting calculation method. The method is proved to require the ideal results. Sources contribution rate to PM can be calculated as Eq. (1) and Eq. (2).

\[
C = \sum_{i=1}^{m} \sum_{j=1}^{n} F_{ij} \times S_j
\]

(1)

\[
\eta_j = \frac{S_j}{C} \times 100\%
\]

(2)

In this equation, \( C \) is the concentration of the all chemical components in the atmospheric particulate matter of the receptor, \( \mu g/m^3 \); \( F_{ij} \) is a measured value of the chemical component \( i \) in the particulate matter of the \( j \) source, \( g/g \); \( S_j \) is the calculated concentration of the contribution of the \( j \) source, \( \mu g/m^3 \); \( j \) is the number of the source, \( j = 1, 2... n \); \( i \) is the number of chemical components, \( i = 1, 2... m \); \( \eta_j \) is the contributing rate of each source.

**Quality control.** Each PM\(_{2.5}\) filter was weighed three times with the 1/100000 analytical balance to ensure that the error was less than 0.05 mg each time. Comparing the PM\(_{2.5}\) mass concentration measured by the filter collected from the manual sampling instrument at the same sampling online sites and the same period, it was found that the measure deviation was within 10%, which ensured the filter samplings’ mass concentration accuracy. The accuracy of a standard curve is the key to experimental quality control. In this study, the component contents of the prepared mixed standard solution were measured at different five concentrations to draw standard curves; the correlation coefficient (\( R^2 \)) between five concentration levels of every ion, every element and carbon component was above 0.99997. The recovery rates of blank filter and samples added standard solution

| No. | contents           | Analysis method                        | Instrument                        |
|-----|--------------------|----------------------------------------|-----------------------------------|
| 1   | PM\(_{2.5}\) mass  | Weight method                          | Metler Toledo AX205               |
| 2   | Anion analysis     | Ion chromatography                     | Dionex ICS-1000                   |
| 3   | Carbon analysis    | Thermal-optical carbon analysis        | Multiwavelength Carbon Analyzer DRI Model 2015 |
| 4   | NH\(_4^+\)         | Ultraviolet and visible spectrophotometry | Ultraviolet and Visible Spectrophotometer TU-1810 |
| 5   | Metal elements     | Inductively coupled plasma spectroscopy | ICP-MS (ICP-5000)                |
| 6   | Si                 | Inductively coupled plasma spectroscopy | ICP-OES (EXPEC-7000)             |

Table 1. Analysis methods and instruments used for the filter samples.
respectively by each ion were 90–110%, 82–108% and by each element were 89–113% and 85–116%, by OC/EC with glucose standard solution were all 80–115%, which meet the EPA requirements. Every sample was detected parallel for at least three times, which was used to calculate the uncertainty of every component with the relative standard deviation for the reproducibility test, which is no more than 10% deviations for ion and OC/EC, 5–10% deviations for metal elements and 10% for Si. At least 7 pieces Quartz and organic blank filters respectively were treated by the same sample treatment process and then used to quantify the limit of method detection (LOD) with 3.14 times the relative standard deviation. The LOD for the analyzed ions are between 0.01 μg/m³ and 0.085 μg/m³, for OC and EC respectively 0.1 μg/m³, for 19 elements between 0.009 and 0.270 μg/m³, for Si 0.010 μg/m³. For the detecting accuracy of ions, elements and carbon components, a blank filter was conducted analysis every 10 samples to control the quality.

The input data of the model consisted of the chemical composition spectra and its uncertainty of environmental receptors and emission sources. Its uncertainty is the standard deviation (SD) calculated by the all data of the same component. The results of CMB model are mainly evaluated by sum of squares of residuals (χ²), regression coefficient (R²) and mass percent (% mass). When χ² < 1, R² > 0.8 and 80% < mass percent < 120%, the results of CMB analysis are considered to be better. All of the calculation fit the model requirements.

### Results and Discussion

**Pollution characteristics of atmospheric particulate matter.** Coefficient of Divergence (CD) of PM₁₂.₅ between each two sampling sites.

