



A three-year investigation of metals in the atmospheric wet deposition of a basin region, north China: Pollution characteristics and source apportionment

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ARTICLE INFO

Keywords:

Metals
Wet deposition
Temporal variations
Source apportionment
Back trajectory

ABSTRACT

Precipitation samples were collected in Taiyuan, China, from January 2013 to December 2015. Thirteen elements were detected by inductively coupled plasma-mass spectrometry (ICP-MS). The total concentration of soluble and insoluble materials averaged $9695.26 \mu\text{g L}^{-1}$. Si was the most abundant element, accounting for 94.61% of the total, followed by Al and Fe. The wet deposition flux of the 13 elements was $3065.14 \text{ mg m}^{-2}\text{yr}^{-1}$, with the highest flux detected in the summer and the lowest in the spring. The order of deposition flux was as follows: $\text{Si} > \text{Al} > \text{Fe} > \text{Zn} > \text{Ba} > \text{Cu} > \text{Mn} > \text{Cr} > \text{Sr} > \text{Pb} > \text{Ni} > \text{As} > \text{Cd}$. The elements mainly consisted of insoluble materials and accounted for 56.1–98.5% of the total. Per the enrichment factor (EF) results, Zn, Cu, Pb, As, and Cd were derived mainly from anthropogenic activities, while Al and Fe were derived mainly from crustal dusts. Positive Matrix Factorization (PMF) was used to identify 4 sources of soluble materials in 2015. Results revealed that industrial activities were the leading source, contributing to 50.47% of the total, followed by coal combustion (26.09%), vehicle emissions (13.59%), and dusts (9.85%). Combined with 3 years of back trajectory data, southeasterly air masses (with a proportion of 39%) were the main direction from which the precipitation in Taiyuan originated and had a considerable influence on pH and flux.

1. Introduction

Atmospheric wet deposition has attracted worldwide attention over the past few decades as it effectively removes atmospheric pollutants, such as particulate matter, polycyclic aromatic hydrocarbons (PAHs), and metals (Hovmand et al., 2008). Some deposited pollutants (e.g., metals) are particularly dangerous to the environment and human health due to their bioaccumulation, toxicity, and carcinogenicity (Khillare and Sarkar, 2012; Pu et al., 2015; Widziewicz and Rogul-Kozowska, 2017). Heavy metals are a group of 40 electropositive elements that are natural constituents of the earth's crust, have a density > 5 , and may have a long-term effect on the ecosystem as they are difficult to remove from the soil and water (Cheng, 2003; Pacyna et al., 2009). Recent developments have been made in the investigations of

the atmospheric deposition of metals. For example, it was previously discovered that metal depositions were significantly higher in urban and industrial areas than at suburban or rural sites (Kicińska, 2016; Kicińska and Bożęcki, 2018). Specifically, the wet deposition fluxes of metals in Beijing ($238.2 \text{ mg m}^{-2}\text{yr}^{-1}$), Tianjin ($316.5 \text{ mg m}^{-2}\text{yr}^{-1}$), and Tangshan ($404.2 \text{ mg m}^{-2}\text{yr}^{-1}$) were higher than those in Cangzhou ($163.3 \text{ mg m}^{-2}\text{yr}^{-1}$) and Xinglong ($101.0 \text{ mg m}^{-2}\text{yr}^{-1}$) (Li et al., 2012; Pan, 2015). The metal deposition fluxes and ratios of wet deposition to dry deposition in different regions are affected by emission source, emission intensity, prevailing wind direction, and precipitation (Kara et al., 2014; Mijić et al., 2010). The wet deposition in Spain and France accounted for 70–97% of total metal deposition, while the Mediterranean Sea and semi-arid regions with less precipitation exhibited the opposite contribution trend (Avila and Rodrigo,

Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

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<https://doi.org/10.1016/j.apr.2020.01.007>

Received 3 August 2019; Received in revised form 14 January 2020; Accepted 17 January 2020

Available online 20 January 2020

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2004; Migon et al., 1997). Metals are considered to be markers of some typical sources. For example, Al is a crustal-related element, As is the main tracer of coal combustion, and Mn is regarded as an indicator of industrial emissions and an important source of crustal dust (Shi et al., 2015; Yu et al., 2011). Changes in the emissions of these metals are a leading cause of seasonal variations, more so than changes in long-range transport (Kim et al., 2012). Previously, it was discovered that the wet deposition fluxes of Cu, Pb, Zn, and Cd in the summer during the rainy season contributed the most to seasonal variations at 10 sites in Northern China (Pan, 2015). During the winter and spring, the wet deposition fluxes of trace elements along the Japan Sea coast were strongly affected by the long-range transport of air pollutants from the Asian continent (Sakata et al., 2006).

Taiyuan is a typical city that is coal-powered in the winter, as well as a heavy industrial city. Coal combustion, exhaust emissions, and traffic are its leading sources of air pollution. Previous studies have shown that PAHs and water-soluble ions (WSIs) in Taiyuan were relatively high, especially in the winter, when the proportion of coal combustion was > 50% (He et al., 2017b, 2017a; Li et al., 2016). The sources of metals were different from those of PAHs. In order to better understand the quality of regional soil ecological environment, it is necessary to explain the source of metals. It is of great significance to study the characteristics of metals in atmospheric precipitation and to analyze the sources of metals for understanding the geochemical cycle of pollutants and the quality of regional soil ecological environment and the prevention and control of pollution in the study area. Therefore, this study used Taiyuan as an example for investigating the change in metal characteristics in precipitation from 2013 to 2015.

The objectives of this study were to: (1) analyze the content and variation characteristics of metals in soluble and insoluble materials in the precipitation of Taiyuan, (2) analyze the wet deposition fluxes of metals in soluble and insoluble materials in precipitation, and (3) discuss possible sources of metals and assess the ecological risk of metals in precipitation.

2. Materials and methods

2.1. Study area and sampling

Taiyuan is the capital city of Shanxi Province located in Northern China. It is surrounded by mountains on three sides. It has a temperate monsoon climate, is hot and rainy in the summer, cold and dry in the winter, and has an average annual precipitation of 456 mm. The Fen River flows from north to south. Along the Fen River Basin are industrial enterprises, including coal coking plants and the largest stainless steel production area in China, which produces 10 million tons (Fig. 1). In 2015, the total emission of sulfur dioxide was 1.1206 million tons and the total emission of nitrogen oxide was 9307 million tons (industries 1, 2, 3, and 4) (Fig. 1).

