

## Short communication

## Accumulation and fractionation of rare earth elements in atmospheric particulates around a mine tailing in Baotou, China



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## ABSTRACT

Rare earth elements (REEs) have been increasingly emitted into the atmosphere with a worldwide increase in use of these metals. However, the research on REEs in atmospheric particulates is fairly limited. In this paper, atmospheric particulates including total suspended particulate (TSP) matter and particles with an equivalent aerodynamic diameter less than 10  $\mu\text{m}$  (PM<sub>10</sub>) were collected around a rare earth mine tailing in Baotou, the largest rare earth industrial base in China, in August 2012 and March 2013, for the analyses of REE levels and distributions. The total concentrations of REEs for TSP were 172.91 and 297.49  $\text{ng}/\text{m}^3$ , and those for PM<sub>10</sub> were 63.23 and 105.52  $\text{ng}/\text{m}^3$ , in August 2012 and March 2013, respectively. Enrichment factors for all 14 analyzed REEs in the TSP and PM<sub>10</sub> indicated that the REE enrichment in atmosphere particulates was caused by anthropogenic sources and influenced by the strong wind in spring season. The spatial distribution of REEs in TSP showed a strong gradient in the prevailing wind direction. The chondrite-normalized patterns of REEs in TSP and PM<sub>10</sub> were similar with the conspicuous fractionation between light REEs and heavy REEs.

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## 1. Introduction

Rare earth elements (REEs) are located at the bottom of Mendeleev's Periodic Table, including fifteen lanthanides, from La to Lu, Sc and Y (Liang et al., 2008). REEs are divided into heavy REEs (HREEs) and light REEs (LREEs) depending on their atomic masses and radii. LREEs include La, Ce, Pr, Nd, Pm, Sm and Eu, while HREEs include Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu (Zhang et al., 2001; Wang et al., 2011). These elements form a coherent group of elements with similar chemical properties and are often found together in mineral deposits. REEs have become vital and indispensable components of many high-tech products. It is reported that with a complete technological system in mining, dressing, smelting and separating of rare earth ores, China can produce over 400 varieties of rare earth products in more than 1000 specifications (Chen, 2011). In 2011, China has produced over 90% of the world's rare earth supply with only 23 percent of the world total reserves (Anonymous, 2012). The large-scale exploitation and application of rare earth resources will inevitably result in substantial increases of REE concentration levels in soil, water and air.

During the past decades, considerable research has focused on the concentration distribution of REEs in soils and water bodies (Zhang et al., 2001; Wang et al., 2008; Liang et al., 2008; Li et al., 2010). However, research on their concentrations in the air is fairly limited because of analytical limitations. Previous studies have investigated the long haul transport of REEs in atmospheric dust from continents to oceans (Lee et al., 2010; Csavina et al., 2012) and levels of REEs in the airborne particulate matter in urban areas (Wang et al., 2001; Kulkarni et al., 2006; Moreno et al., 2010; Shaltout et al., 2013). Air pollution caused by REEs in forms of ambient particles has been found during the combustion of oil in the vicinity of refinery factories (Kitto et al., 1992; Pacyna and Pacyna, 2001) and a steel plant (Geagea et al., 2007), because petroleum-cracking catalyst and products are highly enriched in LREEs (La, Ce and Nd).

Though being the non-essential elements for living organisms (Pang et al., 2001), REEs have positive effects on the growth of farming animals and various plant species (Pang et al., 2001; Hu et al., 2004). Consequently, REEs had been used at low concentrations as feed additives and fertilizers in China for decades (Wang et al., 2008). However, the environmental safety of the application of REEs has always been controversial and human health risk caused by rare earth intake has drawn increasing attention. Many researches have shown that REEs can enter human bodies and the presence of significant amounts of REEs in human bone, blood,

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teeth, liver, kidney and lymph nodes has been observed (Koeberl and Bayer, 1992; Zhang et al., 2000). Chen et al. (2001) reported that REEs could enter the cell and cell organelles and mainly be bound with biological macromolecules. The long-term consumption of food contaminated with REEs may cause chronic poisoning (Hirano and Suzuki, 1996; Jiang et al., 2012). Nevertheless, little information is available about the dose intake and potential health effects of exposure to REEs on human beings living in the rare earth mining and tailing areas.