In order to analyze the spatial difference of PM₁₂.₅ between each two sampling sites, the Coefficient of Divergence (CD) of PM₁₂.₅ were calculated seen as Table 2. CD was used to test the extent of spatial difference.

The CD was defined as follows:

$$CD_{jk} = \sum_{i=1}^{p} \left( \frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2$$

(3)

where j and k represented two sampling sites, and p was the number of chemical components. xᵢ and xⱼK were the average mass concentration for a chemical component i at site j and k. Referring to the literature, if CD < 0.6, the difference between different sites of a certain pollutant is greater; if 0.3 < CD < 0.6, the difference is general; if CD < 0.3, indicating that it has a certain similarity. Our calculated CD was between 0.007 to 0.148, below 0.3, indicating that there were no obvious differences for PM₁₂.₅ at the five sampling sites. So, the average concentrations of PM at five sampling sites can be used to analyze the regional pollution characteristics of the fine particles in Laiwu, China.

**Pollution characteristics of atmospheric particulate matter.** The daily concentrations of PM₂.₅ and PM₁₀ were averaged according to the hourly data from the five online monitoring sites. The monthly averaged values were computed by averaging the daily data in that month. The mean PM concentrations in Laiwu were averaged according to the data from all monitoring sites. The monthly average concentration ranges of PM₂.₅ and PM₁₀ were 33.0–121.2 μg/m³ and 66.8–185.5 μg/m³, respectively, and the detailed results are illustrated in Fig. 2. The respective overall mean mass concentrations for PM₂.₅ and PM₁₀ were 73.5 μg/m³ and 126.8 μg/m³, and the standard deviations were 28.6 μg/m³ and 38.2 μg/m³. The lowest concentrations of PM₂.₅ and PM₁₀ were both observed in August, while the highest concentrations of PM₂.₅ and PM₁₀ were observed in January and April, respectively. Throughout the whole year, the PM₁₀ concentrations were relatively high from March to May during the spring period, and the PM₂.₅ concentrations were relatively high in January and December. These concentrations were mainly attributed to the climatic conditions and local emissions of Laiwu City. In spring, it often occurred the pollution of coarse particles such as road dust, soil dust, and construction dust because of the sandstorm caused by the higher wind speed. In the cold and dry winter, the large amount of coal combustion by residents’ heating, and the geographical conditions that surrounded by mountains on three sides of the city, also tended to cause the accumulation of fine particles. Compared to other cities in China (Table 3), the annual concentration of PM₂.₅ in Laiwu was at the same level as that of Tangshan, higher than that of Beijing (55 μg/m³), Shijiazhuang (65.1 μg/m³) and Zhubai (34.4 μg/m³). The annual concentration of PM₁₀ in Laiwu was lower than most neighboring province cities except Tianjin (86.6 μg/m³). In comparison with cities in same Province, its PM₂.₅ level was lower than Heze (109.1 μg/m³), and higher than Yantai (64.1 μg/m³). According to the Ambient Air Quality Standard (GB 3095–2012), except August, the PM₂.₅ and PM₁₀ concentrations both exceeded their standard second grade limits (35 μg/m³ and 75 μg/m³, respectively). Hence, as a small city in China, its PM₂.₅ pollution was necessary to focus on.

|   | 1# | 2# | 3# | 4# | 5# |
|---|----|----|----|----|----|
| 1# | —  | —  | —  | —  | —  |
| 2# | 0.148 | — | 0.127 | — | — |
| 3# | 0.138 | 0.100 | — | — | — |
| 4# | 0.115 | 0.146 | 0.098 | — | — |
| 5# | 0.039 | 0.002 | 0.007 | 0.012 | — |

Table 2. Coefficient of Divergence (CD) of PM₁₂.₅ between each two sampling sites.