The sampling site was located on the roof of a 16-story building at the main campus of Taiyuan University of Science and Technology located in the urban area of Taiyuan. Rainwater samples were collected using an Eigenbrodt UNS 130/E automatic sampler with an RS 85 humidity sensor. The cover opened when the rain began and closed once the rain stopped. The collection surface was 500 cm². The sampler was set at a height of 2 m above the roof, and a 5 L high-density polyethylene (HDPE) bucket (pre-cleaned with deionized water) was used for collecting rainwater. Snow samples were collected using an open polyethylene container (60 × 35 × 15 cm). All samples were collected during each rainfall or snowfall event, and 84 samples were collected from January 2013 to December 2015. Samples were transferred to 200 mL HDPE bottles immediately and transported to the laboratory within 1 h (Fig. S1; Table S1).

2.2. Chemical analysis

Snow samples were allowed to melt at room temperature. Both rainwater and melted snow samples were weighted by a balance with a sensitivity of 1 µg. The pH and conductivity were measured by a PHS-3C pH meter (Lei Ci, China) and FE30K conductometer (Mettler Toledo, China), respectively. Then, samples were filtered through a 0.45 µm microporous membrane (Lin Teng, China). The filtrate was acidified with mass fraction 68% nitric acid (1% v/v) to analyze the elements in soluble materials and subsequently maintained in a refrigerator at 4 °C. The membranes were cut by ceramic scissors and placed in Teflon tubes with 5 mL mass fraction 68% nitric acid for microwave digestion following the digestion program previously described by Wang et al. (2015). Then, the digested solution was filtered and diluted with ultra-pure water to 100 mL.

The metals were measured by ICAP Q inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo Fisher, USA) at the State Key Laboratory of Organic.

Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou. The working parameters were as follows: analyzer vacuum, 7.51E-07 mbar; plasma power, 1550 W; atomizing chamber temperature, 2.7 °C; peristaltic pump speed, 40 rpm; cooler velocity, 14 L min⁻¹; sampling depth, 6 mm; atomizer flow rate, 1.08 L min⁻¹.

The detection limits (3 × the standard deviation of the blanks) were as follows: Si (0.005 µg L⁻¹), Al (0.005 µg L⁻¹), Cr (0.0002 µg L⁻¹), Mn (0.00007 µg L⁻¹), Fe (0.0003 µg L⁻¹), Ni (0.004 µg L⁻¹), Cu (0.0002 µg L⁻¹), Zn (0.0003 µg L⁻¹), As (0.0006 µg L⁻¹), Sr (0.00002 µg L⁻¹), Cd (0.00009 µg L⁻¹), Ba (0.0002 µg L⁻¹), and Pb (0.008 µg L⁻¹). The analytical error was < 5%, and the recovery rates for the elements were between 85 and 105%. The correlation coefficients (R²) of the calibration curves were ≥ 0.999 for all elements. The field blanks of MilliQ water were analyzed by the same method to ensure the veracity and reliability of the data, of which, the concentrations were below the detection limits and indicated negligible contamination.

2.3. Data analysis

The flux of wet deposition was considered as the amount of a substance in the precipitation per unit area per unit time. Wet deposition fluxes of metals were calculated according to the following equation:

$$F_i = \frac{C_M * p_i}{1000} \quad (1)$$

where C_M is the mean concentration (µg L⁻¹), F_i is the wet deposition flux of element i (mg m⁻²), and p_i is the amount of daily/monthly/annual precipitation (mm).

The Positive Matrix Factorization (PMF) model was used for the air quality management calculations of the profiles and contributions of pollutants (Paatero and Tapper, 2010). In this study, the concentrations of the 13 elements were analyzed using the EPA PMF 5.0 model. The corresponding uncertainties related to the method detection limits (MDL) and error fractions were also obtained. If the concentration was lower than the MDL, the calculation of uncertainty (Unc) was calculated as follows:

$$Unc = \frac{5}{6} \times MDL, \quad (2)$$

If the concentration was higher than the MDL, Unc was calculated as follows:

$$Unc = \sqrt{(Errorfraction \times concentration)^2 + (0.5 \times MDL)^2}, \quad (3)$$

The error fraction values were set to 20%. The classifications of all 13 elements were strong, with a signal/noise ratio (S/N) of 4.0. The values of Q (Robust)/Q (True) were = 1. The R² values for all species