The harmful effects of atmospheric particulates including total suspended particulate (TSP) matter and particles with an equivalent aerodynamic diameter less than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ) on human health are drawing more attention nowadays (Kulkarni et al., 2006; Moreno et al., 2010; Cheng et al., 2013). Previous studies have demonstrated an association between atmospheric pollutants and morbidity and adverse health outcomes such as hospital admissions for cardiovascular and respiratory diseases, urgent care visits, asthma attacks, acute bronchitis and restrictions in activities (Anenberg et al., 2010; Cheng et al., 2013). Atmospheric particulates contain a mixture of solid particles with organic and inorganic pollutants (Lee et al., 2010; Cheng et al., 2013) which are more harmful to human health than the particulates themselves. Along with a worldwide increase in the use of rare earths, these elements have increasingly been emitted into atmosphere. Therefore, it is of importance to analyze and evaluate the levels and distribution of REEs in the air.

Baotou REE tailing was produced by Baotou Iron and Steel Company, China's largest rare earths producer. It contains high levels of REEs and heavy metals from the Bayan Obo mine, the largest light rare earth deposit ever found in the world. Since the tailing is powdery and composed of various mineral matters, it is one of the major pollution sources for the surrounding environment (Guo et al., 2013). A large amount of tailing powders with high REE concentrations can enter the atmosphere easily due to the strong wind occurring frequently all year around in this region. The presence and accumulation of REEs in the atmospheric particulates may have serious consequences on the surrounding ecosystems as well as human health. To assess the potential environmental risk of REEs, in this study, we focused on the concentration and distribution of REEs in the atmospheric particulates in a representative open-air rare earth tailing region of northern China. TSP and  $\text{PM}_{10}$  samples were collected around the mine tailing in August 2012 and March 2013, representing the warm and wet season and the cold and dry season in this area, respectively.

## 2. Materials and methods

### 2.1. Study area

Baotou (40°14'56"–42°43'49"N, 109°15'12"–111°26'25"E) is the capital city of Inner Mongolia which has been known as the largest rare earth industrial base in China since the discovery of the large Bayan Obo Nb–REE–Fe deposit in 1927 (Xu et al., 2008). It is located in the central part of Inner Mongolia, on the Tumochuan and Hetao Plain, with the Yellow River to the south and Mongolia to the north. It has a semi-arid, temperate, continental monsoon climate. The mean annual temperature is 6.5 °C. The average annual precipitation is about 240–400 mm, with an evaporation of 1938–2342 mm. The soil type is mainly chestnut soil. The prevailing wind direction is northwest. Because of the frequent exchange of warm and cold air, dust storms frequently occur in this area from March to May every year. The average wind speed is 3 m/s and the average numbers of days with strong wind, floating dust and the dust storm are about 46 days, 25.9 days and 43.3 days per year, respectively.

The REE ore was mined from the Bayan Obo deposit and transported about 150 km by railroad to milling facilities in Baotou (Xu et al., 2008). About 90% of the mined deposit was stored in the tailing of Baotou Iron and Steel Company, 12 km away from Baotou city for future use. The tailing powders were discharged into the reservoir through open slots by circulating water. The mine tailing was established in 1965 with poor supportive capacity (Guo et al., 2013). It covers an area of 11.5 km<sup>2</sup>, with tailings of  $1.5 \times 10^8$  t, of which about  $9.3 \times 10^6$  t are REE tailings (Li et al., 2010). Compared with the raw ore, the average grade of REEs in the tailings had been increased from 6.8% to 8.85%. After evaporation of water in the tailing reservoir, part of the tailing area is exposed to the air. The particle size of mineral powder was fairly fine and would easily spread to the surrounding environment with the strong wind. This process will inevitably result in accumulation of REEs in the surrounding environment and might affect human health through the food chain (see Fig. 1).

### 2.2. Sampling and measurement

A total of 13 sampling sites were chosen around the rare earth tailings to assess the impact on the surrounding environment. A global positioning system (GPS) was used to record the locations of the sampling sites. The TSP samples were collected for three days from 8:00 am to 8:00 pm during the periods of August 14th–20th, 2012 and March 14th–20th, 2013. The rainy days were avoided, and the sampling periods were chosen after 2 or 3 continuous sunny days. The TSP sampling was conducted using a mid-volume aerosol sampler (TH-150C, Wuhan Tianhong Instrument Co., Ltd, China) at the sampling rate of 100 L min<sup>-1</sup>. The sampling height was about 1.5 m. The filters used were quartz fiber filters ( $\varnothing$  90 mm) with low weight and low blank levels for REEs. Quartz filters were pre-heated (450 °C for 4 h) and pre-weighted (after conditioning for 24 h at 20–25 °C) prior to sample collection, and were stored in a refrigerator (2 °C) prior to sample collection. The filters were weighed (0.1 mg accuracy) before and after sampling to determine the total mass of collected TSP. The filters were sealed in the filter holder with a cover during transport to the sampling sites or back to the laboratory in order to avoid contamination. Meteorological parameters such as wind speed, wind direction, temperature and humidity were also simultaneously measured during the sampling period.