| City          | PM₂.₅ (μg/m³) | PM₁₀ (μg/m³) |
|---------------|---------------|--------------|
| Laiwu         | 73.5±22.6     | 126.8±38.2   |
| Tangshan      | 73.5±22.6     | 126.8±38.2   |
| Beijing       | 55±7.4        | 75±12.5      |
| Shijiazhuang  | 65.1±10.1     | 75±12.5      |
| Zhubai        | 34.4±5.7      | 75±12.5      |
| Tianjin       | 86.6±15.3     | 75±12.5      |
| Heze          | 109.1±18.6    | 75±12.5      |
| Yantai        | 64.1±9.7      | 75±12.5      |
The variation in the PM$_{2.5}$/PM$_{10}$ ratio ranged from 0.45–0.74, and the overall mean value was 0.57. Zhang et al. investigated the PM$_{2.5}$/PM$_{10}$ in typical urban areas of Beijing-Tianjin-Hebei, Yangtze River Delta and Pearl River Delta in 2016, it was found that the PM$_{2.5}$/PM$_{10}$ was ranged from 0.585 to 0.841, and above 0.70 of cities in Beijing-Tianjin-Hebei region$^{33,34}$. Compared with these cities, PM$_{2.5}$/PM$_{10}$ ratio in Laiwu was at a relatively lower level. The overall temporal trend of the pollutant ratios showed a “U”-type distribution, wherein higher PM$_{2.5}$/PM$_{10}$ ratios were detected in December, January, and February and lower PM$_{2.5}$/PM$_{10}$ ratios were detected in March and May. These data suggest that fine particulates play an important role in the air pollution in winter. So it can be concluded that PM$_{2.5}$ was the main pollutant in winter, contributing to the decline in visibility and heavy pollution levels in Laiwu.

PM$_{2.5}$ chemical compositions. Estimation of the existence forms of NH$_4^+$. In order to better explore the relationship between PM and air pollution, the existence of different forms of NH$_4^+$ in PM was investigated. The ratios of the measured NH$_4^+$ and calculated NH$_4^+$ were obtained, and the specific existence of NH$_4^+$ in NH$_4$NO$_3$, NH$_4$HSO$_4$, and (NH$_4$)$_2$SO$_4$ was determined. A Three phase diagram was used to show the existence of NH$_4^+$.$^{35}$ If SO$_4^{2-}$, NH$_4^+$, and NO$_3^-$ exist in the forms of NH$_4$NO$_3$ and NH$_4$HSO$_4$, the estimated concentration of NH$_4^+$ can be calculated according to Eq. (4). If SO$_4^{2-}$, NH$_4^+$, and NO$_3^-$ exist in the forms of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$, the estimated concentration of NH$_4^+$ can be calculated according to Eq. (5). The calculation formulas for NH$_4^+$ are as follows$^{36}$:

\[
[NH_4^+] = 0.29[NO_3^-] + 0.19[SO_4^{2-}] 
\]  
(4)

\[
[NH_4^+] = 0.29[NO_3^-] + 0.38[SO_4^{2-}] 
\]  
(5)

As shown in Fig. 3, when NH$_4^+$ was in the form of NH$_4$HSO$_4$, the slope of the fitted straight line was 0.651, and the square of the Pearson correlation coefficient ($R^2$) was 0.78 (p value < 0.01, two-tailed test). When NH$_4^+$ was in the form of (NH$_4$)$_2$SO$_4$, the slope of the straight line was 0.898, and $R^2$ was 0.83 (p value < 0.01, two-tailed test). The slope in the form of (NH$_4$)$_2$SO$_4$ was closer to 1 than NH$_4$HSO$_4$, hence NH$_4^+$ existed mainly in the form of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ during the four sampling periods.
Proportions of water-soluble secondary ions. Using the weighted relative content data from the five manual sampling sites, the proportions of water-soluble secondary ions $\text{SO}_4^{2-}$, $\text{NH}_4^+$, and $\text{NO}_3^-$ were analyzed for the four different seasons. Proportions of the secondary ions during different seasons were characterized by a ternary phase diagram, and the detailed results were shown in Fig. 4.