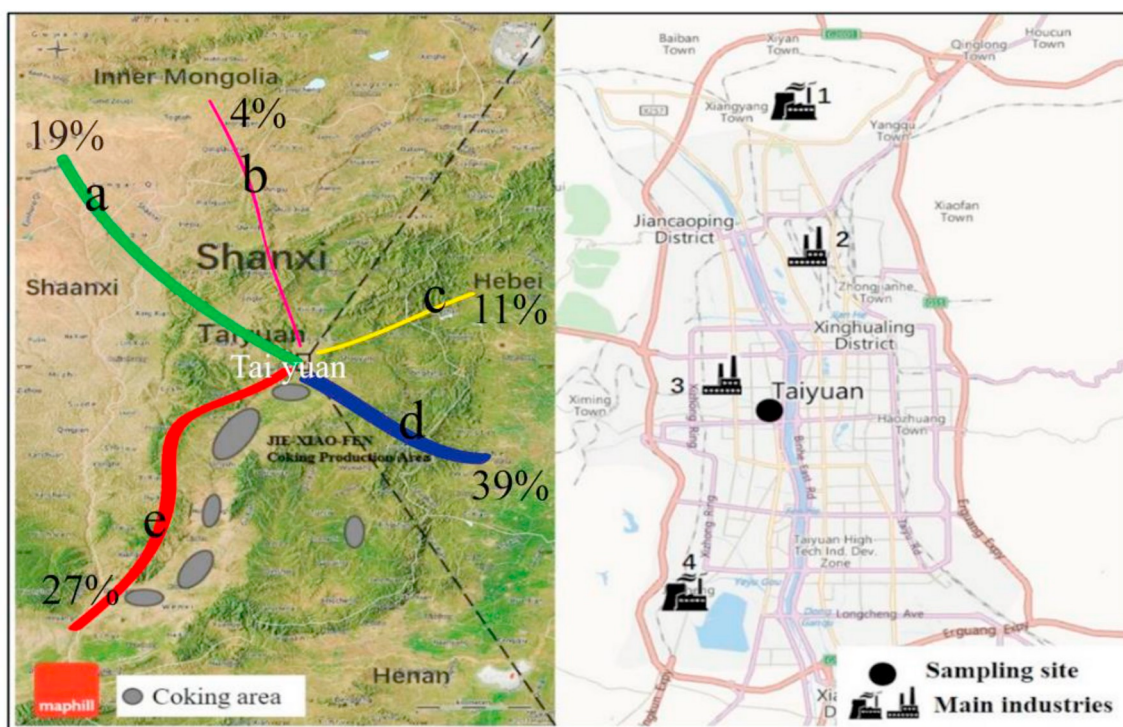


Fig. 1. Location of the sampling site and 48 h air mass backward trajectories of precipitation at 500 m above ground level for 84 precipitation events in Taiyuan. a and b: the northwesterly air masses originated from Neimeng accounted for 19% and 4%, respectively, of the total air mass (green and pink). c: The northeasterly air masses that originated from Hebei accounted for 11% of the total air mass (yellow). d: the southeasterly air masses originated from Jincheng, Changzhi, Jinzhong and accounted for 39% of the total air mass (blue). e: the southwesterly air masses originated from Linyi, Xiaoyi, Jiexiu and accounted for 27% of the total air mass (red). On the right was the main industry in Taiyuan.

were > 0.8.

In order to evaluate the enrichment of metal elements in the precipitation relative to the crust, using Si as the reference element, the enrichment factor (EF) was calculated using the concentration of each element as follows:

$$EF = (C_i(\text{sample})/C_{Si}(\text{sample}))_{\text{precipitation}} / (C_i(\text{crust})/C_{Si}(\text{crust}))_{\text{background}} \quad (4)$$

where EF is the enrichment factor of element i , $(C_i(\text{sample})/C_{Si}(\text{sample}))_{\text{precipitation}}$ is the ratio of element i to the concentration of Si in atmospheric precipitation, and $(C_i(\text{crust})/C_{Si}(\text{crust}))_{\text{background}}$ is the ratio of element i to the concentration of Si in the crust. The concentration of Si is 600 ng/m³ in the crust in Taiyuan, and the concentration of Zn, Ba, Cu, Mn, Cr, Sr, Pb, Ni, As, Al, Cd and Fe are 68 ng/m³, 516 ng/m³, 23 ng/m³, 600 ng/m³, 64 ng/m³, 370 ng/m³, 20 ng/m³, 29 ng/m³, 11.2 ng/m³, 600 ng/m³, 0.1 ng/m³, 500 ng/m³, respectively, in the crust in Taiyuan, (Taylor, 1964). The selected abundance of crustal elements used in this calculation was the global average. If the EF of element i was < 10, it indicated that the element was mainly derived from the crust, $10 < EF < 100$ indicated that the element was moderately enriched and slightly influenced by human sources, and $EF > 100$ indicated that the element was considerably enriched and obviously affected by human activities.

3. Results and discussion

3.1. Metal levels

The concentrations and deposition fluxes of the main elements in both soluble and insoluble materials of wet deposition samples obtained from Taiyuan in 2015 are provided (Table 1). The precipitation concentration of the 13 elements ranged from 3689.24 to 21,230.15 µg L⁻¹ with a mean value of 9695.26 µg L⁻¹. Si had the highest concentration with an average value of 3992.89 µg L⁻¹, followed by Al and Fe, which

had concentrations of 3107.97 µg L⁻¹ and 2071.88 µg L⁻¹, respectively. These 3 elements accounted for 41.18%, 32.06%, and 21.37% of the total, respectively, followed by Zn, Ba, Cu, Mn, Cr, Sr, Pb, Ni, and As. Ca had the lowest concentration of 0.96 µg L⁻¹, which was 3 orders of magnitude lower than Si. The distribution of each element was significantly different across soluble and insoluble materials. The elements were mainly concentrated in insoluble materials, except As. The average value of the 13 elements in insoluble materials was 9102.88 µg L⁻¹ compared with 592.38 µg L⁻¹ in soluble materials. The concentrations of Cr, Pb, and Cd were < 2 µg L⁻¹ in soluble materials; these elements may adversely affect human health as they are easily absorbed by organisms and enter the food chain (Fernández-Olmo et al., 2014; Hsu et al., 2008).

The total deposition flux of the 13 elements was 3065.14 mg m⁻²·yr⁻¹. Si had the highest value at 1262.35 mg m⁻²·yr⁻¹ and accounted for 41.18% of the total, followed by Al and Fe with fluxes of 982.58 mg m⁻²·yr⁻¹ and 655.02 mg m⁻²·yr⁻¹, respectively. Al poisoning can occur when the human body ingests too much Al. Fe is a trace element and usually has a positive effect on the human body. The deposition flux of Cd was the lowest at 0.30 mg m⁻²·yr⁻¹. Cd is a very toxic chemical to both animals and humans. Cd adversely affects the growth, yield, and quality of crops, as well as the health of animals and humans. Cd can damage the bones, kidneys, livers, immune and procreation systems, as well as possible factors that influence Cd absorption. Fluxes were mainly concentrated in insoluble materials, reaching 2877.86 mg m⁻²·yr⁻¹ and accounting for 93.89% of the total deposition, compared to 187.28 mg m⁻²·yr⁻¹ of soluble materials.

In this study, the deposition fluxes of precipitation between Taiyuan and other cities in China were compared; the deposition fluxes of precipitation in cities of China were also compared to cities of other countries (Table 1). The deposition fluxes of Al, Fe, Cu, and Cr were 10–100 × higher than As, Ba, Zn, and Pb in Beijing and Tianjin. In

Table 1
Concentrations ($\mu\text{g}\cdot\text{L}^{-1}$) and fluxes ($\text{mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) of metals in water and particle phases in Taiyuan and other areas.