To measure the participants'  $\text{PM}_{10}$  exposures during normal activities, 24-h personal  $\text{PM}_{10}$  samples were simultaneously collected in a village Wulanji near the tailing reservoir during the same sampling period as the TSP. The personal air sampling-pump (Omni5000IS, Beijing Jinkesantong Instrument Co., Ltd, China) was used to collect  $\text{PM}_{10}$  samples on 37-mm quartz fiber filters around the tailings. The 37-mm filters were pretreated (heating and weighting) in line with the 90-mm filters. At a nominal flow rate of 3 L min<sup>-1</sup>, approximately 4.32 m<sup>3</sup> of air was collected during each 24-h sampling period. Sixteen adult participants living in the Wulanji village were invited to wear the personal air sampling-pump to collect  $\text{PM}_{10}$  samples for 24 h from 8:00 am first day to 8:00 am next day. The sampling inlet was positioned in the breathing zone of each participant at the midline of their chest.

After sampling, all the filters were weighed after equilibrated in a desiccator for 48 h and the net weight of the sampled TSP and  $\text{PM}_{10}$  can be obtained by subtraction. The filters loading samples were cut into small pieces using plastic scissors and subsequently leached for 4 h with 43%  $\text{HNO}_3$  (super pure). The leachate was filtered and transferred to a flask and diluted to 100 ml with de-ionized water. The concentrations of REEs and Al were analyzed by inductively coupled plasma mass spectrometry (ELAN DRC-e, Perkin Elmer SCIEX) (Wang et al., 2011). Each measurement was

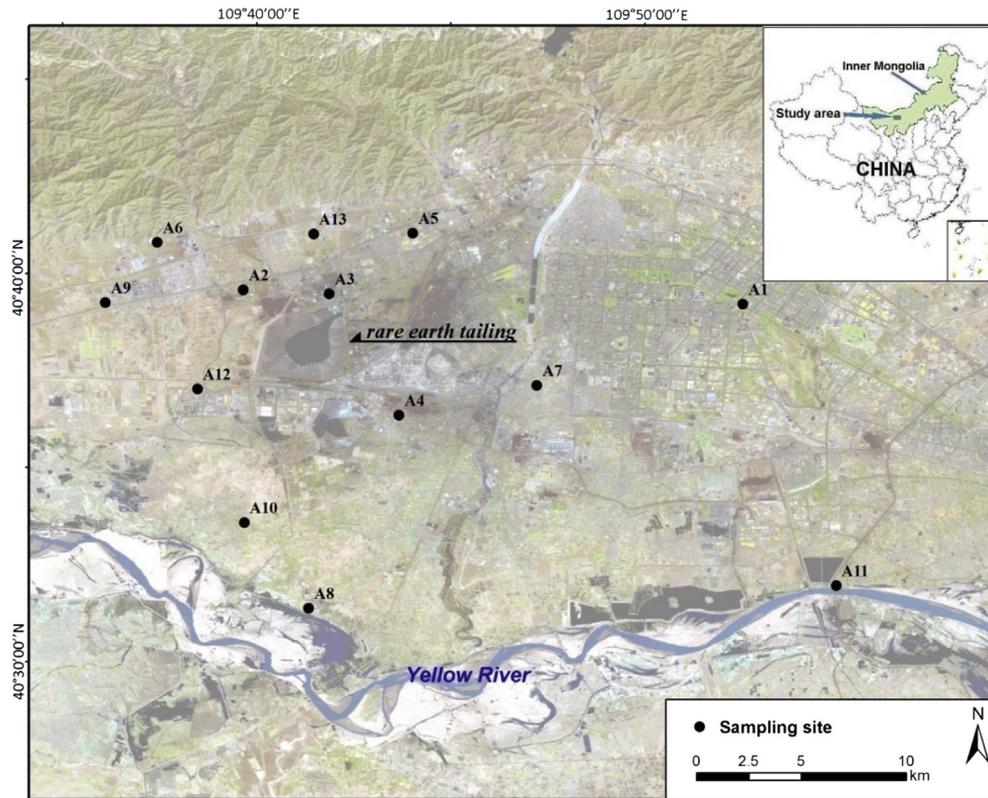


Fig. 1. Map of the study area and sampling site.