As shown in Fig. 4, the data for the secondary water-soluble ions were mainly concentrated in the middle of the graph for all four seasons. During spring, $\text{NO}_3^-$ was the main component, with values exceeding 50%. The proportion of $\text{SO}_4^{2-}$ mainly ranged between 25% and 50%, and the $\text{NH}_4^+$ content was the lowest (less than 25%). The $\text{SO}_4^{2-}$ content in summer exceeded 50%, while that of $\text{NH}_4^+$ ranged between 18% and 37%. The $\text{NO}_3^-$ content was the lowest, with values below 25%. Therefore, the main ions present were $\text{SO}_4^{2-}$ and $\text{NH}_4^+$, and $(\text{NH}_4)_2\text{SO}_4$ was the main form. Lesser amounts of $\text{NH}_4\text{NO}_3$ were also present in spring and summer. The $\text{SO}_4^{2-}$ content mainly ranged from 25% to 55% in autumn, with only a few values exceeding 50%. The $\text{NO}_3^-$ content ranged between 15% and 50%, and that of $\text{NH}_4^+$ was below 37%. The ratios of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ were roughly the same in winter, with values ranging from 25% to 50%. The $\text{NH}_4^+$ content ranged from 24% to 35%. Therefore, the ions existed mainly in two forms, namely, $(\text{NH}_4)_2\text{SO}_4$ and $\text{NH}_4\text{NO}_3$, in autumn and winter. These results are consistent with those from earlier research\textsuperscript{37}, which was conducted in autumn over southern Hebei, China. According to a study at an urban site in Karachi, Pakistan, 4.4% $(\text{NH}_4)_2\text{SO}_4$ existed in PM$_{2.5}$\textsuperscript{38}.

Figure 3. Existence of different forms of $\text{NH}_4^+$.

Figure 4. Proportions of $\text{SO}_4^{2-}$–$\text{NO}_3^-$–$\text{NH}_4^+$ during different seasons.

$\text{OC/EC and SOC.}$ $\text{OC/EC}$ can be used not only to assess the degree of secondary pollution, but also to speculate on the sources of carbon components. $\text{OC/EC}$ indicates vehicle exhaust in the range of 1.0–4.2, and fired sources in the range 2.5–10.5\textsuperscript{38,40}. When it exceeds 2.0, it is suggested there is SOC (Secondary Organic Carbon) generated by the secondary reaction\textsuperscript{41,42}. The annual value of $\text{OC/EC}$ was calculated to be $5.38 \pm 1.70$, higher than 4.2 and lower than 10.5, indicating the sources of carbon components were fired sources such as power plants and steel industries. The seasonal average value of the ratio was $(4.54 \pm 2.07)$, $(6.07 \pm 1.13)$, $(5.01 \pm 1.28)$ and $(5.87 \pm 1.86)$, respectively. The higher $\text{OC/EC}$ in summer may be attributed to high temperatures, strong solar radiation and the easy reaction of hydrocarbons in the atmosphere, which significantly promotes the formation of SOC\textsuperscript{43}. The
SOC can be calculated by the Eq. (6) as reported in the literature\textsuperscript{42,43}. The annual value of was calculated to be \((8.22 \pm 3.93) \mu g/m^3\) for SOC, and \((43.68 \pm 12.98)\%\) for SOC/OC, which was higher in summer and lower in Spring, which was in consistent with the OC/EC.

\[
SOC = OC - (OC/EC)_{min}
\]

\textit{Chemical composition spectrum of PM\textsubscript{2.5} and its pollution sources.} Every chemical composition at five sites in different seasons for PM\textsubscript{2.5} filter samples was averaged as the environmental receptor. Road dust, urban dust, soil dust, construction dust, steel dust, power plants dust and motor vehicle exhaust dust were regarded as pollution sources. Compositional spectrum of environmental receptors and sources were established respectively, as shown in Fig. 5 and Fig. 6.