Element	Taiyuan China (concentrations)				Huelva city Spain ^a (corrections)				Jiao zhou Bay ^b				Beijin ^d		Tianji ^d		Chuncheon ^e		Nakanoto ^f		Kathmandu ^g
	Concentration				Flux				Flux				Flux		Flux		Flux		Flux		
	Soluble	Insoluble	Total	Soluble	Insoluble	Total	Soluble	Insoluble	Total	Soluble	Total	Soluble	Total	Total	Total	Total	Total	Total	Total	Total	
Si	338.9	3654.0	3992.9	107.1	1155.2	1262.4				29.2		14.0	54.6	83.7	10.0					209.6	
Al	54.7	3053.3	3108.0	17.3	965.3	982.6				14.2		21.8	61.2	85.5						246.5	
Fe	58.0	2013.8	2071.9	18.4	636.7	655.0	2.7	704.0	706.8			69.1	52.0	93.0	6.9		27.0			244.4	
Zn	50.9	136.0	186.9	16.1	43.0	59.1	39.0	41.3	80.3	24.1		7.5	10.3	11.8	3.0		7.0			8.3	
Mn	19.8	34.2	54.0	6.3	10.8	17.1	1.9	7.3	9.2	24.2		0.6	0.6	0.7	0.4		1.4			0.7	
Ni	2.0	9.4	11.4	0.6	3.0	3.6	2.6	1.1	3.7			2.0	2.7	2.3	1.2		1.8			1.9	
Cu	2.8	74.2	77.0	0.9	23.5	24.4	9.1	70.1	79.2			0.4	0.3	0.2	0.1		0.3			0.1	
Cd	0.4	0.5	1.0	0.1	0.2	0.3		0.1		0.1		0.4	0.3	0.2	0.1		0.4			1.6	
Cr	1.0	44.5	45.5	0.3	14.1	14.4		1.7		0.7			0.3	0.5							
Sr	15.6	22.0	37.6	4.9	6.9	11.9	3.3	1.6	4.9				1.4	1.1							
As	2.4	1.8	4.2	0.8	0.6	1.3		0.6				1.3									
Ba	44.7	37.4	82.0	14.1	11.8	25.9	3.0	7.1	10.1				27.0	8.0							
Pb	1.1	21.9	23.0	0.3	6.9	7.3		3.5		2.2		6.0	6.4	8.0	1.1		10.0			1.4	

^a Castillo et al. (2013).

^b Xing et al. (2017).

^c Wang et al. (2007).

^d Pan et al. (2015).

^e Kim et al. (2012).

^f Sakata and Asakura (2009).

^g Tripathee et al. (2014).

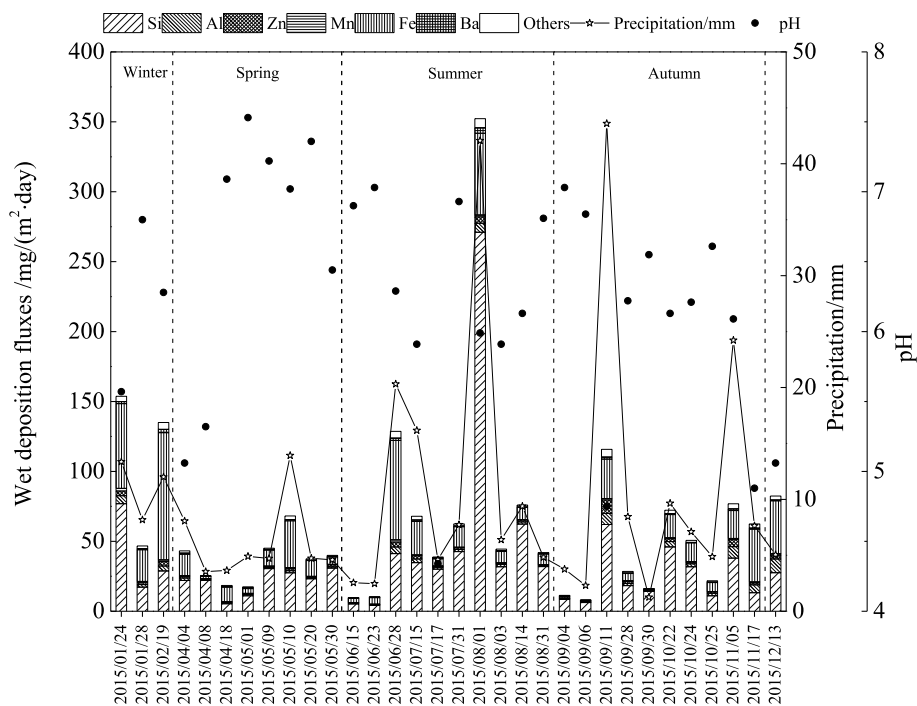


Fig. 2. Wet deposition fluxes (soluble and insoluble material) of metals in 2015.

terms of Taiyuan had obviously lower deposition fluxes in soluble materials than the Kiaochow Bay and Mount Tai areas where several power plants and industries are located in Mount Tai (Xing et al., 2017; Yan et al., 2007). Compared to foreign cities in Korea, Japan, Nepal, and others, the metal fluxes in Taiyuan were relatively high, which may be attributed to its large coal consumption (1.27×10^4 million tons yr^{-1}) and industry cluster located in the Taiyuan basin (Sakata and Asakura, 2009; Tripathi et al., 2014). The deposition fluxes of metals in the soluble and insoluble materials of Taiyuan and Huelva were roughly the same (Castillo et al., 2013).

3.2. Temporal variations

For some reasons, we cannot get the part of date about insoluble metals the phase in 2013–2014. We analysis the soluble metals and insoluble metals in 2015 samples. Figures involving insoluble metals show only in 2015. The variation in pH, composition, and fluxes of metals in the precipitation of Taiyuan city in 2015 are presented (Fig. 2). The pH ranged from 4.34 to 7.53, and 56.25% of the precipitation showed weak acidity. The pH of precipitation also exhibited a certain seasonal variation, being higher in the spring and lower in other seasons. SO_2 , NO_x , CO_2 , NH_4^+ and rain wash were important factors affected the pH of precipitation (Grimshaw and Dolske, 2002). In the winter, due to coal combustion, pollutants are easy to accumulate in the atmosphere, which leads to high concentration of SO_2 and NO_x in precipitation and increased and the pH of precipitation was lower than the other three seasons. Taiyuan city was located in the north of China, the wind speed in spring is significantly higher than that in winter, although there was no lack of acidic substances in the atmosphere, but there were more alkaline substances increased in the atmosphere, including Ca^{2+} , Mg^{2+} , and NH_4^+ , among others, which are mainly derived from soil and atmospheric particles (Connan et al., 2013; Grimshaw and Dolske, 2002; Migliavacca et al., 2005). Therefore, the pH of precipitation in spring was higher than that in winter. Additionally, the precipitation in the summer and autumn was significantly higher than that in the spring. The formation of acid rain depends on the relative content of acid-base ions in the atmosphere. Specifically, alkaline cations exist in dust particles that are larger in size