conducted in duplicate. National reference samples, replicates, and blanks were applied to ensure accuracy of the results. Both the relative errors for the reference samples and the differences for duplicate analyses of the samples were better than 5%. Differences in REE concentrations of TSP and PM<sub>10</sub> between the two sampling periods were assessed using Student's *t* test.

The enrichment factor (EF) was widely used to detect the contribution of anthropogenic emissions of trace elements to the environment (Cheng et al., 2012; Liu et al., 2013). The formula used to calculate EF was:

$$EF = (C_i/C_r)_{\text{sample}} / (C_i/C_r)_{\text{crust}}$$

where  $C_i$  is the concentration of the element considered in the sample or the crust and  $C_r$  is the concentration of a reference element in the sample or the crust. EF can be used to assess the degree of anthropogenic influence. Elements with EF values significantly higher than 1 may be attributed to anthropogenic sources. EF of an element was based on the standardization of a measured element against a reference element characterized by low occurrence variability, such as relatively common elements Al, Fe, Mn, K and Si (Cheng et al., 2012). In this study, Al was used as reference element to calculate the enrichment factors of REEs. Concentrations of REEs and Al in the upper continental crust were taken from Wedepohl (1995).

### 3. Results and discussion

#### 3.1. Concentrations of TSP and PM<sub>10</sub>

Box charts were produced to show the overall features of TSP and PM<sub>10</sub> mass concentrations around the tailing reservoir in different samplings (Fig. 2). The averages (ranges) of TSP in August

2012 and March 2013 were 0.64 mg/m<sup>3</sup> (0.27–1.55) mg/m<sup>3</sup> and 1.61 mg/m<sup>3</sup> (0.73–3.17) mg/m<sup>3</sup>, respectively. The average concentrations (ranges) of PM<sub>10</sub> in August 2012 and March 2013 were 0.26 mg/m<sup>3</sup> (0.21–0.55) mg/m<sup>3</sup> and 0.54 mg/m<sup>3</sup> (0.21–0.93) mg/m<sup>3</sup>, respectively. The concentrations of TSP and PM<sub>10</sub> in March 2013 were significantly higher than those in August 2012 respectively ( $p < 0.05$ ). According to the secondary standard of Chinese Air Environment Quality Standard (GB 3095–1996), the daily average concentration for TSP and PM<sub>10</sub> in an inhabited area should be 0.30 mg/m<sup>3</sup> and 0.15 mg/m<sup>3</sup>, respectively. Therefore, the TSP and PM<sub>10</sub> in most of the sampling sites were higher than the secondary standard of China.

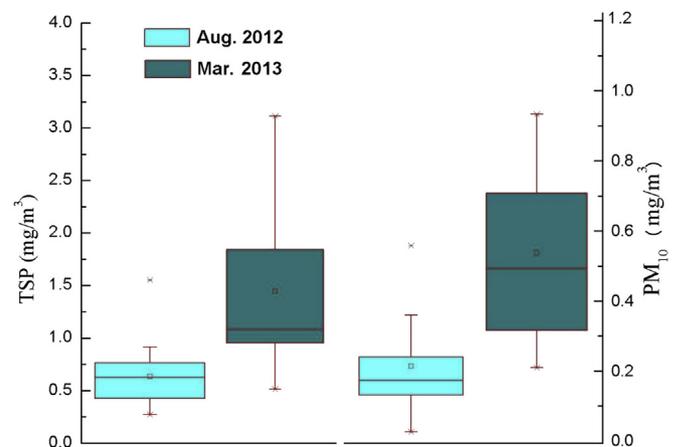


Fig. 2. TSP and PM<sub>10</sub> concentrations.