\textit{Composition spectrum of sources.} As shown in Fig. 5, for main elements, the concentration of Si in urban dust and soil dust was higher (0.10 g/g and 0.16 g/g) and the concentration of Ca, Fe were also higher, which showed the similar and complex sources. Lai \textit{et al.} reported the same results\textsuperscript{44}. However, Si is an element associated to crustal dust and coal-fired power plants\textsuperscript{45}. For construction dust, steel dust, power plant dust, the higher main element was Ca, Fe and Al, respectively, which in consistent with the results of other literatures\textsuperscript{46}, while Al and Ca could be also associated to road dust and soil dust\textsuperscript{45}. For minor elements, the concentration of Zn and Mn was high in most sources especially steel dust and power plant dust, showing the complexity of their sources, in consistent with the conclusion of relevant literatures\textsuperscript{46}. Ti was abundant in natural sources including urban dust, soil dust and construction dust,
and literatures reported the similar results. Pb was rich in steel dust and power plant dust, and former researches showed that, with the widespread use of unleaded gasoline, the contribution of automobile exhaust to Pb grew to decline, while industrial emissions became the main contributor. The concentration of Cr was high in urban dust and power plant dust, references also showed the industrial productions were the crucial emission sources to Cr. For water soluble ions, the concentration of NH$_4^+$ (0.15 g/g) in construction dust was higher, which showed that construction dust was also affected by secondary transformation. For power plants dust, SO$_4^{2-}$ was the highest concentration component (0.18 g/g), in consistent with the conclusion of the reported literature. The higher components of motor vehicle exhaust dust were OC and EC, seen as the main chemical component. The characteristic components were Si, Fe and Ca in urban dust and soil dust; Ca, Mg and NH$_4^+$ in construction dust; Fe, Ca and SO$_4^{2-}$ in steel dust; OC, EC and Si in motor vehicle exhaust dust; SO$_4^{2-}$, Al and NH$_4^+$ in power plant dust.

Composition spectrum of PM$_{2.5}$. As seen in Fig. 6, for main elements, the concentrations of Si, Ca, Fe, Al were higher than that of other elements, with annual average values of 3.35, 3.15, 1.32 and 0.87 $\mu$g/m$^3$, respectively, especially in winter and spring in accordance with the main components of soil dust, construction dust, steel dust and power plants dust in Fig. 5. The concentration of other main elements ranged between 0.60 and 1.17 $\mu$g/m$^3$. For minor elements, the annual average concentration of Zn (0.210 $\mu$g/m$^3$) was much higher compared with the value of heavy metals elements such as Pb, V, Mn, Ni, Cd between 0.003 and 0.093 $\mu$g/m$^3$. As shown in Fig. 5, the concentration of these minor elements all appeared higher in power plants dust and steel dust. The results were consistent with literature reports that these elements had high content in power plants dust, steel dust, or motor vehicles exhaust. The annual average concentration of heavy metals elements with high toxicity was all below the WHO annual concentration limits. This showed that heavy metals pollution in Laiwu was not serious. Compared with other cities at home and abroad, it was found that the concentrations of main elements in Laiwu were significantly higher than these in foreign cities, and at a medium level in China, higher than that in Hangzhou, Yantai and Haikou, while lower than that in Ningbo, Tianjin and Qingdao, while the concentration levels of minor elements in Laiwu were much lower than these cities, indicating a slightly pollution status of minor elements. The seasonal distributions of both main elements and minor elements were characterized by higher concentration in winter and spring. This may be mainly due to the large amount of pollutants discharged by the increase of coal combustion in winter, and the impact of dust weather in spring, which is consistent with the results of relevant references. For water soluble ions, the annual concentrations of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$, with the value of 15.42, 13.84 and 9.53 $\mu$g/m$^3$, respectively, were higher compared with the value of F$^-$ and Cl$^-$ between 2.47 and 6.48 $\mu$g/m$^3$. SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were the secondary pollutants and mainly concentrated in power plants dust, motor vehicle exhaust and construction dust compared to Fig. 5. OC and EC also showed a relatively high annual concentration, 14.91 and 3.27 $\mu$g/m$^3$, respectively. All water soluble ions and carbon components showed the higher concentration in winter except for SO$_4^{2-}$ that higher in summer, mainly due to the fact that the higher temperature in summer was beneficial to the transformation of SO$_4^{2-}$.