and are first washed into the soil by precipitation and it was more affected by rain wash. The longer the precipitation time, the higher the acid ion content in the air, and the lower the precipitation pH. However, the pH was still higher than the winter pH. The pH of precipitation exhibited a downtrend during continuous precipitation or when the interval was 1 day (Fig. 3). Acidic precipitation can help dissolve particle metals (Herut et al., 1995). Ba, Sr, Ar, and Ca in insoluble materials moved into soluble materials, resulting in the increase of the proportion of these elements in soluble materials. Metal fluxes were also affected by precipitation intervals. The maximum flux of the 13 elements occurred on August 1, with a diurnal variation range from 8.43 to 358.75 $\text{mg m}^{-2}\text{day}^{-1}$; the precipitation was as high as 42.07 mm. The lowest flux occurred on September 6, which was 8.43 $\text{mg m}^{-2}\text{day}^{-1}$, and the precipitation was 2.30 mm. The flux of metal elements was positively correlated with precipitation, and R^2 changed from 0.353 (Al) to 0.882 (Cr) (Table S2). The flux was higher in August and September due to high and frequent precipitation. Additionally, the wet deposition flux decreased when the precipitation interval was < 6 days (Fig. S2). However, the wet deposition flux increased when the precipitation interval was > 6 days due to the accumulation of pollutants in the atmosphere in the absence of precipitation (Gunawardena et al., 2013). Fluxes were also positively correlated with deposition concentrations (Fig. S3; Table S3). For example, on September 11, 2015, the precipitation was as high as 43.60 mm and the flux was 121.35 $\text{mg m}^{-2}\text{day}^{-1}$. On January 24 and February 19, 2015, the precipitation was only 13.36 mm and 12.00 mm, respectively, and the deposition flux reached 157.46 $\text{mg m}^{-2}\text{day}^{-1}$ and 139.82 $\text{mg m}^{-2}\text{day}^{-1}$, respectively.

The highest seasonal wet deposition flux was obtained in the summer (1487.28 $\text{mg m}^{-2}\text{day}^{-1}$), followed by autumn (599.40 $\text{mg m}^{-2}\text{day}^{-1}$), winter (586.67 $\text{mg m}^{-2}\text{day}^{-1}$), and spring (391.79 $\text{mg m}^{-2}\text{day}^{-1}$). This was mainly due to the variation in precipitation in different seasons, that is, precipitation increased to its highest level in the summer and reduced to its lowest in the spring. Although precipitation was relatively low in the winter, the wet deposition flux was high as a result of the increase in air pollutants due to heating supply. Changes in the metal concentrations in precipitation and atmospheric SO_2 in 2015 are provided (Fig. S4). The concentrations

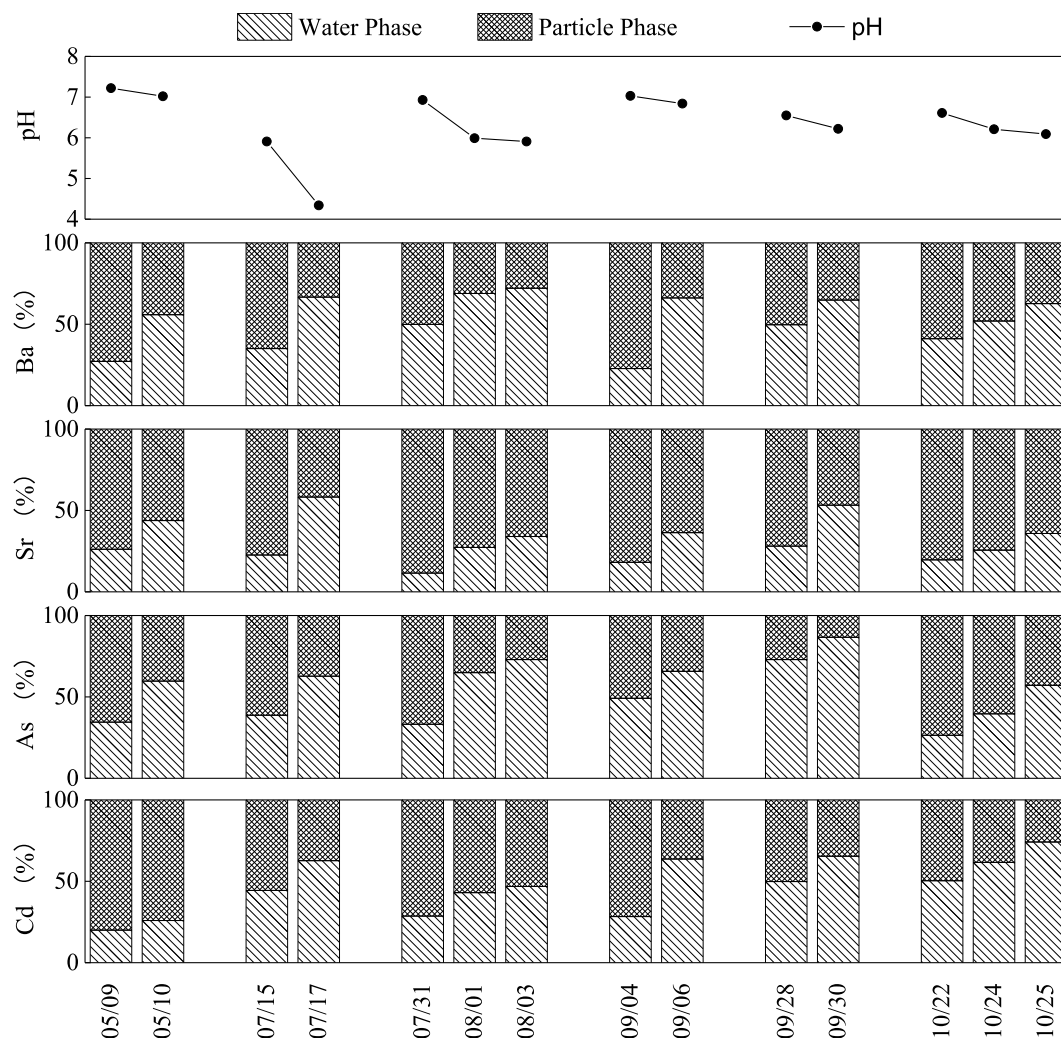


Fig. 3. Trends of pH and distributions of Ba, Sr, As, and Cd in soluble and insoluble material during the continuous precipitation or when the precipitation interval was one day.

of both atmospheric SO_2 and deposited metals were significantly higher in the winter than in other seasons due to coal combustion emissions. Additionally, the concentration of As, a tracer of coal combustion, increased to $8.99 \mu\text{g L}^{-1}$ in the winter, but remained at low levels in the spring ($4.15 \mu\text{g L}^{-1}$), summer ($3.40 \mu\text{g L}^{-1}$), and autumn ($3.25 \mu\text{g L}^{-1}$).