### 3.2. REE concentrations in TSP and PM<sub>10</sub>

REE concentrations in TSP and PM<sub>10</sub> in different sampling periods are shown in Table 1. The total concentrations of REEs ( $\sum$ REE) for TSP in August 2012 and March 2013 were 172.91 and 297.49 ng/m<sup>3</sup>, respectively. The  $\sum$ REE in TSP in the present study were significantly higher than those in atmospheric particulate matter at three sampling sites (24.06, 83.14 and 31.85 ng/m<sup>3</sup>) in Beijing and that in the Netherlands (4.056 ng/m<sup>3</sup>) (Wang et al., 2001). The  $\sum$ REE for PM<sub>10</sub> in August 2012 and March 2013 were 62.23 and 105.52 ng/m<sup>3</sup>, respectively. The investigations about REEs in the atmospheric environment especially in the PM<sub>10</sub> in the vicinity of tailings and the related scientific data in the literature are limited. The concentrations of individual REE in PM<sub>10</sub> in the present study were 1–2 order higher than those reported by Fanizza et al. (2008) and Bozlaker et al. (2013). Meanwhile,  $\sum$ REE in TSP and PM<sub>10</sub> in March 2013 were greater than those in August 2012, and the difference was statistically significant ( $p < 0.05$ ).

The concentrations of La, Ce, Pr, Nd, Sm, Eu, Gd, Ho in TSP in March 2013 were significantly higher than those in August 2012 ( $p < 0.05$ ). However, although the average of Tb, Dy, Er, Tm, Yb and Lu concentration increased in March 2013, there was no significant differences between the two periods ( $p > 0.05$ ). The concentrations of La, Ce, Pr, Nd, Sm, Eu and Gd of PM<sub>10</sub> in March 2013 were significantly higher than those in August 2012 ( $p < 0.05$ ). There was no significant differences of Tb, Dy, Ho, Er, Tm, Yb and Lu in PM<sub>10</sub> in the two periods, even though their concentrations in March 2013 were slightly higher than those in August 2012.

It can also be observed from Table 2 that the average concentrations of REEs in TSP and PM<sub>10</sub> around the tailing reservoir followed the order: Ce > La > Nd > Pr > Sm > Gd > Dy > Er > Yb > Eu > Tb > Ho > Tm > Lu. The order was similar to that in Bayan Obo ores (Xu et al., 2012), and similar to the order of REEs in sediments (Zhu et al., 1997), animals, plants, environmental and geological materials (Wang et al., 1995, 2001). The concentrations of single REE conformed to the distribution law of odd–even numbers. Meanwhile, there is a statistically significant correlation ( $R^2 > 0.92$ ;  $p < 0.05$ ) between all the elements examined. This suggests that

**Table 2**

EFs of REEs in atmospheric particulates around the mine tailing.

Element	TSP ( $n = 13$ )		PM <sub>10</sub> ( $n = 16$ )	
	Aug. 2012	Mar. 2013	Aug. 2012	Mar. 2013
La	25.0	39.6	9.4	13.9
Ce	28.9	64.8	8.3	16.5
Pr	19.9	42.1	6.6	13.2
Nd	20.2	40.7	8.2	19.9
Sm	10.0	38.9	6.6	10.5
Eu	11.9	39.7	3.9	11.2
Gd	10.7	33.1	5.0	15.0
Tb	30.1	42.4	2.7	17.0
Dy	5.8	8.4	0.5	0.6
Ho	4.5	7.7	1.2	1.5
Er	4.2	7.0	1.3	1.5
Tm	5.6	8.8	1.2	1.1
Yb	6.0	7.2	2.3	2.8
Lu	4.8	5.5	2.4	2.5

the accumulation and distribution of REEs in atmospheric particles were affected by the rare earth mineral exploitation. Moreover, the LREE accounted for more than 87% of the total atmospheric REE burden. Such distribution patterns of LREE enrichment are similar to those in Bayan Obo ores (Xu et al., 2012).

### 3.3. Enrichment factors of REEs

The calculated EF values for all 14 REEs in the TSP and PM<sub>10</sub> are listed in Table 2. The average EFs of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Tm in TSP for both August 2012 and March 2013 were greater than 10, implying significant influences of non-crustal sources. Meanwhile, the EF values in March 2013 were higher than those in August 2012, suggesting that the enrichment of REEs was caused by anthropogenic sources and influenced by the strong wind in spring. The mean values of EF ranged between 4.2 and 6.0 for Dy, Ho, Er, Tm, Yb and Lu suggesting these elements also originated from anthropogenic sources. The average EF values of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Tm in PM<sub>10</sub> for March 2013 were greater than 10,

**Table 1**

REE concentrations in atmospheric particulates around the mine tailing and the significance levels of *t*-test for the differences between the two periods.