CMB Sources apportionment results. Based on the Eq. (3), CD of every chemical component between each two sampling sites for four seasons were calculated. The CD ranged from 0.36 to 0.50 in Si, from 0.11 to 0.57 in metal elements, from 0.09 to 0.36 in OC, from 0.15 to 0.48 in EC, from 0.12 to 0.38 in ions, all below 0.6. In general, the larger CD were observed in metal elements between S3 and S4, indicating the statistic significant differences likely due to the influence of human traffic and urban emission. The analysis of CD gave an reasonable agreement that the statistic significant differences likely due to the influence of human traffic and urban emission. The contribution rates of the primary pollution sources apportionment for power plants dust and steel dust were 11% and 6%, respectively. Worthily, motor vehicle exhaust accounted for 13%, which should be paid more attention by the local government. The contribution rates of surface resuspension dust sources including soil dust, construction dust and urban dust were 7%, 6% and 2%, respectively, a total of 15%. Moreover, the annual contribution rate of secondary generation sources including sulfate, nitrate and SOC of PM$_{2.5}$ was 17%, 17% and 13%, respectively, which were nearly half of the total sources, and the primary sources of these sources should be taken care in the future research study. Kim used the receptor Model (PMF model), and Contini associated PMF Model with CMB model to obtain the SOC source contribution in PM$_{2.5}$. The results of sources apportionment were shown in Fig. 7. The contribution rates of the primary pollution sources apportionment for power plants dust and steel dust were 11% and 6%, respectively. Worthily, motor vehicle exhaust accounted for 13%, which should be paid more attention by the local government. The contribution rates of surface resuspension dust sources including soil dust, construction dust and urban dust were 7%, 6% and 2%, respectively, a total of 15%. Moreover, the annual contribution rate of secondary generation sources including sulfate, nitrate and SOC of PM$_{2.5}$ was 17%, 17% and 13%, respectively, which were nearly half of the total sources, and the primary sources of these sources should be taken care in the future research study. Kim used the receptor Model (PMF model), and Contini associated PMF Model with CMB model to analyze the sources of particulate matter. They both found that secondary generation sources were the most important contributor to particulate matter. Therefore, more attention should be paid on secondary generation sources as well as the motor vehicle exhaust and road dust caused by their transportation.
Conclusions
Online monitoring data for atmospheric particulate matter (PM) during the whole year in 2016 and manual filters sampling of PM$_{2.5}$ during four seasons in Laiwu, Northern China, were used to study the characteristics and chemical compositions of pollutants in PM at a typical steel industrial urban site. PM pollution sources, including soil dust, urban dust, construction dust, coal-fired power plants dust, steel dust and motor vehicle exhaust dust were sampled, respectively. The results showed that the average concentrations of PM$_{10}$ and PM$_{2.5}$ were (126.8 ± 38.2) µg/m$^3$ and (73.5 ± 28.6) µg/m$^3$, respectively. The PM$_{2.5}$/PM$_{10}$ ratio was the highest in winter, indicating PM$_{2.5}$ was the dominant pollutants in this period. Water-soluble secondary ions mainly existed in the form of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ during the sampling periods. The annual value of OC/EC was 5.38 ± 1.70, higher in summer and lower in winter, and the calculated SOC/OC value was (43.68 ± 12.98) %. The characteristic components were Si, Fe and Ca in urban dust and soil dust; Ca, Mg and NH$_4$ in construction dust; Fe, Ca and SO$_4^{2-}$ in steel dust; OC, EC and Si in motor vehicle exhaust dust; SO$_4^{2-}$, Al and NH$_4$ in power plant dust, respectively. The CMB model results showed that the contribution rates of the primary pollution sources apportionment for power plants dust and steel dust were 11% and 6%, and the annual contribution rate of secondary generation sources including sulfate, nitrate and SOC to PM$_{2.5}$ was 17%, 17% and 13%, respectively.

Data availability
The data of the compounds are available from the authors. 2020 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Received: 31 December 2019; Accepted: 14 April 2020;
Published online: 06 May 2020

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Acknowledgements
We would like to thank the Laiwu City Environmental Protection Agency (Project Number: BM2015-210), and the Science and Technology Development Project of Shandong Province (2014GSF117002) for providing funding support for this study.

Author contributions
Guiqin Zhang conceived of the presented idea, formulated research objectives, led paper writing, and ran the model. Chun Ding conducted the samples collecting and pretreated samples experiment, analyzed the data and interpreted results discussion. Xiaojing Jiang conducted the experiment and analyzed the data. Guang Pan contributed data and analysis tools. Xiaofeng Wei performed the analytic calculations. Youmin Sun designed the original idea, analyzed the data, and helped to the final version of the manuscript. All authors read and approved the submitted manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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