The annual wet deposition flux in soluble materials exhibited an upward trend (170.24 mm in 2013, 216.87 mm in 2014, and 316.15 mm in 2015). This was consistent with the trend of precipitation ($104.22 \text{ mg m}^{-2}\text{day}^{-1}$ in 2013, $113.45 \text{ mg m}^{-2}\text{day}^{-1}$ in 2014, and $187.28 \text{ mg m}^{-2}\text{day}^{-1}$ in 2015) (Table S4). The annual deposition flux of Si increased from $32.08 \text{ mg m}^{-2}\text{day}^{-1}$ in 2013 to $68.18 \text{ mg m}^{-2}\text{day}^{-1}$ in 2014 and then to $107.14 \text{ mg m}^{-2}\text{day}^{-1}$ in 2015 due to large-scale urban village reconstruction in Taiyuan, which released huge amounts of dust. The variations in metals fluxes of soluble materials from 2013 to 2015 are provided (Fig. 4). The deposition fluxes of most metals were the lowest in 2014, except Si, Sr, and Ni. The highest metal deposition flux of $21.04 \text{ mg m}^{-2}\text{day}^{-1}$ was obtained on June 20, 2013, when the precipitation was 26.15 mm. The lowest flux of $0.61 \text{ mg m}^{-2}\text{day}^{-1}$ occurred on September 6, 2015, when the precipitation was 2.30 mm. These results suggest that the deposition flux of metals in soluble materials was markedly influenced by the level of precipitation.

3.3. EFs

Generally, EF values are indicators of metal sources. When $\text{EF} < 10$, elements are derived from natural sources, while $\text{EF} > 100$ suggests that elements are derived from anthropogenic sources (Berg and Steinnesb, 1994; Odabasi et al., 2002). When $10 < \text{EF} < 100$, elements are influenced by both natural and anthropogenic sources. The EFs of heavy metals in the wet deposition in Taiyuan in 2015 are presented (Fig. 5). The EFs of Zn, As, Sr, and Cd in soluble materials were obviously higher than those in insoluble materials. The EFs for Al and Fe were < 10 , indicating that these elements were derived from natural sources (Gao et al., 2014). Cr, Mn, Ni, and Sr were influenced by both natural and anthropogenic sources, with an EF ranging from 10 to 100. Previously, it had been indicated that Cr and Ni are mainly emitted from coal combustion, industrial, and traffic activities (Lu et al., 2017), while Mn and Sr are derived from industrial sources and dust (Lu et al., 2016, 2017; Wei et al., 2015). Cr was significantly correlated with Mn, Ni, and Sr ($R^2 = 0.875, 0.730, \text{ and } 0.630$, respectively) (Table S5), which may be derived from the same sources. The EFs for Cu, Zn, As, Cd, Ba, and Pb were > 100 , while the EFs for Zn, As, and Cd in soluble materials were > 1000 , indicating that they were affected by severe anthropogenic sources. Among Cd, As, and Zn R^2 was > 0.6 , indicating that these elements may be emitted from industrial, coal combustion, or traffic activities (Rajesh Kumar et al., 2008). Additionally, the R^2 between Cr and As was 0.605, indicating that these elements were

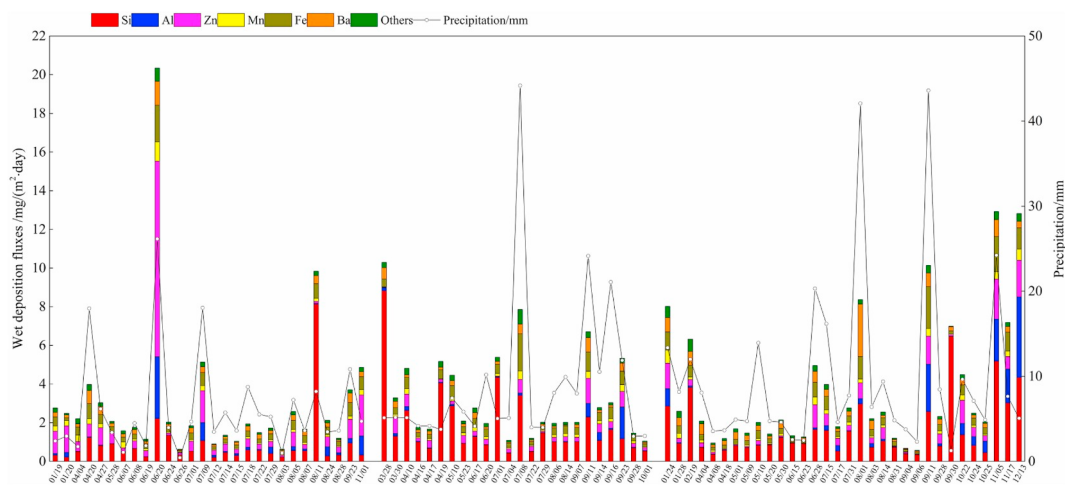


Fig. 4. Wet deposition fluxes of metals in soluble phase from 2013 to 2015 from left to right.

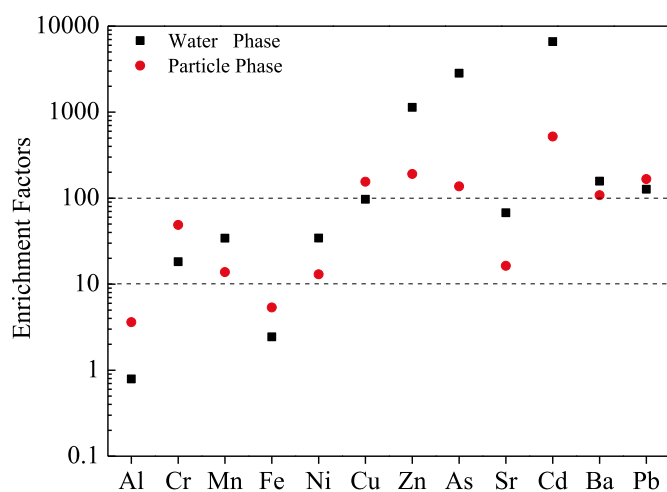


Fig. 5. Enrichment factors of metals in wet deposition in Taiyuan in 2015.

significantly correlated and may be derived from coal combustion.