REEs	TSP ( $n = 13$ )			PM <sub>10</sub> ( $n = 16$ )		
	Aug. 2012	Mar. 2013	<i>p</i>	Aug. 2012	Mar. 2013	<i>p</i>
La	36.26 ± 20.86	57.49 ± 25.39	<0.05	13.64 ± 2.49	20.26 ± 4.95	<0.05
Ce	83.99 ± 27.00	143.08 ± 45.79	<0.05	26.69 ± 4.93	47.91 ± 7.39	<0.05
Pr	7.89 ± 1.79	16.73 ± 4.63	<0.01	2.61 ± 0.99	5.23 ± 1.24	<0.01
Nd	27.38 ± 11.26	55.09 ± 16.63	<0.01	11.14 ± 2.68	19.92 ± 5.84	<0.01
Sm	6.91 ± 3.86	11.22 ± 4.41	<0.01	2.62 ± 0.53	3.92 ± 0.30	<0.01
Eu	1.34 ± 0.34	1.64 ± 0.24	<0.01	0.74 ± 0.22	0.98 ± 0.17	<0.01
Gd	2.79 ± 0.89	3.66 ± 1.13	<0.01	1.81 ± 0.09	2.13 ± 0.27	<0.01
Tb	0.44 ± 0.17	0.57 ± 0.23	>0.05	0.31 ± 0.07	0.36 ± 0.16	>0.05
Dy	2.09 ± 0.28	3.17 ± 0.91	>0.05	1.39 ± 0.27	1.81 ± 0.23	>0.05
Ho	0.39 ± 0.20	0.52 ± 0.08	<0.05	0.27 ± 0.14	0.32 ± 0.08	>0.05
Er	1.57 ± 0.62	1.95 ± 0.75	>0.05	0.88 ± 0.31	1.21 ± 0.28	>0.05
Tm	0.26 ± 0.10	0.35 ± 0.15	>0.05	0.16 ± 0.05	0.22 ± 0.08	>0.05
Yb	1.37 ± 0.41	1.73 ± 0.62	>0.05	0.84 ± 0.10	1.09 ± 0.26	>0.05
Lu	0.23 ± 0.06	0.28 ± 0.05	>0.05	0.13 ± 0.03	0.18 ± 0.04	>0.05
$\sum$ REE	172.91 ± 53.05	297.49 ± 77.86	<0.05	63.23 ± 5.82	105.52 ± 10.48	<0.05
LREE	150.55 ± 34.02	285.25 ± 97.08	<0.05	57.44 ± 11.84	98.21 ± 19.88	<0.05
HREE	9.15 ± 1.23	12.23 ± 1.52	<0.05	5.79 ± 0.56	7.31 ± 0.51	<0.05
LREE/HREE	16.46	23.32		9.92	13.44	
LREE/ $\sum$ REE	0.87	0.96		0.91	0.93	
(La/Yb) <sub>N</sub>	17.99	22.57		11.09	12.55	
(La/Sm) <sub>N</sub>	3.28	3.20		3.25	3.23	
(Gd/Yb) <sub>N</sub>	1.65	1.71		1.75	1.57	
$\delta$ Eu	0.78	0.62		0.98	0.93	
$\delta$ Ce	1.15	1.10		1.02	1.10	