The EFs of heavy metals in the precipitation samples from 2013 to 2015 are provided (Fig. 6). EF values decreased as precipitation increased due to the decrease in metal concentrations. Si remained relatively stable when precipitation increased. Most EFs exhibited the

following trends: winter > spring > summer > autumn. In the winter, due to increased coal heating and industrial emissions and less precipitation, metal content and EFs were higher. In the summer and autumn, due to heavy, high, and rapid precipitation, atmospheric pollutants were diluted during the process of precipitation, resulting in lower EFs. The EFs of different metals also exhibited differences due to seasonal variations. Specifically, the EFs of Al and Fe were the highest in the spring due to the dry and windy conditions and increase in ground dust.

The EFs of Cd remained high regardless of the changes in precipitation, indicating that this element was greatly influenced by human activities. The EFs of Zn increased to 16,884.76 and 2087.19 on June 20, 2013, and September 11, 2015, respectively, during which time, the precipitation levels were high. This may be attributed to the high solubility of Zn in water.

The seasonal wind speed from 2013 to 2015 was as follows: spring (2.74 m/s) > winter (2.65 m/s) > autumn (2.22 m/s) > summer (2.18 m/s). Regardless of the level of precipitation, the EF for Cd was always high, indicating that human activities greatly influenced this element. For Zn, EFs remained high (16,884.76 and 2087.19) when the precipitation of individual samples was high (on June 20, 2013 and September 11, 2015, respectively), which was likely due to its high solubility. These results are consistent with the findings of Morselli et al. (2003).

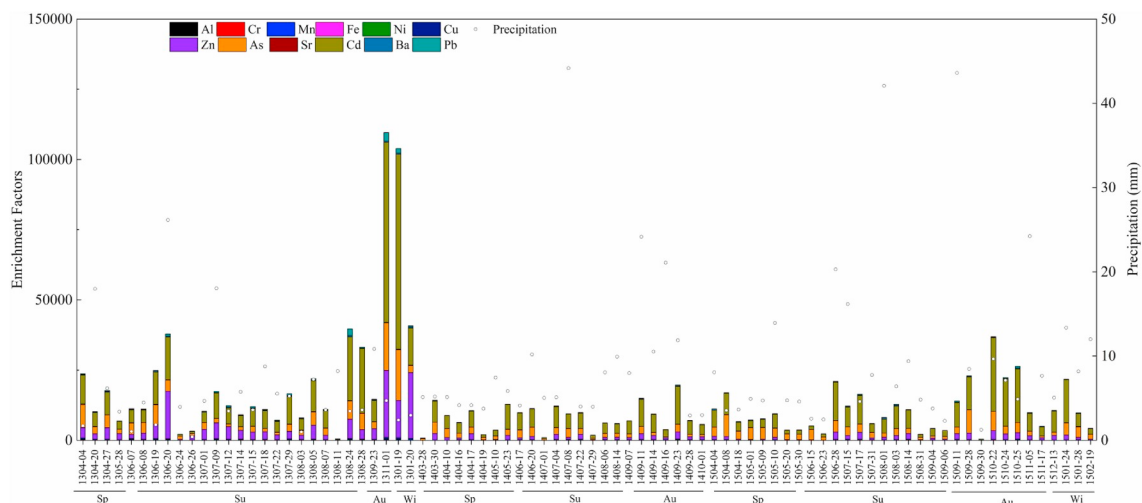


Fig. 6. Variation of enrichment factors of metals in soluble phase from 2013 to 2015 (Sp: Spring; Su: Summer; Au: Autumn; Wi: Winter).

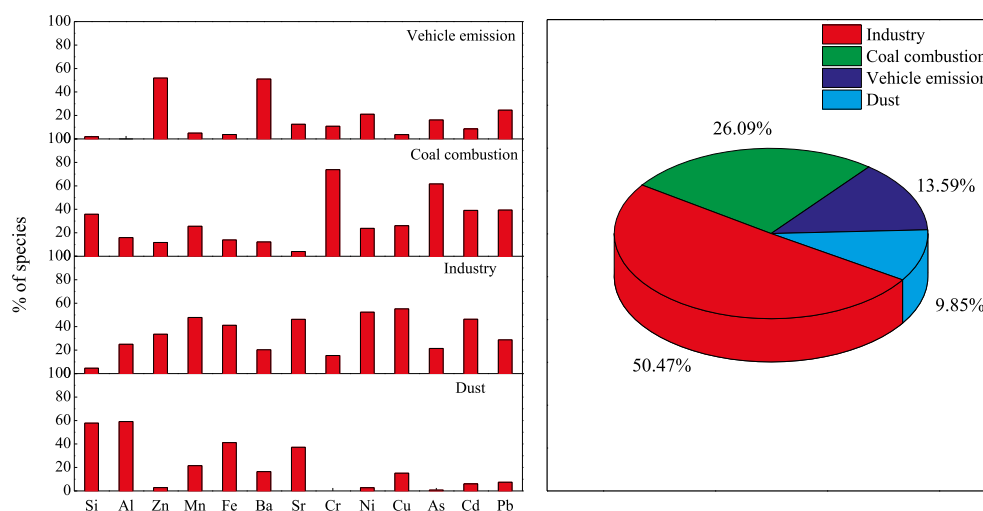


Fig. 7. Profiles and contributions of four sources of metals in 2015 obtained from PMF model.

3.4. Source apportionment

A PMF analysis of measured metals was conducted (Fig. 7). Four factors, vehicle emissions, coal combustion, industrial activities, and dust, were obtained by EPA PMF 5.0 to determine the sources of the total metal amounts (i.e., the sum of amounts in soluble and insoluble materials) in the precipitation in 2015 (Fig. 7).

Zn and Ba were mainly derived from factor 1, which contributed 13.59% of the total metal amount (Fig. 7). Zn is the main additive of automobile lubricants, and Zn and Ba are also widely used in automotive tires and brake pads (Wei et al., 2015). The number of motor vehicles in Taiyuan increased to 1.1229 million in 2015 with an average annual growth rate ranging from 10.5 to 13.5% from 2013 to 2015 (Weerasundara et al., 2017). Therefore, factor 1 should be vehicle emissions. Thus, the effects of vehicle emissions on metals should be paid more attention. Factor 2 accounted for 26.09% of the total metal amounts; a large proportion of Cr and As were derived from factor 2. Arsenic is a tracer of coal combustion emissions. Coal is the main energy source of Taiyuan. The coal consumption of this city reached 66.22, 64.08, and 63.06 million tons in 2013, 2014, and 2015, respectively (Duzgoren-Aydin, 2007; Tian et al., 2010). These results suggest that factor 2 should be coal combustion. Factor 3 had the largest proportion of 50.47% and contained large amounts of Mn, Ni, Cu, Sr, and Cd, which is in accordance with metal industrial activities, such as metal processing and smelting. Si, Al, and Fe are considered earth crust elements and were rich in factor 4 with a contribution of 9.85%, indicating that factor 4 could be identified as dust.

Additionally, the results from the total metals analysis in 2015 were consistent with the soluble material data from 2013 to 2015 (Figs. S5 and S6). In summary, the leading contributors of heavy metals in precipitation were metal industrial activities, followed by coal combustion, vehicle emissions, and dust.

3.5. Trajectory analysis

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) was used to analyze 48 h and 500 m high air masses in 84 instances of precipitation from 2013 to 2015 in Taiyuan (Table 2). Air masses can transport air pollutants or clean the air and affect the amount and chemical composition of precipitation. The air masses during precipitation in Taiyuan mainly originated from the southeast and southwest, accounting for 66% of the total precipitation (Table 2). The average pH of precipitation was 5.43 from 2013 to 2015. Sixteen instances of precipitation had pH values < 5.6. Among them, 10 air masses originated from the southeast and 6 from the southwest. The pH

of precipitation was relatively high when air masses originated from the northwest or northeast.

The flux and amount of metals were different when the pathway of air masses changed. The deposition fluxes of the southeasterly and southwesterly air masses were higher than those from the northwest and northeast. The southeasterly air masses, originating from Jincheng, Changzhi, and Jinzhong, accounted for 39% of the total air mass and contributed the most to metal deposition fluxes (Fig. 1). Large-scale thermal power plants, including Yangcheng and Zhangze, are located in Southeast Taiyuan, resulting in higher proportions of coal combustion-related elements, including Si (35.44%), Fe (34.24%), Ni (34.00%), and Cu (35.87%). Moreover, 27% of the total air mass originated from the southwest, the main coking region of Shanxi (i.e., Linyi, Xiaoyi, Jiexiu, and other cities), which contributed the most Al, Cr, Mn, Zn, As, Cd, and Pb in the proportions of 43.60%, 31.60%, 36.96%, 32.84%, 36.99%, 40.78%, and 36.86%, respectively (Table 2). The metal deposition fluxes in Taiyuan were less affected by the northerly air masses, which were relatively clean. The northerly and northeasterly air masses accounted for 19% and 11%, respectively, which contributed relatively little to the overall heavy metal deposition fluxes. These results are consistent with the findings of Pu et al. (2015).

4. Conclusions

The total concentrations of the 13 metals in soluble and insoluble materials in the precipitation of Taiyuan ranged from 2655.81 to 16,292.90 $\mu\text{g L}^{-1}$ with a mean value of 9695.26 $\mu\text{g L}^{-1}$ in 2015. Si, Al, and Fe were the main components found in soluble and insoluble materials. The deposition flux of the 13 elements was 3065.14 $\text{mg m}^{-2}\text{yr}^{-1}$ in 2015 and reached its highest value in the summer, followed by autumn, winter, and spring. From 2013 to 2015, the deposition flux in soluble materials increased every year due to the increase in precipitation and pollutant emission intensity. Cd, Zn, and As were highly enriched due to anthropogenic activities, while Si, Al, and Fe were mainly derived from the crust. Four sources (i.e., industrial activities, vehicle emissions, coal combustion, and dust) were identified from soluble and insoluble materials in 2015 using the PMF model. Industrial activities and coal combustion were found to be the main sources of the 13 elements, with relative contributions of 50.47% and 26.09%, respectively. Combined with the back trajectory analysis, the precipitation in Taiyuan was mainly affected by the southerly air mass. The southeasterly and southwesterly air masses, which were transported through the coal-powered industrial and coking zones, contributed 39% and 27% of the total precipitation, respectively, and greatly influenced the wet deposition of metals in Taiyuan.

Table 2Contribution of pH and wet deposition fluxes ($\text{mg m}^{-2} \text{yr}^{-1}$) of metals in water phase from air masses of four typical transport pathways.

Element	SE		SW		NE		NW	
	Flux	Rate/%	Flux	Rate/%	Flux	Rate/%	Flux	Rate/%
N	33		23		9		19	
Precipitation/mm	278.1		192.5		78.4		164.0	
pH	5.6		5.7		6.1		5.9	
Si	43.1	35.4	37.9	31.2	14.8	12.2	25.7	21.2
Al	8.7	32.7	11.7	43.6	3.7	14.0	2.6	9.7
Cr	0.3	30.5	0.3	31.6	0.1	13.4	0.2	24.5
Mn	4.1	29.0	5.2	37.0	1.9	13.7	2.9	20.3
Fe	13.4	34.2	12.5	32.1	5.1	13.0	8.1	20.7
Ni	0.4	34.0	0.4	35.0	0.1	10.5	0.3	20.5
Cu	0.7	35.9	0.6	32.5	0.2	12.3	0.4	19.3
Zn	12.5	25.2	16.3	32.8	12.7	25.7	8.1	16.3
As	0.4	28.6	0.5	37.0	0.2	12.3	0.3	22.1
Sr	3.0	32.4	3.2	34.7	1.3	13.7	1.8	19.2
Cd	0.1	29.5	0.1	40.8	0.0	10.2	0.1	19.6
Ba	7.4	29.8	7.1	28.6	3.4	13.6	7.0	28.0
Pb	0.3	34.1	0.3	36.9	0.1	14.8	0.1	14.3

SE represents trajectory of d; SW represents trajectory of e; NE represents trajectory of c; NW represents trajectory of a and b.

Author contributions

Study concept and design: Xiao Tian, Qiusheng He, Acquisition of date: Xiao Tian, Ailing Ye, Analysis and interpretation of date: Xiao Tian, Ailing Ye. Drafting of manuscript: Xiao Tian, Qiusheng He and Zhentao Wang, Critical revision of the manuscript for important intellectual content: Qiusheng He, Zhentao Wang, Yuhang Wang, Statistical analysis: Xiao Tian, Administrative, technical, or material support: Lili Guo, Laiguo Chen, Ming Liu, Study supervision: Lili Guo, Laiguo Chen, Ming Liu.

Declaration of competing interest

The authors declare no competing financial interest.

Acknowledgments

This study was supported by the funding of the National Natural Science Foundation of China (No. 41472311). We gratefully acknowledge the partial supports from the One-hundred talent program supported by The Organization Department of Shanxi Province Committee.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apr.2020.01.007>.

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