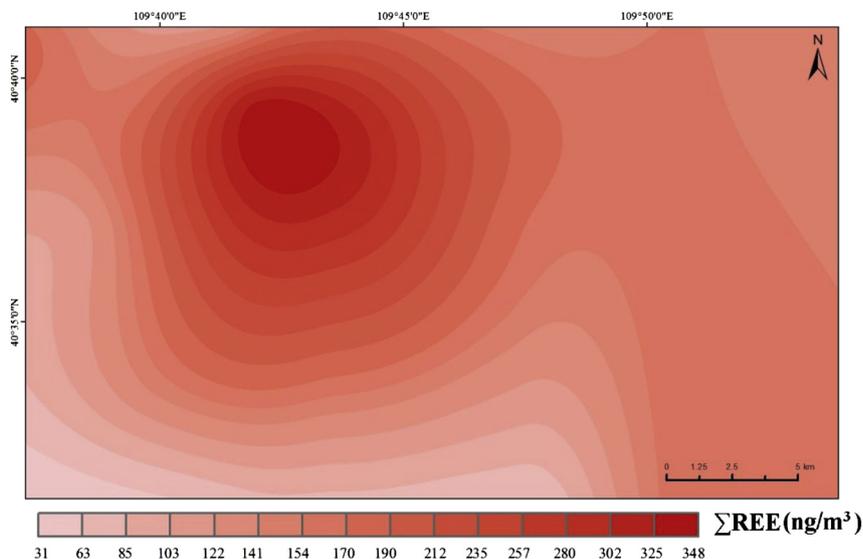


Fig. 3. Spatial distribution of total REE concentration for TSP in August 2012.

whereas, they were lower than 10 in  $PM_{10}$  in August 2012. The EF values for Dy, Ho, Er, Tm, Yb and Lu in  $PM_{10}$  were close to 1 suggesting these elements originated mainly from the local natural sources, including the atmospheric dust from the weathered soils and rocks.

#### 3.4. Spatial distribution of REEs in TSP

The spatial distribution maps of REE concentrations in TSP are shown in Figs. 3 and 4. These maps show obviously elevated REE concentrations in TSP in the vicinity of the tailing and they decreased with the increase of distance away from the tailing. There was also a strong gradient concentration in the prevailing wind direction in March 2013 (Fig. 4), which could be caused by the strong wind in spring in this region.

#### 3.5. Distribution patterns of REEs in TSP and $PM_{10}$

The widely used chondrite normalization method was used to reveal the distribution patterns of REEs in the TSP and  $PM_{10}$ . The

normalized patterns provide useful information of REE abundance relative to a major source (e.g. average upper continental crust) (Li et al., 2010) and the relationship between adjacent elements. The REE values in chondrite were reported by Taylor and McLennan (1995) and the normalized curves are presented in Fig. 5. The chondrite-normalized patterns of REEs in TSP and  $PM_{10}$  are similar, with a steep declining trend in the LREE section and stable change in the HREE section.

The ratio of LREE/HREE is used as a measure of the fractionation between LREEs and HREEs, and the ratios of  $(La/Sm)_N$  and  $(Gd/Yb)_N$  are used to measure the degree of LREE fractionation and that of HREE fractionation respectively. The distribution patterns of REEs in TSP are characterized by obvious fractionation of LREE and HREE with the LREE/HREE ratios of 16.46 and 23.32,  $(La/Yb)_N$  of 17.99 and 22.57 for August 2012 and March 2013 respectively. This means that the atmospheric particles originated from a light REE type source. The degree of LREE fractionation with  $(La/Sm)_N$  of 3.28 and 3.20 is higher than that of HREE fractionation with  $(Gd/Yb)_N$  of 1.65 and 1.71 for August 2012 and March 2013 respectively. The fractionation patterns of

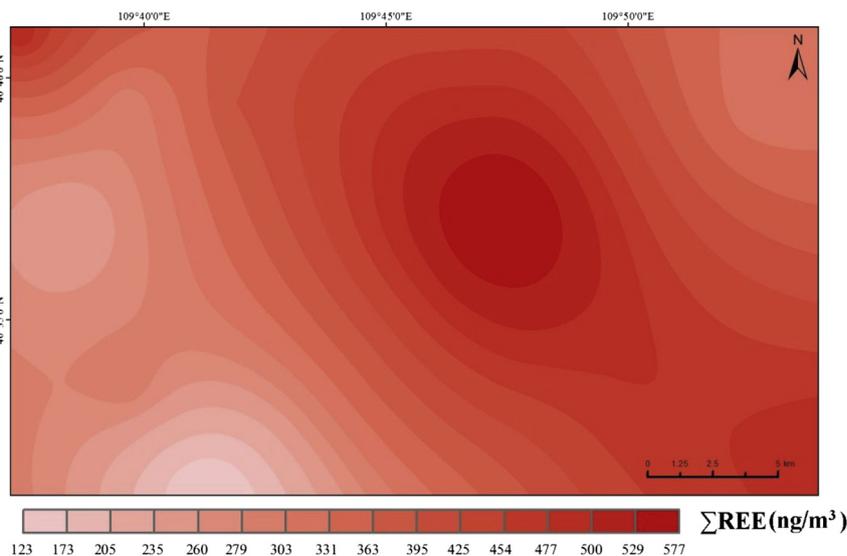


Fig. 4. Spatial distribution of total REE concentration for TSP in March 2013.

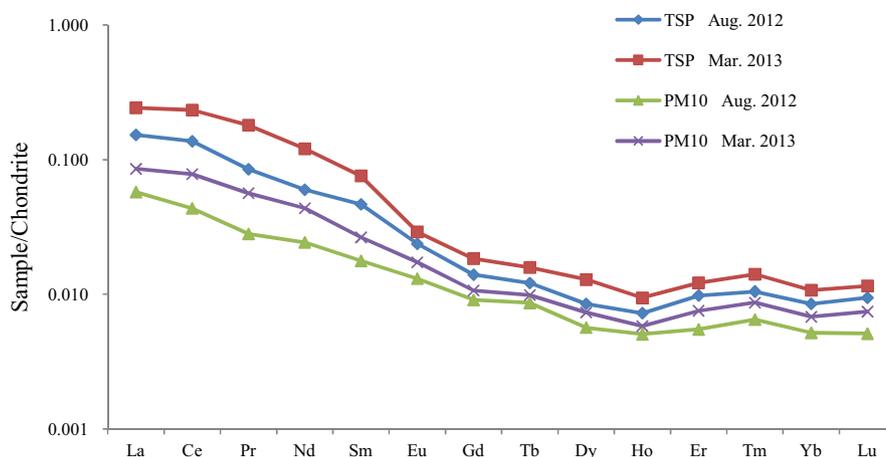


Fig. 5. Chondrite normalized REE distribution patterns in atmospheric particulates.

relative LREE enrichment are similar to those in Bayan Obo ores (Xu et al., 2012), indicating the influences of rare earth tailing on the surrounding environment. Slight positive Ce anomaly with  $\delta\text{Ce}$  of 1.15 and 1.10 on average, and obviously negative Eu anomaly with  $\delta\text{Eu}$  of 0.78 and 0.62 on average are also observed. Individual anomalies showed differentiation between selected elements (e.g. Ce and Eu) and the other REEs. The depletion or enrichment of the other REEs may be linked to their fixation under specific conditions and changes in their mobility (Semhi et al., 2009; Lai and Yang, 2013).

Similar to TSP, conspicuous fractionation between LREEs and HREEs is observed in the  $\text{PM}_{10}$  samples, with LREE/HREE ratios of 9.92 and 13.44,  $(\text{La}/\text{Yb})_N$  of 11.09 and 12.55 for August 2012 and March 2013 respectively. Meanwhile, there is also a discrepancy between the high degree of LREE fractionation and the low degree of HREE fractionation, with the ratios of  $(\text{La}/\text{Sm})_N$  of 3.25 and 3.23 and  $(\text{Gd}/\text{Yb})_N$  of 1.75 and 1.57 for August 2012 and March 2013 respectively. The  $\text{PM}_{10}$  samples also displayed positive Ce anomalies and negative Eu anomalies, with average  $\delta\text{Ce}$  values of 1.02 and 1.10 and average  $\delta\text{Eu}$  values of 0.98 and 0.93 for August 2012 and March 2013 respectively. All atmospheric particles including TSP and  $\text{PM}_{10}$  were enriched in LREE and depended on the rock type in this region, although the LREE/HREE ratios were different and influenced by different factors such as wind disturbance in the different season.

#### 4. Conclusion

The total concentrations of REEs in TSP were 172.91 and 297.49  $\text{ng}/\text{m}^3$ , and those for  $\text{PM}_{10}$  were 62.23 and 105.52  $\text{ng}/\text{m}^3$ , in August 2012 and March 2013, respectively. Enrichment factor for all 14 REEs in the TSP and  $\text{PM}_{10}$  indicated that REE enrichment in atmosphere particulates was caused by anthropogenic sources and influenced by the strong wind in springtime. The degree of LREE fractionation with  $(\text{La}/\text{Sm})_N$  of 3.28 and 3.20 is stronger than that of HREE fractionation with  $(\text{Gd}/\text{Yb})_N$  of 1.65 and 1.71 for August 2012 and March 2013 respectively. Slight positive Ce anomaly and obviously negative Eu anomaly are also observed. The spatial distribution of REEs in TSP showed a strong gradient in the prevailing wind direction. The chondrite-normalized REE patterns of TSP and  $\text{PM}_{10}$  were similar and the normalized curves showed conspicuous fractionation between the light REEs and heavy REE.

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